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UNIVERSITY OF DURHAM

A THESIS

entitled

CHEMISTRY OF HEXAFLUOROBUT-2-YNE

Submitted by

COLIN GERHART PRYCE JONES, B.Sc. (Dunelm)

(University College)

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A candidate for the degree of Doctor of Philosophy

1980

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TO MY PARENTS

ACKNOWLEDGEMENTS

I would like to thank Professor R.D. Chambers for his considerable help and encouragement during the course of this work.

I would also like to express my gratitude to the many technical and laboratory staff for their assistance and to Dr. S. Bartlett for typing this thesis.

Finally, thanks are also due to the Science Research Council for providing a maintenance grant.

MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1977 and September 1980. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

Part of this work has been the subject of the following paper:

R.D. Chambers, C.G.P. Jones, G. Taylor, and R.L. Powell, *J. Chem. Soc. Chem. Commun.*, 1979, 433.

NOMENCLATURE

1. The prefix perfluoro is used before a name to denote that the compound or the part of the compound following the prefix is fully fluorinated.
2. A capital F in a ring (e.g. ) denotes that the ring and its unspecified substitutents are fully fluorinated.

ABSTRACT

This thesis is concerned with the preparation and reactions of hexafluorobut-2-yne (H.F.B.).

Attempts to improve the somewhat unsatisfactory literature method for preparing this acetylene were unsuccessful. However, the pyrolysis of perfluorocyclobutene over fluoride ion, a reaction first reported by a previous worker in this laboratory, has been developed to provide a new high yield route to H.F.B.

Free radical additions to H.F.B. have been investigated and a series of novel adducts was obtained. The behaviour of H.F.B. was found to differ considerably from that of fluoroalkenes, which have been studied previously.

A number of reactions of H.F.B. involving the use of caesium fluoride as an initiator have been studied. Copolymers of various compositions were obtained from reactions with acetylenic esters and several interesting co-oligomers were prepared from fluoroalkenes.

The additions of a variety of nucleophiles to H.F.B. were investigated with a view to obtaining cyclic products. Most of these experiments gave polyhexafluorobut-2-yne as the only product but a reaction with sulphur did give a thiophene derivative. A reaction with dimethyl sulphoxide gave an interesting sulphonium ylid of surprisingly high thermal and chemical stability.

A series of reactions was carried out in order to investigate some of the factors which influence the stereochemistry of nucleophilic addition to H.F.B. These experiments showed that both catalysed and uncatalysed additions of alcohols give mainly *anti* addition products. Only in the case of uncatalysed reactions employing an inert aprotic solvent does *syn* addition predominate.

CONTENTS

APPENDICES

INTRODUCTION

GENERAL INTRODUCTION

In 1836 Dumas and Peligot prepared methyl fluoride by what appears to be the first recorded synthesis of a fluorine containing organic compound.[1] However, it was not until the beginning of this century that the foundations of organofluorine chemistry were firmly established by Swarts' work on simple aliphatic fluoro-compounds.[2] Between about 1890 and 1938 he prepared a large number of partially fluorinated compounds by halogen exchange reactions. This work made it possible for Midgley and Henne to introduce dichlorodifluoromethane as a refrigerant.[3]

The chemistry of perfluorinated compounds began with the isolation of carbon tetrafluoride, which was not characterised till 1930.[4,5] Since then methods have been devised to prepare a wide range of fully fluorinated compounds and the subject has been extensively reviewed.[6]

Besides their use as refrigerants, fluorocarbons have found industrial applications in areas as diverse as fire extinguishers, aerosol propellants, dyes and surfactants.[7] Polytetrafluoroethylene, for example, is a polymer with unique physical properties which make it ideal for use in the manufacture of non-stick coatings for cooking utensils etc. The use of fluorine containing compounds in the pharmaceutical industry is becoming increasingly common. Methods have been developed to introduce fluorine into almost all of the available positions of the steroid nucleus and some of the resulting fluorinated steroids exhibit considerably enhanced pharmacological activity.

However, the value of a study of fluorocarbon chemistry lies not only in the industrial applications of the new materials that are being discovered. Another important aspect of this study has been

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the development of a new area of chemistry displaying a variety of novel types of reaction mechanism. The introduction of fluorine into a molecule has a major effect on the electronic environment of neighbouring functional groups and often alters their reactions completely. The study of the behaviour of fluorocarbon derivatives presents considerable challenges to established theories of mechanism and reactivity.

This thesis intends to discuss the chemistry of perfluorinated acetylenes, an area which has not been extensively studied and is still comparatively young. The synthesis of the first perfluoroacetylene, hexafluorobut-2-yne, was not reported till 1949.[8]

Although approximately 15 others have been reported to date, they are all either too unstable or too difficult to prepare in large quantities for their chemistry to be studied in detail. Only hexafluorobut-2-yne has received more than a superficial investigation, largely because it is the only commercially available perfluoroacetylene. However, most of the work using this acetylene has not been aimed at studying the properties of the system per se but instead has treated it as a novel compound with which to investigate some other field of chemistry. For example, a vast amount of work has been published, especially in recent years, on the use of hexafluorobut-2-yne as a ligand in organometallic chemistry. Another example of this type of approach is the exploitation of the powerful dienophilic properties of hexafluorobut-2-yne to prepare a wide range of Diels-Alder adducts.

The work described in this thesis involves the exploration of various aspects of the chemistry of hexafluorobut-2-yne.

CHAPTER I

PREPARATION OF FLUORINATED ACETYLENES

This chapter intends to summarise the methods used to prepare highly fluorinated acetylenes and for this purpose it is convenient to treat 1-fluoroacetylenes separately from bisperfluoroalkyl acetylenes. First, however, it will be worthwhile to give a brief general discussion of the effects of fluorine on the chemistry of fluoroaliphatic compounds, with particular reference to fluoroacetylenes.

I.A General Aspects of Organofluorine Chemistry

I.A.1 Introduction

The replacement of a hydrogen atom by fluorine can cause profound modifications in the chemical properties of a compound. These changes are mainly due to differences in the electronic properties of hydrogen and fluorine but steric factors also have some influence. A brief summary of these effects is given below and the subject is covered in greater detail by several authors.[9]

I.A.2 Effects of Fluorine in Organic Molecules

The fluorine atom, although it has 7 electrons in the second quantum shell, is only slightly larger than the hydrogen atom (van der Waals radii ca. 1.35Å for F, 1.20Å for H). Therefore it is possible to replace all the hydrogen in a saturated hydrocarbon by fluorine without introducing significant overcrowding or

distortion. Fluorine is more effective than hydrogen at shielding the carbon skeleton of an alkane from chemical attack, not just because of its greater size but, perhaps more importantly, because it has a dense electron cloud surrounding it. Also, the C-F bond is considerably stronger than the C-H bond and both these factors contribute to the comparative inertness of saturated fluorocarbons.

However, the differences between the chemistry of fluorocarbon and hydrocarbon systems arise largely from electronic effects. These may be divided into three types:

a) Fluorine is the most electronegative element and the C-F bond is highly polar. Inductive effects are therefore very important in fluorocarbon chemistry.

b) Fluorine has three lone pairs in the valence shell, whereas hydrogen has none. Coulombic repulsion between electron pairs on fluorine and π electrons have been proposed to explain certain aspects of the reactivity of unsaturated fluorocompounds.

c) The electron affinity of fluorine is much higher than that of hydrogen. Therefore fluoride ion is more readily displaced than hydride ion. Positively charged fluorine containing species are less likely than the analogous hydrocarbon systems because of the higher ionisation energy of fluorine.

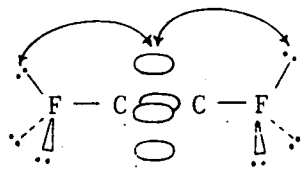
These generalisations lead one to expect highly fluorinated compounds to react rather differently from hydrocarbons.

I.B Effects of Fluorine in Acetylenes

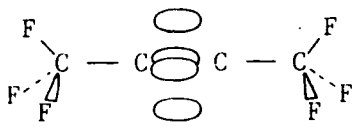
From the considerations discussed above it is possible to predict some of the properties of fluoroacetylenes. The substitution of an acetylene with fluorine or perfluoroalkyl groups reduces the

electron density in the triple bond. This has the effect of making the acetylene electrophilic in character. Fluoroacetylenes are therefore resistant to electrophilic attack but are very reactive towards nucleophiles.

Acetylenes with a fluorine atom directly attached to the triple bond are very unstable. This is probably due to repulsive interactions between the lone pairs on fluorine and the π electrons of the triple bond. The energy of the system is therefore raised.



arrows represent repulsive interactions



Also, as the electronegativity of carbon increases in the series sp^3, sp^2, sp, the C-F bond strength decreases correspondingly.

Acetylenes with perfluoroalkyl substitutents are much more stable, the fluorine lone pairs being further removed from the triple bond than in 1-fluoroacetylenes.

I.C 1-Fluoroacetylenes

I.C.1 General

Compared to the large number of acetylenes with chlorine, bromine and iodine attached to the triple bond, very few 1-fluoroacetylenes are known. This is due partly to difficulties in their preparation and partly to their instability. They can only be prepared by elimination type reactions from fluoroolefins, whereas other haloacetylenes are obtained by a variety of routes[10] and are therefore more readily accessible. The high reactivity of 1-fluoroacetylenes makes their isolation difficult. In fact, several 1-fluoroacetylenes which have not been isolated are proposed as high energy intermediates in a number of reactions.[11]

e.g. $C_6H_5CH{=}CFCl \xrightarrow{LiN(R)_2} [C_6H_5C{\equiv}CF] \xrightarrow{LiN(R)_2} C_6H_5C{\equiv}CN(R)_2$

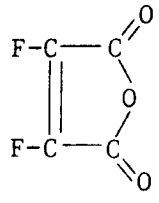
The only 1-fluoroacetylenes known are monofluoroacetylene, difluoroacetylene, perfluoropropyne, fluoropropiolyl fluoride, fluorochloroacetylene, t-butyl fluoroacetylene, difluorobutadiyne, tetrafluoropenta-1,3-diyne and 1-fluoro-2-cyanoacetylene.

I.C.2 Mono- and Difluoroacetylenes

Monofluoroacetylene has been prepared in 6 - 7% yield by dehalogenation of 1,1-difluoro-2-bromoethylene with magnesium in tetrahydrofuran, the major product being 1,1-difluoroethylene.[12] Debromination of 1,2-dibromo-1-fluoroethylene[13] or 1,1,2,2-tetrabromo-1-fluoroethane (either using magnesium[14] or electrochemically[15]) gives better yields.

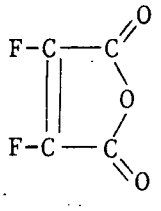
$$FCBr{=}CHBr \xrightarrow{Mg/THF} FC{\equiv}CH \qquad (80\%)$$

An almost quantitative yield was obtained when fluoromaleic anhydride was pyrolysed at 650 °C.[16]



$$\xrightarrow[5 - 7 \text{ mm Hg}]{650\,^\circ} FC{\equiv}CH + CO + CO_2 \quad (100\%)$$

Pyrolysis of difluoromaleic anhydride gives some difluoroacetylene as well as fluoropropiolyl fluoride.[17]



$$\xrightarrow{600\,^\circ} FC{\equiv}CF + FC{\equiv}C{-}COF + CO + CO_2$$

Difluoroacetylene is one of the components produced when tetrafluoroethylene is photolysed[18] and has been isolated from the product mixture by gas chromatography. Difluoroacetylene is also believed to be produced by radiolysis[19] and pyrolysis[20,21] of suitable fluorocarbons. It is also reported to be formed from the reaction of carbon and fluorine at 2500 - 3000K.[22] More recently, difluoroacetylene was shown to be one of several fluoroacetylenes produced when electrical discharges were passed through hexafluorobenzene, pentafluoropyridine or pentafluorobenzonitrile.[23] Difluorobutadiyne, tetrafluoropenta-1,3-diyne and 1-fluoro-2-cyanoacetylene are also isolable from these reactions.

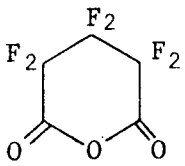
I.C.3 Tetrafluoropropyne

Tetrafluoropropyne has been prepared by debromination of 1,2-dibromohexafluoropropene, which in turn is made from 1,1-difluoro ethylene and dibromodifluoromethane.[24,25]

$$CF_2Br_2 + CH_2{=}CF_2 \xrightarrow[110^\circ]{(PhCO)_2O_2} CF_2BrCH_2CF_2Br \xrightarrow[1\text{ mm Hg}]{C,\ 300^\circ} CF_2BrCH{=}CF_2$$

$$CF_2BrCH{=}CF_2 \xrightarrow{Br_2\ h\nu} CF_2BrCHBrCF_2Br \xrightarrow{KOH_{aq}} CF_2{=}CBrCF_2Br \xrightarrow{AlBr_3} CF_3CBr{=}CFBr \xrightarrow{Zn/Dioxan} CF_3C{\equiv}CF$$

Another route to this acetylene starts from hexafluoroglutaric anhydride.[24]



$$\xrightarrow[1-2\text{ mm Hg}]{KF\quad 420^\circ} CF_2{=}CFCF_2COF \xrightarrow{F^-} CF_3CF{=}CFCOF \xrightarrow{NaOH} CF_3CF{=}CFCOONa \xrightarrow{220-240^\circ} CF_3C{\equiv}CF$$

Tetrafluoropropyne is also formed by the mercury sensitised decomposition of tetrafluorocyclopropene.[26]

I.D Bisperfluoroalkyl acetylenes

I.D.1 General

The most common methods for preparing perfluoroalkylacetylenes involve elimination of hydrogen halides or halogens from the appropriate olefin. Elimination of halogens generally gives better yields.[27] Dichloroolefins are the most common starting materials and these can be made by coupling 1,1,1-trichloropolyfluoroalkanes followed by elimination of chlorine.[28]

$$CF_2{=}CF_2 + CCl_4 \xrightarrow{275^\circ} Cl(CF_2CF_2)_nCCl_3 \qquad n = 1,2,3 \text{ or } 4$$

$$\downarrow \text{ Cu powder } 180^\circ/15 \text{ hr.}$$

$$Cl(CF_2CF_2)_nCCl{=}CCl(CF_2CF_2)_nCl$$

$$\downarrow \text{ Zn/acetic anhydride } 135^\circ$$

$$Cl(CF_2CF_2)_nC{\equiv}C(CF_2CF_2)_nCl$$

Another method for preparing bisperfluoroalkyl-dichloroolefins consists of heating a perfluoroalkanoic acid chloride, nickel carbonyl and 1,1-dichloro-2,2-difluoroethylene at 150°.

$$2R_FCOCl + Ni(CO)_4 \longrightarrow 2R_FCO\cdot + NiCl_2 + 4CO$$

$$R_FCO\cdot \longrightarrow R_F\cdot + CO$$

$$R_F\cdot + CF_2{=}CCl_2 \longrightarrow R_FCF_2CCl_2\cdot$$

$$2R_FCF_2CCl_2\cdot \longrightarrow R_FCF_2CCl_2CCl_2CF_2R_F$$

$$R_FCF_2CCl_2CCl_2CF_2R_F + Ni(CO)_4 \longrightarrow R_FCF_2CCl{=}CClCF_2R_F + NiCl_2 + 4CO$$

Besides elimination reactions, several other methods have been used to prepare bisperfluoroalkylacetylenes. These include the fluoride ion induced isomerisation of dienes, the use of sulphur tetrafluoride

as a selective fluorinating agent and various miscellaneous methods of limited applicability.

I.D.2 Hexafluorobut-2-yne

Hexafluorobut-2-yne (1) is the simplest member of the series of bisperfluoroalkylacetylenes. It is the only commercially available perfluoroacetylene and has been made by a variety of routes.

I.D.2.a Dehalogenation and dehydrohalogenation reactions

The methods for preparing dichloroalkenes outlined above are only applicable for hex-3-enes and higher homologues. 2,3-Dichlorohexafluorobut-2-ene, the precursor of hexafluorobut-2-yne, is generally prepared from hexachlorobuta-1,3-diene.[29,8]

$$CCl_2{=}CClCCl{=}CCl_2 \xrightarrow[155°]{SbF_3/SbF_3Cl_2} CF_3CCl{=}CClCF_3 \quad (85\%)$$

$$CF_3CCl{=}CClCF_3 \xrightarrow[10\ days\ 40°]{Zn/EtOH} CF_3C{\equiv}CCF_3 \ (1)\ (48.7\%) + CF_3CH{=}CClCF_3 \ (27.6\%) + CF_3CH_2CH_2CF_3 \ (1.4\%) + CF_3CF{=}C{=}CF_2 \ (0.4\%) + 10.1\%\ \text{recovered starting material}$$

The dechlorination was originally carried out using zinc dust in ethanol.[8,30] However, this method gives low conversions to the butyne and large quantities of reduction products, as well as being very slow. Acetic anhydride appears to be a more satisfactory solvent,[28,31] giving better yields (63%) with less by-products and in a shorter

time (7 hrs.).

Hexafluorobut-2-yne (1) has also been made by dehydrohalogenation of 2-halogenobut-2-enes with excess potassium hydroxide but dehalogenation was found to be a more satisfactory reaction.[27]

$$CF_3CH{=}CXCF_3 \xrightarrow[KOH \quad 10°]{300\% \text{ excess}} CF_3C{\equiv}CCF_3$$

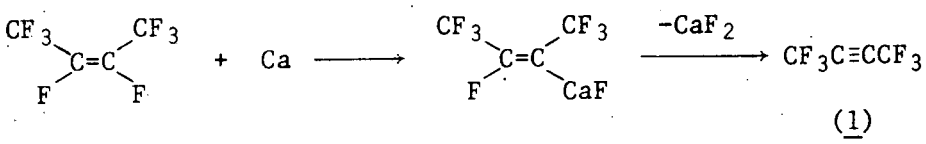
X = Cl 36%

X = Br 68%

$$CF_3CBr{=}CBrCF_3 \xrightarrow[\text{reflux, 4 hrs.}]{Zn/EtOH} CF_3C{\equiv}CCF_3 \quad (90\%)$$

$$CF_3CCl{=}CClCF_3 \xrightarrow[\text{acetic acid}]{Zn/\text{glacial}} CF_3C{\equiv}CCF_3 \quad (70\%)$$

Hexafluorobut-2-yne is produced in 13% yield when octafluorobut-2-ene and calcium vapour are condensed simultaneously onto a liquid nitrogen cooled surface.[32] The mechanism proposed for the defluorination involves the oxidative insertion of a calcium atom into a vinylic C-F bond, followed by a rapid elimination of calcium fluoride.



(1)

I.D.2.b Isomerisation of Dienes

The caesium fluoride catalysed isomerisation of hexafluorobuta-1,3-diene gives (1) in yields of up to 83%.[33] The mechanism involves two S_N2' substitutions by fluoride ion.

$$CF_2{=}CFCF{=}CF_2 \xrightarrow{F^-} CF_3CF{=}C{=}CF_2 \xrightarrow{F^-} CF_3C{\equiv}CCF_3$$

(1)

Conditions	Yield of butyne	Recovered butadiene
150°, 0.5 hr	68%	-
100°, 0.5 hr	83%	1%
RT , 100 days	76%	-
200°, 22 secs§	22%	40%

§ Flow reaction

I.D.2.c Fluorination Reactions

Sulphur tetrafluoride is a very useful selective fluorinating agent for converting carbonyl compounds to the corresponding difluorides and carboxylic acids to acid fluorides and trifluoromethyl derivatives.[34] It reacts with acetylene dicarboxylic acid at 70° in the presence of methylcyclohexane (which acts as a diluent) to give the diacid fluoride. At 170°, using a titanium fluoride catalyst the fluorination goes to completion giving hexafluorobut-2-yne.

$$2SF_4 + HOOCC{\equiv}CCOOH \xrightarrow[6\ hrs]{70°/diluent} FOCC{\equiv}CCOF\ (51\%) + 2HF + 2SOF_2$$

$$4SF_4 + HOOCC{\equiv}CCOOH \xrightarrow[170°\ 8\ hrs]{TiF_4\ catalyst} CF_3C{\equiv}CCF_3\ (1) + 2HF + 4SOF_2$$

Acetylenedicarbonyl fluoride has also been prepared using phenyl sulphur trifluoride instead of SF_4, or by using the dipotassium salt of the acid.[35,36]

I.D.3 Octafluoropent-2-yne

Octafluoropent-2-yne has been prepared by fluoride ion induced isomerisations of octafluoropentadienes.[33,37,38]

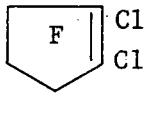
			Yield	Ref.
$CF_2=CFCF_2CF=CF_2$	(a)		68%	33
$CF_2=CFCF=CFCF_3$	(b)	$CF_3C\equiv CCF_2CF_3$	98%	37
$CF_2=C=CFCF_2CF_3$	(c)		95%	38

Conditions: (a) CsF 80° 0.5 hr; (b) Flow reaction CsF 240° 140 sec contact time; (c) CsF 100° 0.1 mm Hg.

Similarly a mixture of isomeric hexynes was produced from perfluorohexa-1,5-diene.[33]

$$CF_2=CFCF_2CF_2CF=CF_2 \longrightarrow CF_3C\equiv CC_3F_7 + C_2F_5C\equiv CC_2F_5$$

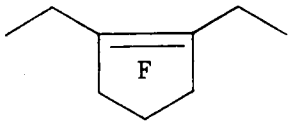
Octafluoropent-2-yne has also been prepared by treatment of 1,2-dichloroperfluorocyclopentene with SbF_3Cl_2, which gives the ring opened alkene, followed by dechlorination.[39]



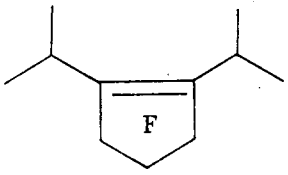
$$\xrightarrow{SbF_3Cl_2} CF_3CCl=CClC_2F_5 \xrightarrow{Zn/EtOH} CF_3C\equiv CC_2F_5$$

I.D.4 Other Bisperfluoroalkyl acetylenes

Perfluorohex-3-yne is one of the minor components obtained when perfluoro-(1,2-diethylcyclopentene) is photolysed.[40] Similarly photolysis of the di-isopropyl analogue gives di-isopropyl acetylene.



$\xrightarrow{h\nu}$ $C_2F_5C{\equiv}CC_2F_5$ + 4 other products



$\xrightarrow{h\nu}$ i-$C_3F_7C{\equiv}C$(i-C_3F_7) + 4 other products

Perfluoro-(2,2-dimethylpent-3-yne) has been prepared[41] by treating perfluoroisobutene with caesium fluoride to form the tertiary butyl carbanion, which was then reacted with 1-chloro-perfluoropropyne.

$$(CF_3)_2C{=}CF_2 + CsF \longrightarrow (CF_3)_3C^- \; Cs^+$$

$$(CF_3)_3C^- + ClC{\equiv}CCF_3 \longrightarrow (CF_3)_3C\text{-}C{\equiv}CCF_3 + Cl^-$$

I.D.5 Hexafluorohexa-2,4-diyne

Perfluorohexa-2,4-diyne was prepared by the coupling of the zinc derivative of trifluoropropyne using cupric chloride.[42]

$$CF_3CCl{=}CCl_2 \xrightarrow[DMF]{Zn} CF_3C{\equiv}CZnCl \xrightarrow{CuCl_2} CF_3C{\equiv}CCuCl \xrightarrow{x2} CF_3C{\equiv}C\text{-}C{\equiv}CCF_3$$

CHAPTER II

THE CHEMISTRY OF FLUORINATED ACETYLENES

II.A Introduction

The chemistry of fluorinated acetylenes was reviewed by Bruce and Cullen in 1969[43] and therefore this chapter gives only a brief summary of earlier work together with a more detailed discussion of recent developments in the field.

The unique electronic properties of fluorine, which account for many of the unusual aspects of fluoroacetylene chemistry, were discussed in Chapter I. Fluorine and perfluoroalkyl substitutents increase the electrophilicity of the triple bond rendering fluorinated acetylenes very susceptible to attack by electron rich species. 1-Fluoroacetylenes are unstable and this is probably because of repulsion between unshared electron pairs on the fluorine and electrons in the triple bond; this explains why they oligomerise and polymerise so readily. Their instability accounts for the fact that very little work on these systems has been published. Bisperfluoroalkyl acetylenes are comparatively stable because the fluorine lone pairs are further removed from the π system. Largely because of its commercial availability, hexafluorobut-2-yne has been more extensively studied than other perfluoroacetylenes.

The reactions of fluoroacetylenes can be divided into five basic types:

1) Oligomerisation and polymerisation

2) Free radical additions

3) Nucleophilic additions

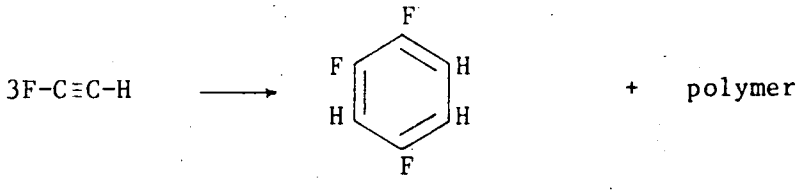
4) Cycloadditions

5) Reactions with organometallic compounds

A large amount of work has been reported concerning the use of fluorinated acetylenes as ligands in organometallic chemistry but no attempt will be made to discuss this particular area as it lies outside the scope of this thesis and has been reviewed elsewhere.[43]

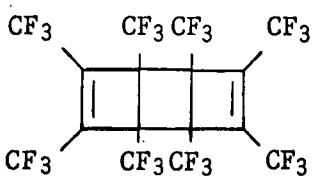
II.B Oligomerisation and Polymerisation

Mono-[16] and difluoroacetylenes[17] polymerise spontaneously at room temperature; in addition monofluoroacetylene trimerises slowly to give 1,2,4-trifluorobenzene.

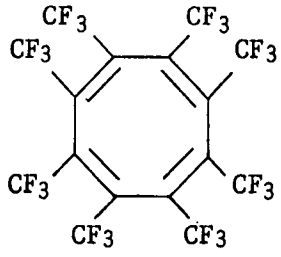


Tetrafluoropropyne is stable at 25°/10 cm Hg for at least one month but slowly polymerises under autogenous pressure at 18°.[24,25]

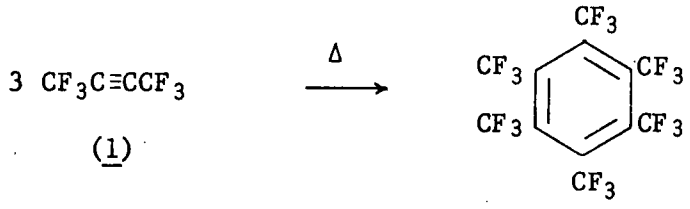
Hexafluorobut-2-yne is much more stable, a temperature of 275° being necessary to cause trimerisation.[44] The product of this thermal reaction was originally believed to be a tetramer and was assigned the tricyclic structure (2).[45] Further examination led to the incorrect assignment of the structure as the cyclooctatetraene (3).[46] The compound was finally identified as the trimer hexakistrifluoromethylbenzene (4).[44,47] Some tetramer is also claimed to be formed.[48]



(2)



(3)

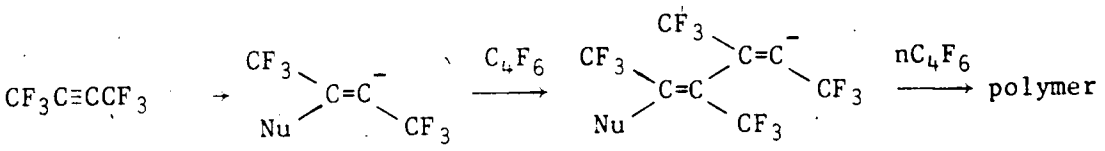


(4)

a)	275-285°	14 hr.	14% [44]
b)	375°	60 hr.	68% [47]

The thermal trimerisation of hexafluorobut-2-yne is catalysed by iodine,[44] trifluoroiodomethane,[44] and bisacrylonitrile-nickel.[49] Surprisingly, octafluoropent-2-yne does not give a trimer on heating, even in the presence of iodine.[50]

Hexafluorobut-2-yne[51,52] and octafluoropent-2-yne[3,7] both polymerise on irradiation with high energy particles from a ^{60}Co source. Trifluoromethyl hypofluorite causes hexafluorobut-2-yne to polymerise under very mild conditions but more conventional free radical initiators such as persulphates and peroxides are ineffective.[55] Several transition metal complexes have been reported to initiate the polymerisation of hexafluorobut-2-yne,[49] as has a mixture of nitrosyl hexafluoroarsenate and boron trifluoride in the presence of u.v. radiation[53] but the mechanism of these reactions is not clear. Certain types of nucleophiles cause hexafluorobut-2-yne to polymerise under mild conditions via an anionic mechanism which can be represented by the following general equation.



Nu^-
(or Nu:)

$Nu^- = F^-$ [89-92], $C_6F_5S^-$ [79]

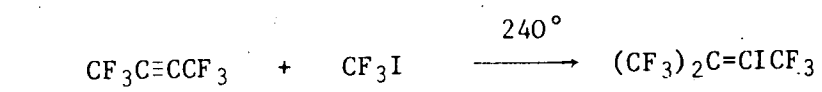
Nu: = $(CH_3)_3N$, $(C_6H_5)_3P$ [54]

These reactions will be discussed more thoroughly in the section devoted to nucleophilic additions to fluoroacetylenes.

II.C Free Radical Additions

Chlorine and bromine add readily to hexafluorobut-2-yne on u.v. irradiation[27] whereas the addition of iodine requires heat[56] but no information about the isomer distributions of the resulting 2,3-dihalogeno-but-2-enes was given. Chlorine reacts in the presence of cupric chloride in DMF to give the *trans* addition product together with a small amount of a compound which is probably the hydrogen chloride adduct.[42]

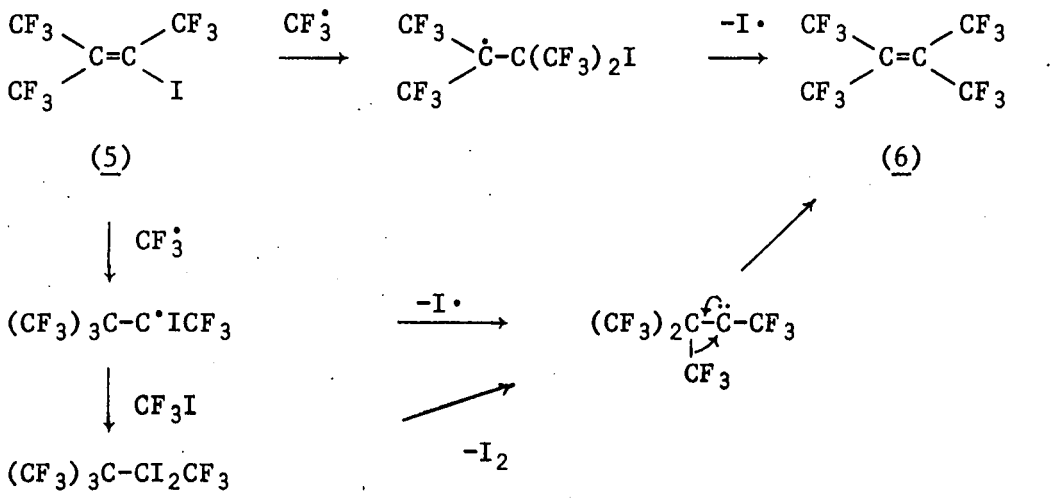
The addition of hydrogen halides is catalysed by Lewis acids[57] and appears to proceed by electrophilic attack. Hydrogen bromide, however, also adds under the influence of u.v. irradiation. Trifluoroiodomethane adds across the triple bond of hexafluorobut-2-yne at 240° to give the corresponding vinyl iodide (5)[58] and the reaction goes further at 350° using a 2:1 excess of CF_3I to give perfluoro-(2,3-dimethylbut-2-ene) (6).



(5)

$$CF_3C{\equiv}CCF_3 + 2CF_3I \xrightarrow[5\ \text{days}]{350^\circ} \underset{(6)}{(CF_3)_2C{=}C(CF_3)_2} + I_2$$

Two mechanisms have been proposed for the addition of the second molecule of trifluoromethyl iodide involving attack by $CF_3^\bullet$ at either end of the double bond in (5).



Further examples of simple radical additions to hexafluorobut-2-yne are summarised in Table II.1. However, several free radical reactions have been reported which gave rather more complicated products. The simple adducts (7), (8) and (9) are not isolated from thermal reactions of hexafluorobut-2-yne with trifluoromethyl pentafluorosulphide,[66] bistrifluoromethyl trioxide,[59] and bistrifluoromethyl nitroxide.[64] Instead products (10) - (17) are formed but the mechanisms of these reactions have not been clearly established.

Table II.1

Free Radical Additions to Hexafluorobut-2-yne

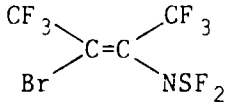
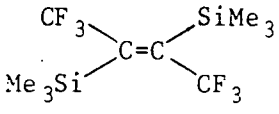
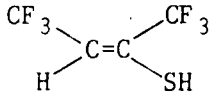
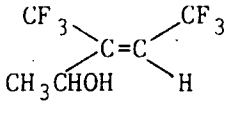
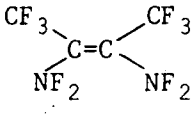
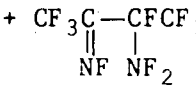
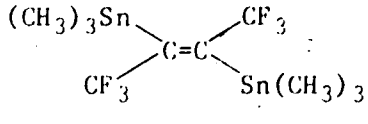
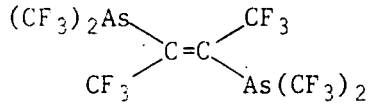
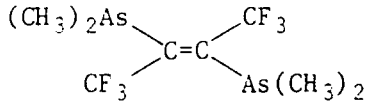
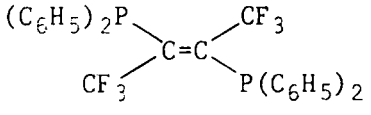
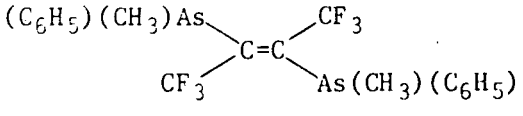
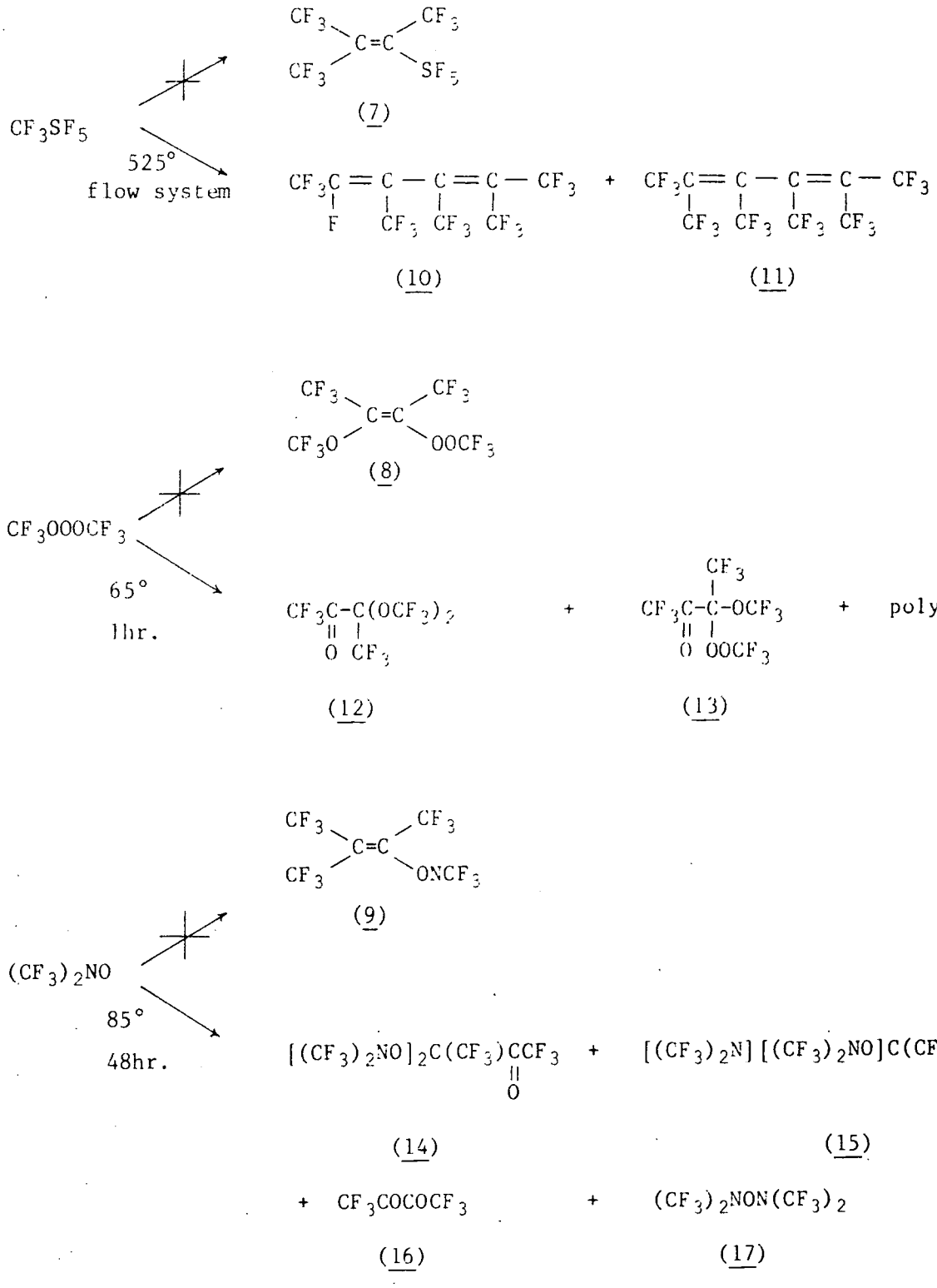
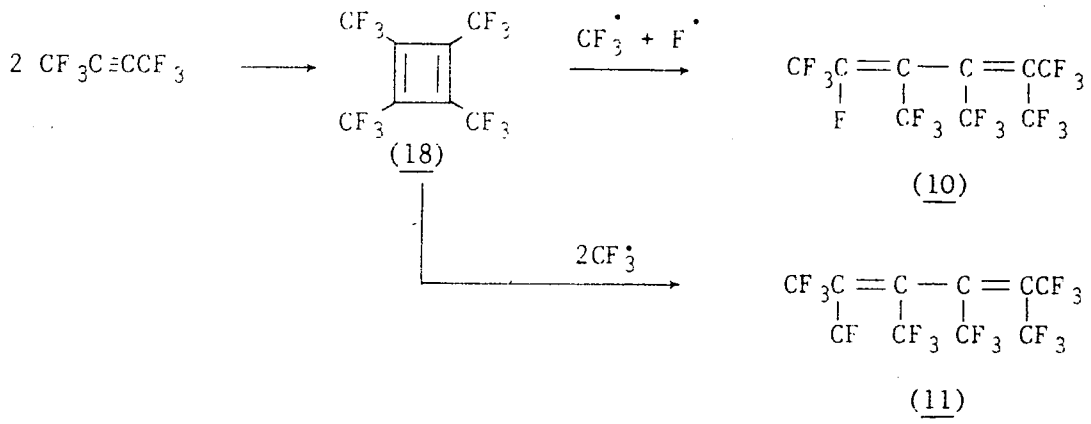
Reactant	Conditions	Products (yield)	Reference
R_FI	240-270°	$CF_3CI=C(CF_3)R_F$ (R_F = *iso*-C_3F_7 55%; R_F *n*-C_3F_7 57%; R_F C_2F_5 67%)	69
$BrNSF_2$	u.v.	 (56% *cis* 44% *trans*)	62
$Hg(SiMe_3)_2$	u.v.	 (95%)	60
H_2S	X ray	 + 2:1 adduct	63
C_2H_5OH	γ ray	 (30% *cis* 37% *trans*)	65
N_2F_4	170°	 (42% *cis* 58% *trans*) (92%); +  (1%)	61
$(CH_3)_3SnSn(CH_3)_3$	u.v.	 mainly *trans*	68

Table II.1 (continued)

$(CF_3)_2AsAs(CF_3)_2$	u.v.	 mainly *trans*	68
$(CH_3)_2AsAs(CH_3)_2$	-20°	 mainly *trans*	67
$(C_6H_5)_2PP(C_6H_5)_2$	130°		54
$(C_6H_5)(CH_3)AsAs(CH_3)(C_6H_5)$	20°		70



The mechanism proposed for the formation of hexadienes (10) and (11) involves the initial dimerisation of hexafluorobut-2-yne to tetrakistrifluoromethyl cyclobutadiene (18), which is then attacked by $CF_3^{\bullet}$ and $F^{\bullet}$ radicals generated from CF_3SF_5.

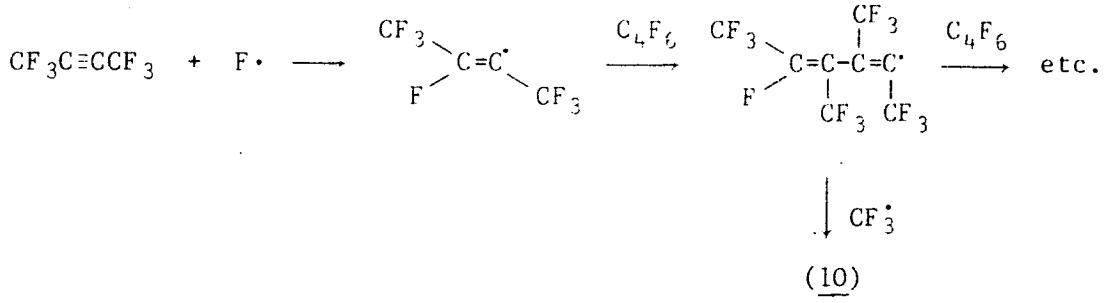


(18)

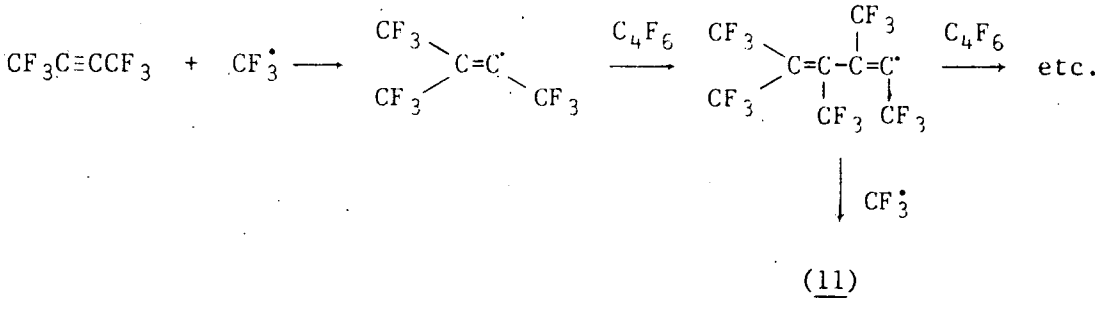
(10)

(11)

However, in view of the complexity of the products and the low yields of (10) and (11) which were obtained in this reaction, the following mechanism, which does not call for the intermediacy of the high energy dimer (18), seems most appropriate.

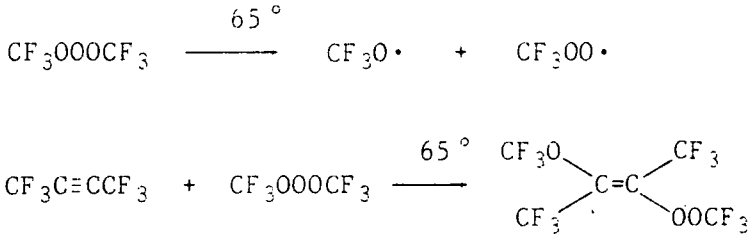


(10)

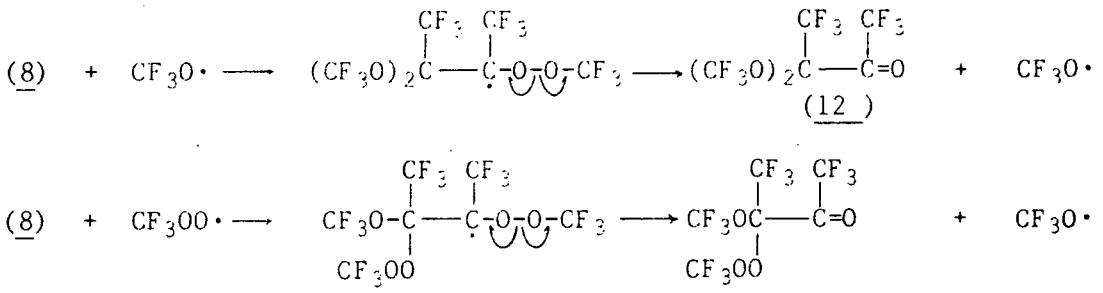


(11)

The reaction with bistrifluoromethyl trioxide is believed to proceed via the simple adduct (8) which reacts with $CF_3O\cdot$ and $CF_3OO\cdot$ radicals to give (12) and (13) respectively.

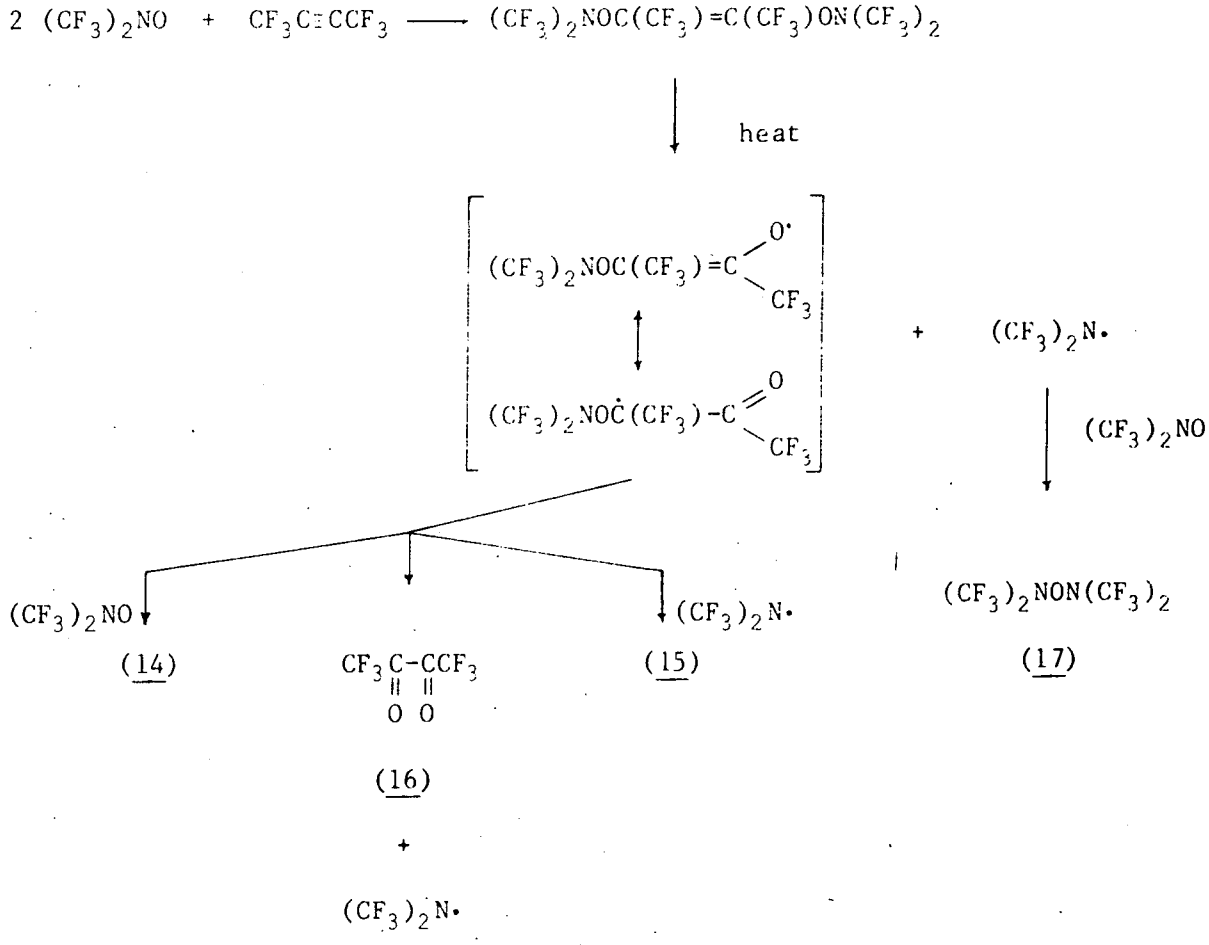


(8)



(13)

Of the several mechanisms proposed for the reaction with bistrifluoromethyl nitroxide, that shown below is the most probable.[64]



II.D Nucleophilic Additions

II.D.1 Introduction

Hexafluorobut-2-yne reacts with a wide range of nucleophiles of the type R_nEH, where E is an element from groups IV, V or VI of the periodic table, to give alkenes which are generally resistant to further addition. However, a second molecule of the nucleophile will sometimes add under forcing conditions.

$$R_nEH + CF_3C{\equiv}CCF_3 \longrightarrow R_nEC(CF_3){=}CHCF_3$$

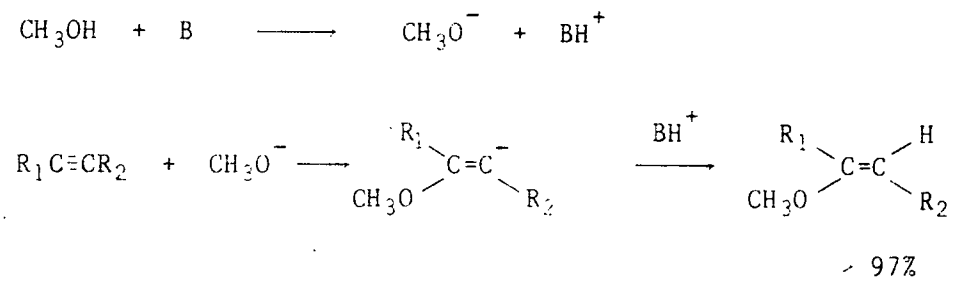
Information on the stereochemistry of these additions is quite limited but most of the available data point towards a general tendency to form *trans* addition products. A few examples of nucleophilic additions giving cyclic products have also been reported.

II.D.2 O Nucleophiles

Methanol and ethanol addition requires a basic catalyst and 2:1 adducts are obtained at elevated temperatures.[57]

$$CF_3C{\equiv}CCF_3 + ROH \xrightarrow[30°]{RONa} CF_3C(OR){=}CHCF_3 \xrightarrow[RONa]{ROH\ \ 70°} CF_3C(OR)_2{-}CH_2CF_3$$

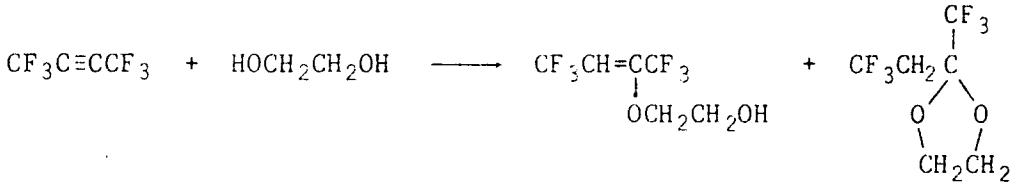
The base catalysed reaction of methanol with hexafluorobut-2-yne (1) and trifluoropropyne (19) gave predominantly *trans* addition products.[71]

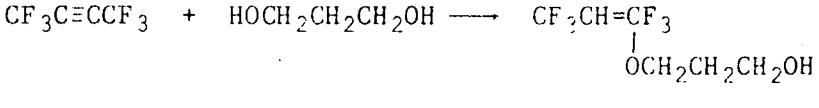


(1) $R_1 = R_2 = CF_3$

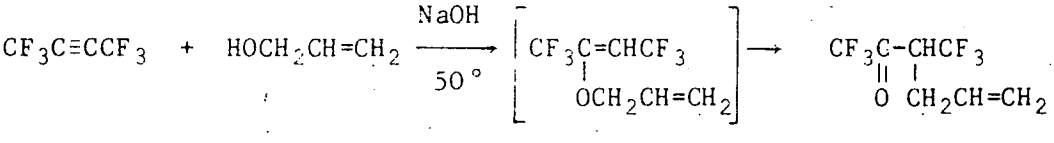
(19) $R_1 = H$, $R_2 = CF_3$

Dihydric alcohols add to hexafluorobut-2-yne in base catalysed reactions to give both cyclic and acyclic products.[72]





Addition of allyl alcohol is accompanied by a Claisen rearrangement.[73]

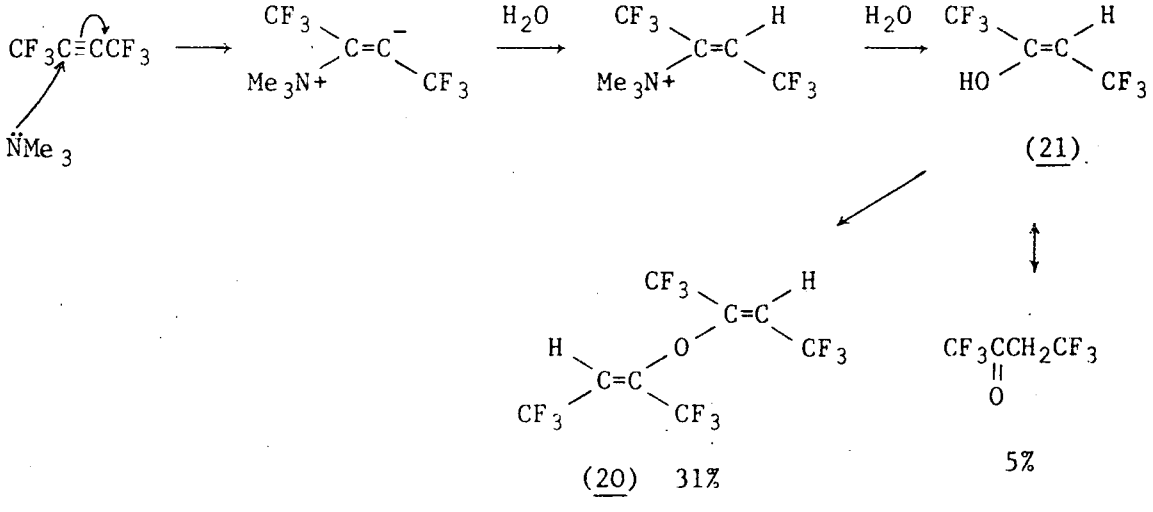


Acetic acid adds to hexafluorobut-2-yne to give an enol acetate and a diacetate, together with substantial quantities of decomposition products.[74]

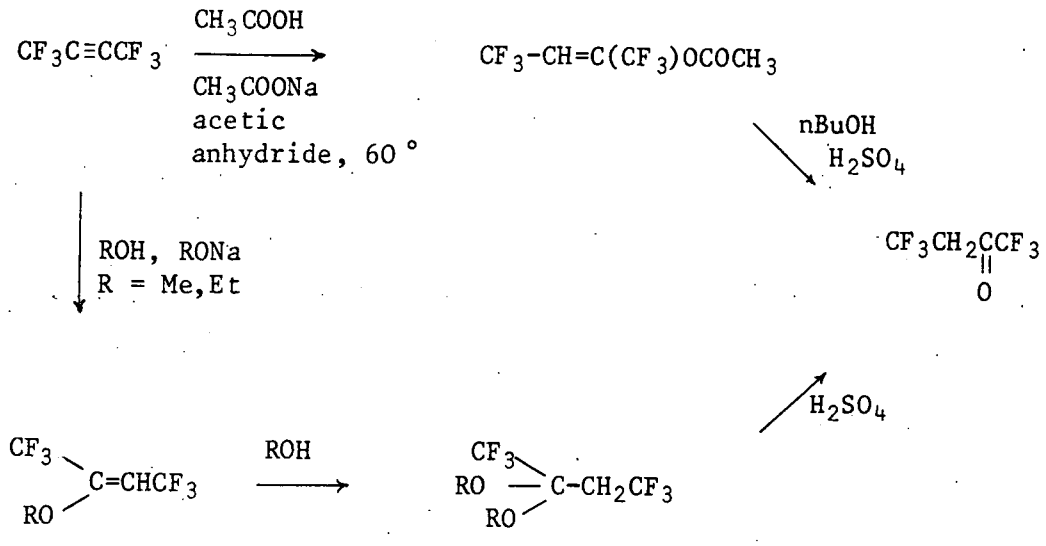
$$CF_3C{\equiv}CCF_3 + CH_3COOH \xrightarrow[CH_3COONa\ (CH_3CO)_2O]{60^\circ} CF_3CH{=}C(CF_3)OCOCH_3\ (40\%) + CF_3COCH_3\ (34\%)$$

+ some $CF_3CH_2C(CF_3)(OCOCH_3)_2$

Hexafluorobut-2-yne reacts with water in the presence of triethylamine but many products are formed.[54] Hexafluorobutan-2-one, the expected hydrolysis product, is produced in only 5% yield. The main product is the ether (20), formed by attack of the enol (21) on a further molecule of butyne. The formation of the other products (carbon dioxide, N,N-dimethylaminohexafluorobut-2-ene and *trans*-2H-heptafluorobut-2-ene) suggests that breakdown of both the butyne and the amine catalyst occurs.

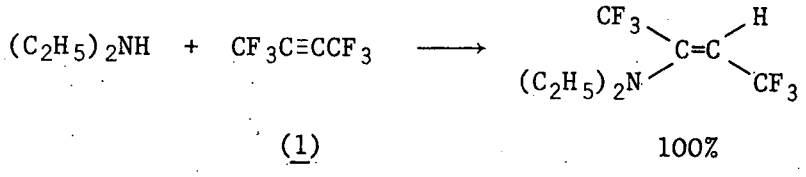


Hydration of hexafluorobut-2-yne has been achieved indirectly by hydrolysis of the 1:1 acetic acid[74] and 1:2 alcohol[57] adducts.

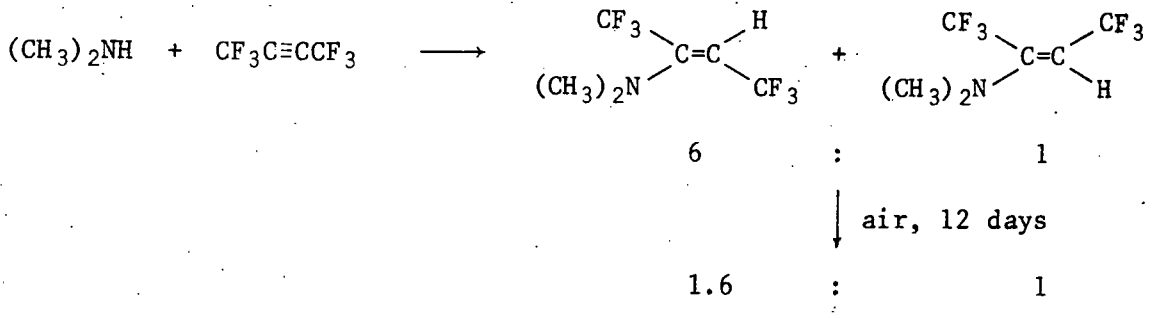


II.D.3 N Nucleophiles

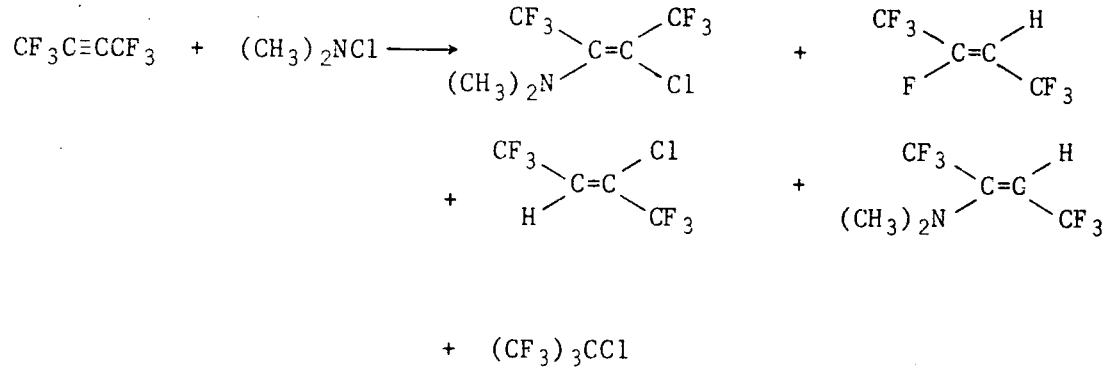
Diethylamine adds to hexafluorobut-2-yne to give a 1:1 adduct which is 100% *trans*,[57] whereas dimethylamine gives a 6:1 mixture of *trans* and *cis* isomers as the initial reaction product.[75] Oxygen apparently catalyses the isomerisation of this mixture, since leaving it exposed to air at 20° results in an increase in the *cis* isomer content.



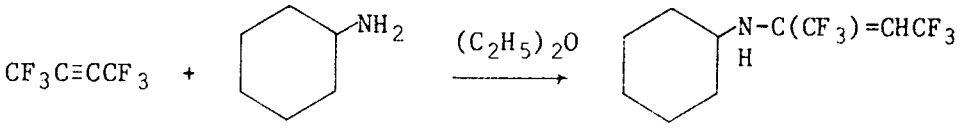
(1) 100%



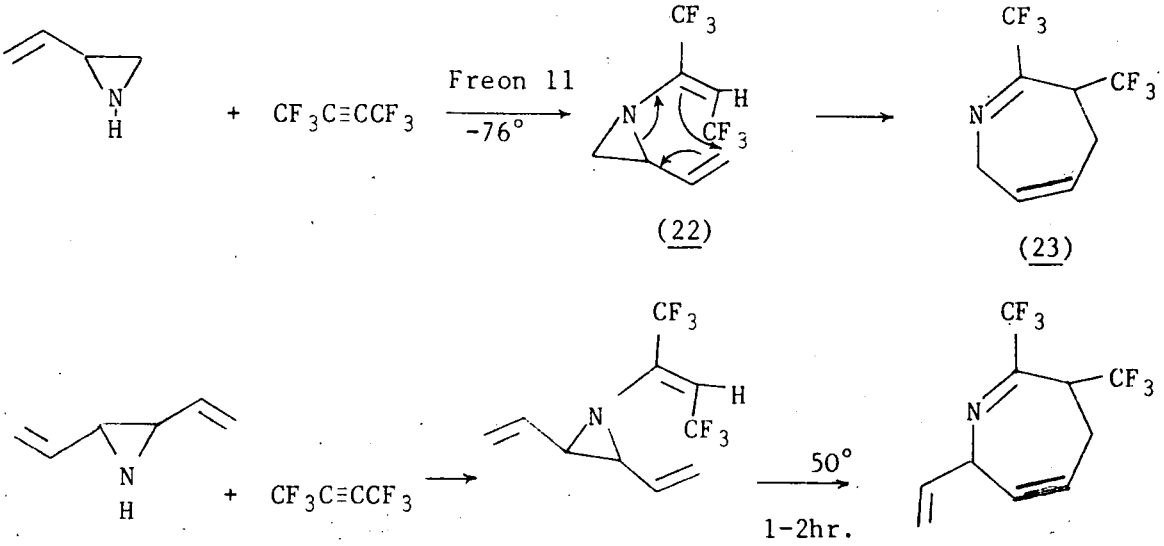
Reaction with chlorodimethylamine[54] at 85° gave a complex mixture of products including the expected 1:1 adduct. Interestingly, only the *cis* isomer was detected and it is possible that this reaction involves free radical addition rather than nucleophilic attack by nitrogen.



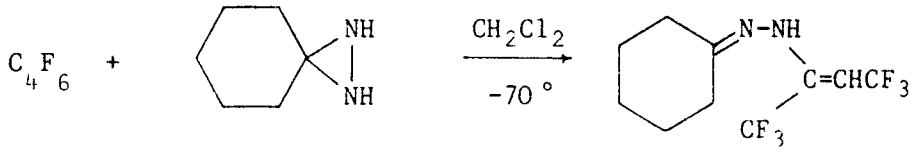
Cyclohexylamine forms a 1:1 adduct of unknown stereochemistry.[76]



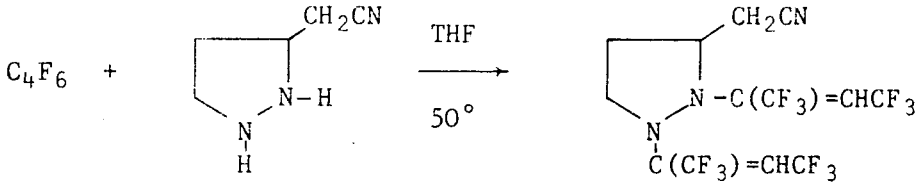
The addition of 2-vinylaziridine[77] to hexafluorobut-2-yne at low temperature gave the divinylaziridine (22), which on standing at room temperature isomerised to the azepine (23). Similarly, the divinylaziridine (24) gave (25) and (26).



Another example of the formation of ring opened products from strained cyclic amines is given below. As might be anticipated, the less strained pyrazolidine gives the simple 2:1 adduct.

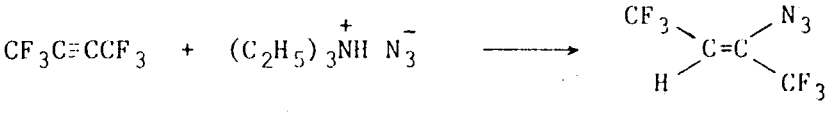


[103]



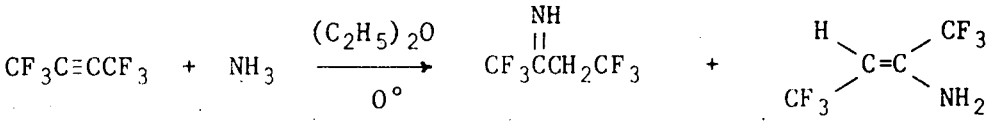
[145]

Triethylammonium azide reacts with hexafluorobut-2-yne to give the *trans* hydrazoic acid adduct (27).[78]



(27)

Ammonia and hydrazine add to hexafluorobut-2-yne[79] to give good yields of imines. In addition, ammonia gives some vinylamine (29) and these tautomeric products were shown not to interconvert at 25°.



(28) (29) 100% *trans*

$$CF_3C{\equiv}CCF_3 + NH_2NH_2 \xrightarrow[-60^\circ]{(C_2H_5)_2O} CF_3\overset{\overset{NNH_2}{\|}}{C}-CH_2CF_3$$

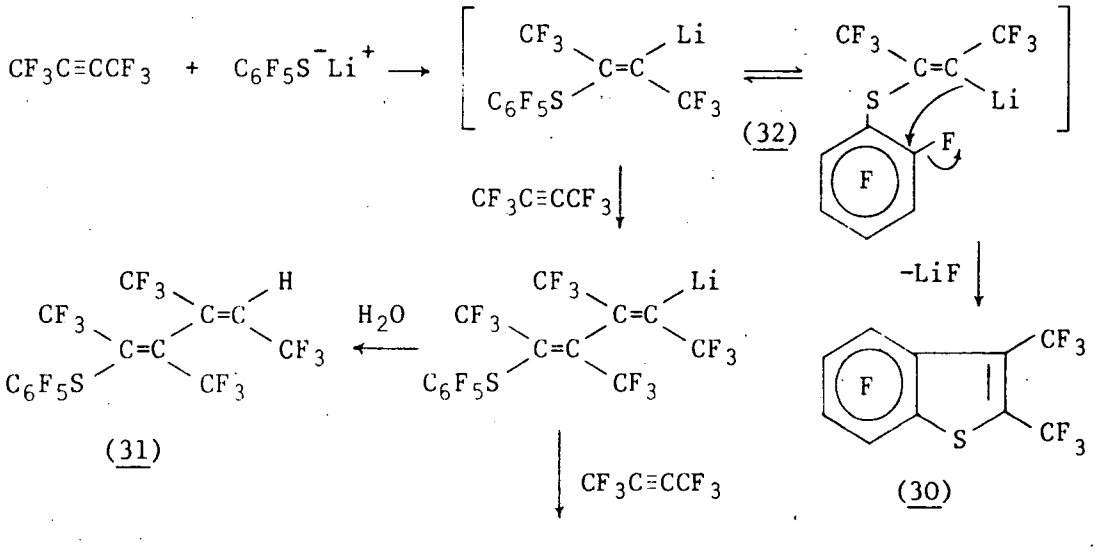
II.D.4 S Nucleophiles

Hexafluorobut-2-yne has been reacted with thiols in the presence of base[80] but no stereochemical information on the products was given.

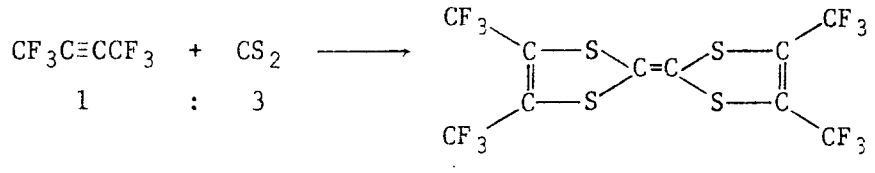
$$RSH + CF_3C{\equiv}CCF_3 \xrightarrow[\text{or } Me_3N]{NaOEt} RSC(CF_3){=}CHCF_3$$

$R = C_2H_5$, HOC_2H_4, C_4H_9, C_6H_5

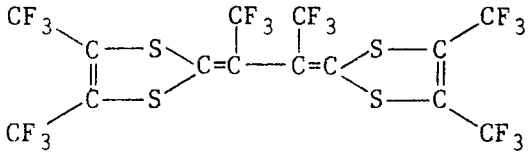
Lithium pentafluorophenylthiolate reacts with hexafluorobut-2-yne at -70° to give (30) and (31) together with a large amount of polymer.[81] These products are thought to arise from the lithio derivative (32), which probably exists as an equilibrium mixture of *cis* and *trans* isomers. The *cis* isomer can cyclise by elimination of lithium fluoride to give the benzothiophene (30). Addition of a further acetylene molecule to (32) gives rise to the diene (31).



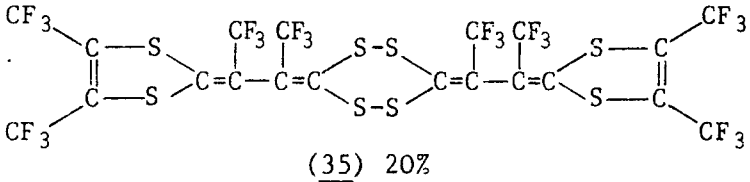
Adducts (33) - (35) were obtained from the reaction with carbon disulphide at 100°.[82]



(33) 2%

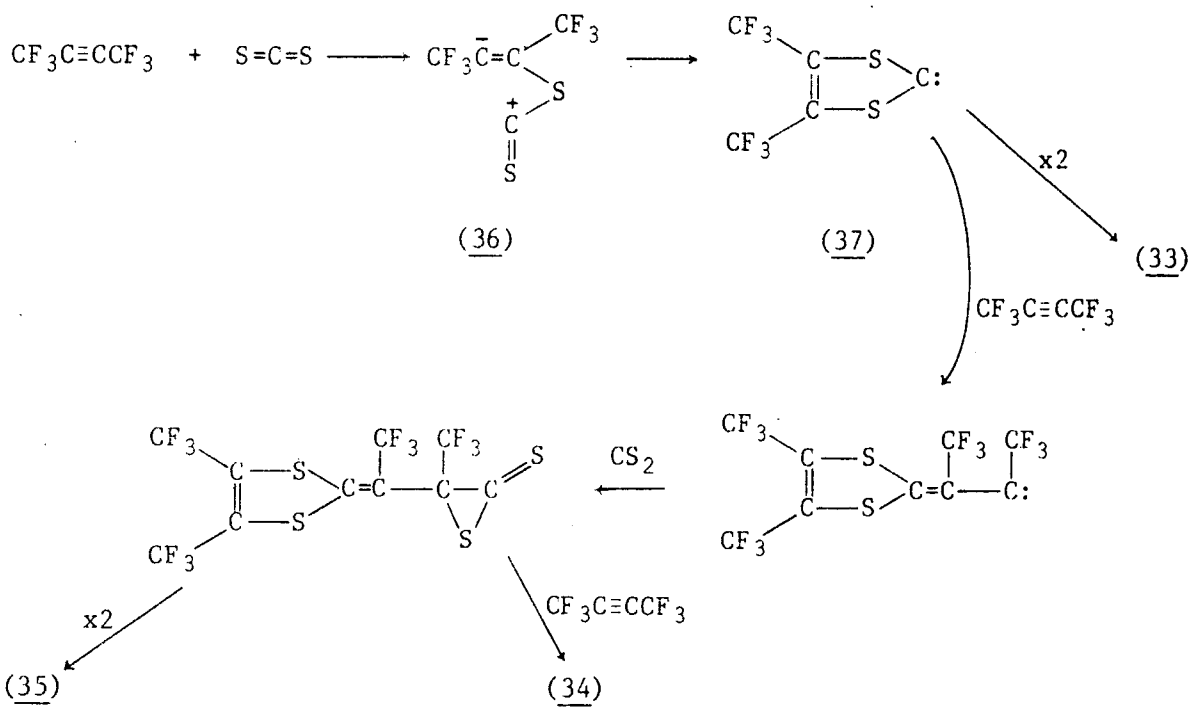


(34) 60%



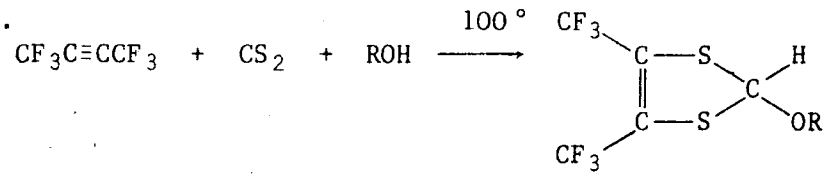
(35) 20%

The mechanism of this reaction is believed to involve an initial nucleophilic attack by sulphur to give the zwitterion (36), which cyclises producing the carbene (37). This can either dimerise to give (33) or react with more hexafluorobut-2-yne to produce (34) and (35).

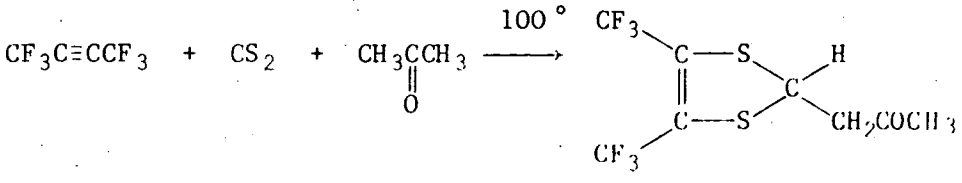


Carbene (37) can also be trapped with reagents other than hexafluorobut-2-yne provided that they react more rapidly. Alcohols, phenols, acids, aliphatic aldehydes and ketones, and aromatic aldehydes have been used to produce a large number of heterocyclic derivatives.

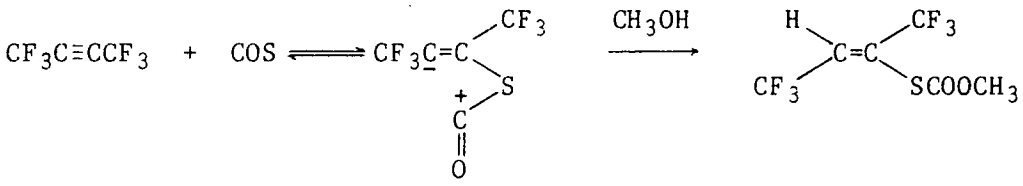
e.g.



R = Me, Et No (33), (34) or (35) formed

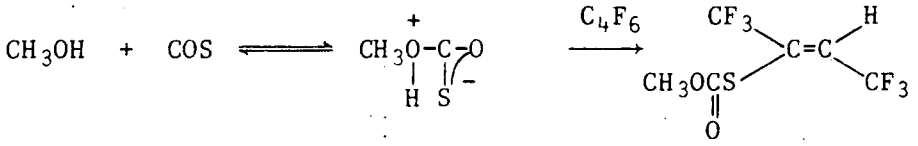


Carbonyl sulphide, however, does not react with hexafluorobut-2-yne unless methanol is present. It was suggested that a reversible nucleophilic attack occurs, producing zwitterion (38) which, in the absence of suitable trapping agents, collapses back to starting materials. A carbene analogous to (37) is not formed from (38), for this would necessitate nucleophilic attack at the oxygen of the carbonyl group.

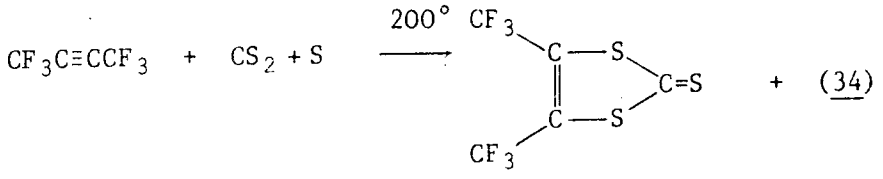


(38)

However, this mechanism does not explain why (38) does not react further with hexafluorobut-2-yne. The failure to observe products analogous to (33), (34) and (35) is probably due to the lower nucleophilicity of carbonyl sulphide compared with carbon disulphide and hence (38) is not the primary intermediate in this reaction. An alternative mechanism, involving the initial formation of an adduct between the alcohol and carbonyl sulphide, seems more likely.

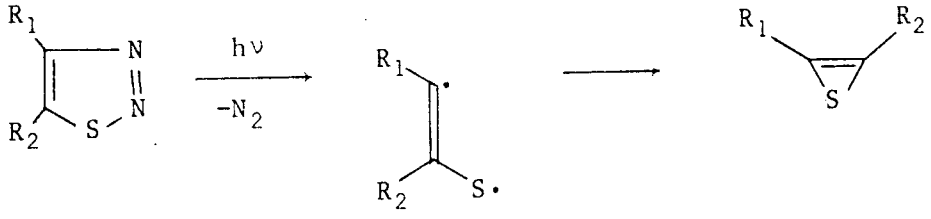


Reaction of hexafluorobut-2-yne with sulphur and carbon disulphide at 200° gave the cyclic trithiocarbonate (39) along with some (34).[83]



(39)

The formation of bistrifluoromethyl thiophenes from photolyses of 1,2,3-thiadiazoles (40) in the presence of hexafluorobut-2-yne probably involves a nucleophilic attack by the proposed thiirene intermediates (42).[84] Direct addition of the diradical (41) to the acetylene can be ruled out because (40b) would give the 4-methyl thiophene (43b), whereas, in fact, both (40b) and (40c) give the same product (43c). This is rationalised by assuming that the acetylene adds to (42) across the less crowded side of the molecule.



(40) a $R_1 = R_2 = H$

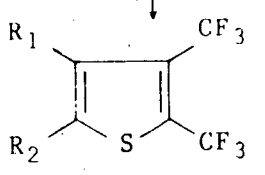
b $R_1 = CH_3$, $R_2 = H$

c $R_1 = H$, $R_2 = CH_3$

(41)

(42) a $R_1 = R_2 = H$

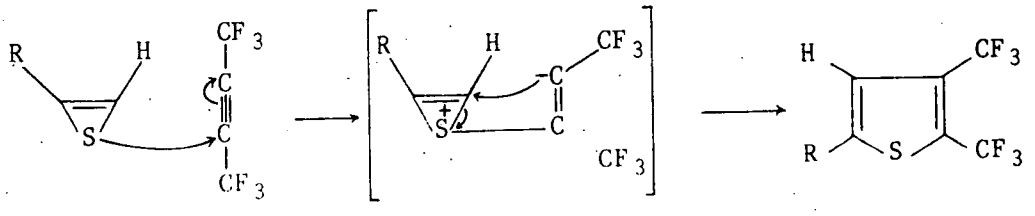
b ≡ c $R_1 = H$, $R_2 = CH_3$



(43) a $R_1 = R_2 = H$

b $R_1 = CH_3$, $R_2 = H$

c $R_1 = H$, $R_2 = CH_3$



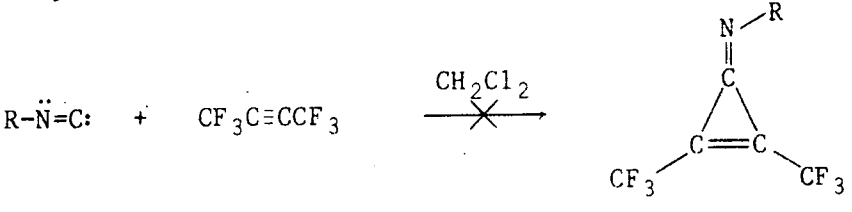
(42)

(43) a R = H

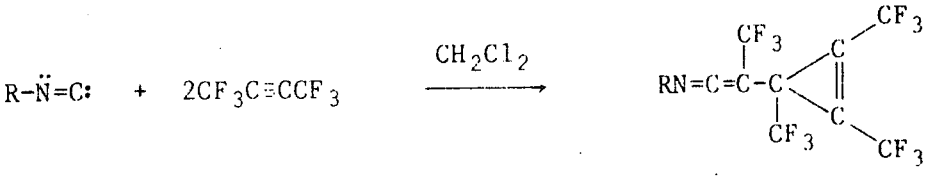
c R = CH_3

II.D.5 C Nucleophiles

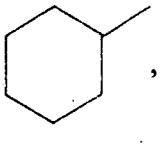
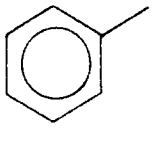
Reaction of isocyanides with hexafluorobut-2-yne in inert solvents gave rather unusual products.[85] Instead of the expected 1:1 adducts (44), the products (45) were found to arise from reaction of two molecules of butyne with one of the isocyanide.



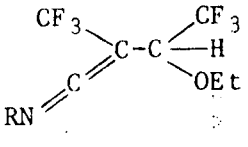
(44)



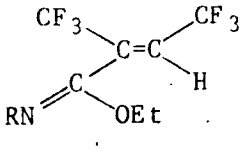
(45)

R =  ,  , t-Bu

When the reaction was carried out in ethanol, two different 1:1:1 adducts (46) and (47) were isolated.

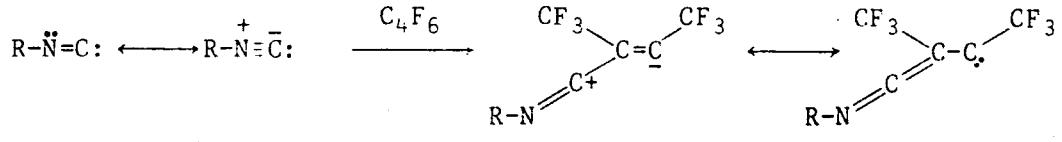


(46)



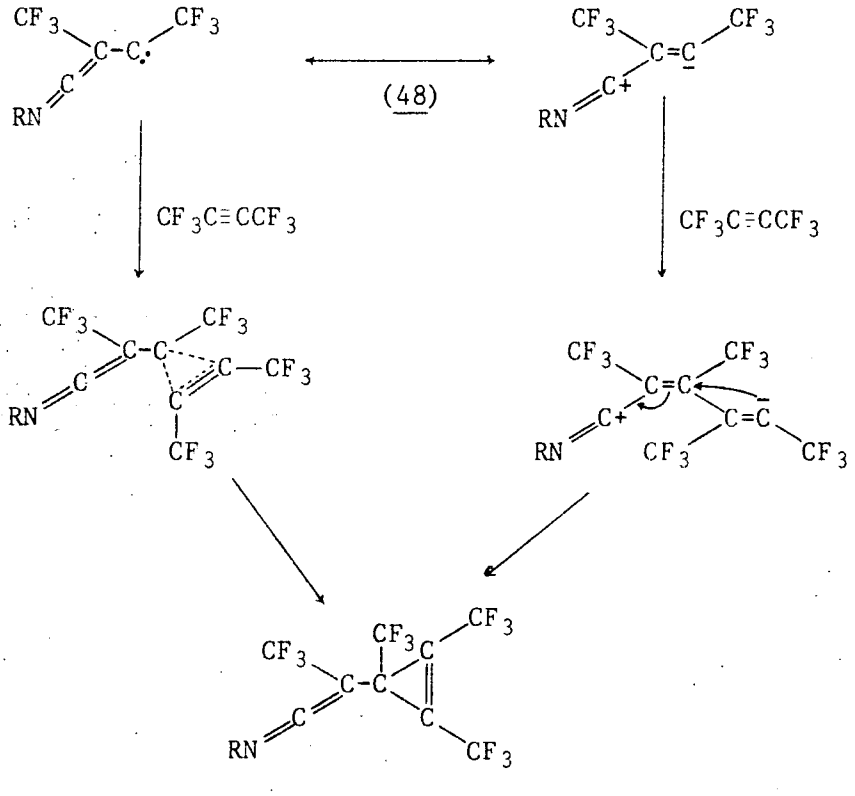
(47)

The mechanism proposed to account for these products involved the initial nucleophilic attack by the carbon of the isocyanide group on the acetylenic triple bond to give a 1,3 dipolar adduct (48).



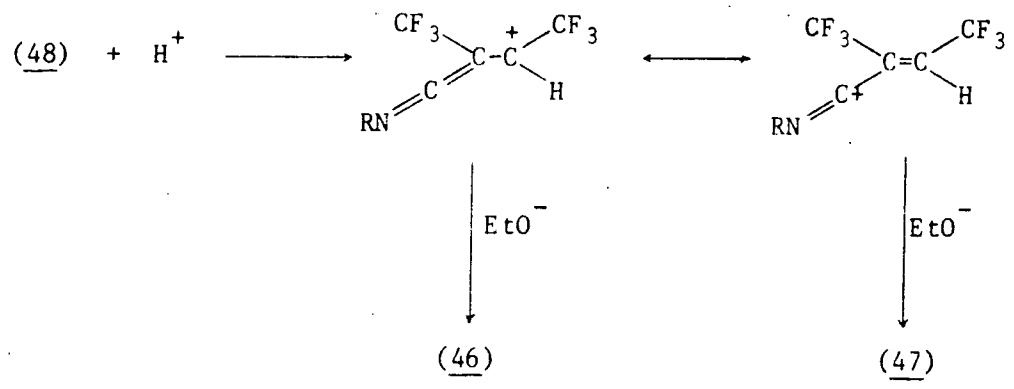
(48)

The intermediate (48) can then react either as a carbene or as a carbanion to give the 2:1 adduct (45).

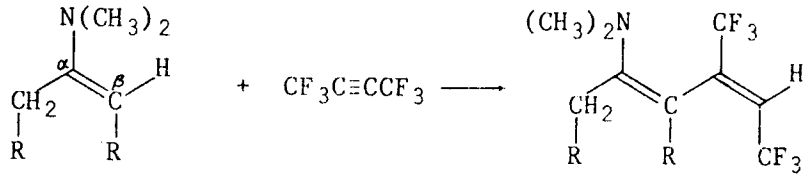


(45)

In ethanol the intermediate (48) is first protonated and then ethoxide ion adds in one of two positions to give the ketenimine (46) and the imino ester (47).



Enamines (49) and (50) react with hexafluorobut-2-yne to give products resulting from nucleophilic attack by the β carbon.[86]



(49) R = $-(CH_2)_3-$

(50) R = CH_3

II.D.6 Addition of Metalloidal and Metal Hydrides

A wide range of compounds containing M-H bonds, where M is an element from Groups IV and V or a transition metal, have been added to hexafluorobut-2-yne under various conditions. A summary of some of these reactions is given in Table II.2.

As can be seen the adducts have a predominantly *trans* configuration indicating that they are formed by *anti* addition of the hydride. However, it seems unwise to speculate on the mechanism of hydride addition on the basis of *cis-trans* iosmer ratios in the product, particularly as

Table II.2

Reactions of Hydrides with Hexafluorobut-2-yne

Reactant	*Trans* Isomer%	Conditions	Ref.
$(CH_3)_3SiH$	84-92	Dark reaction 235°	87
	100[b]	u.v. irradiation	87
$(C_2H_5)_3GeH$	92	u.v. irradiation	87
$(CH_3)_3SnH$	100	Dark reaction T ≤ 20°	87
$(C_2H_5)_3SnH$	98	Dark reaction T ≤ 20°	87
$(C_4H_9)_2SnH_2$	-[a]	Dark reaction T ≤ 20°	87
$(C_4H_9)_3SnH$	∿ 100	Dark reaction T ≤ 20°	87
$(CH_3)_2NH$	86	Dark reaction T ≤ 20°	75
$(CH_3)_2PH$	100	Dark reaction T ≤ 20°	54
$(C_6H_5)_2PH$	80	Dark reaction T ≤ 20°	54,75
$(CF_3)_2PH$	80	u.v. irradiation	54
$(CH_3)_2AsH$	86	Dark reaction T ≤ 20°	75
$(CH_3)(C_6H_5)AsH$	92	Dark reaction T ≤ 20°	75
$(CF_3)_2AsH$	100	Dark reaction 210°	75
$(CO)_5MnH$	100	Dark reaction T ≤ 20°	88
$(CO)_5ReH$	100	Dark reaction T ≤ 20°	89
$[(C_2H_5)_3P]_2PtClH$	0	Mild heating	90

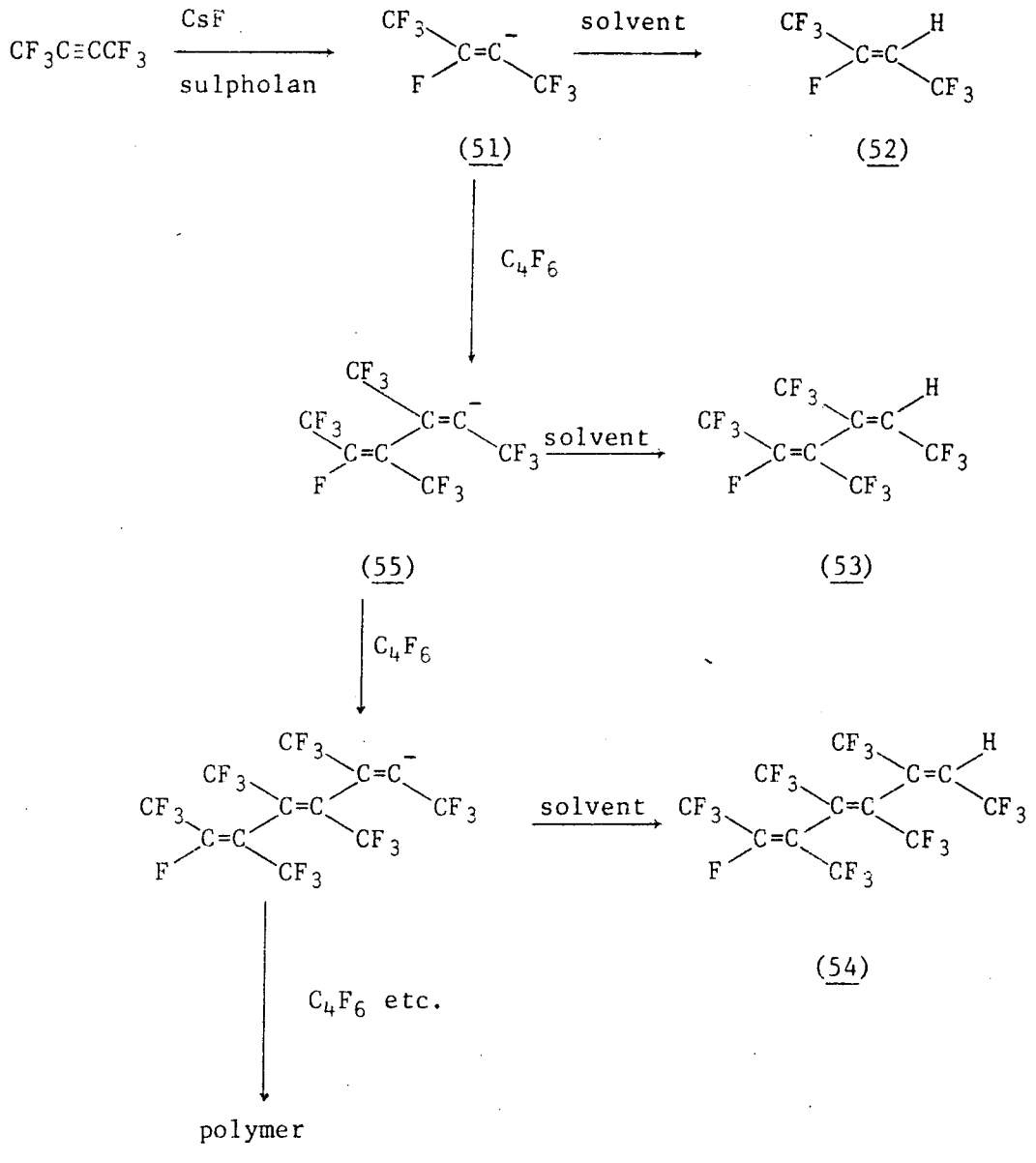
a gives $(C_4H_9)_2Sn(C(CF_3)=CHCF_3)_2$

b also gives 2:1 adduct $(CH_3)_3SiCH(CF_3)-CH(CF_3)Si(CH_3)_3$

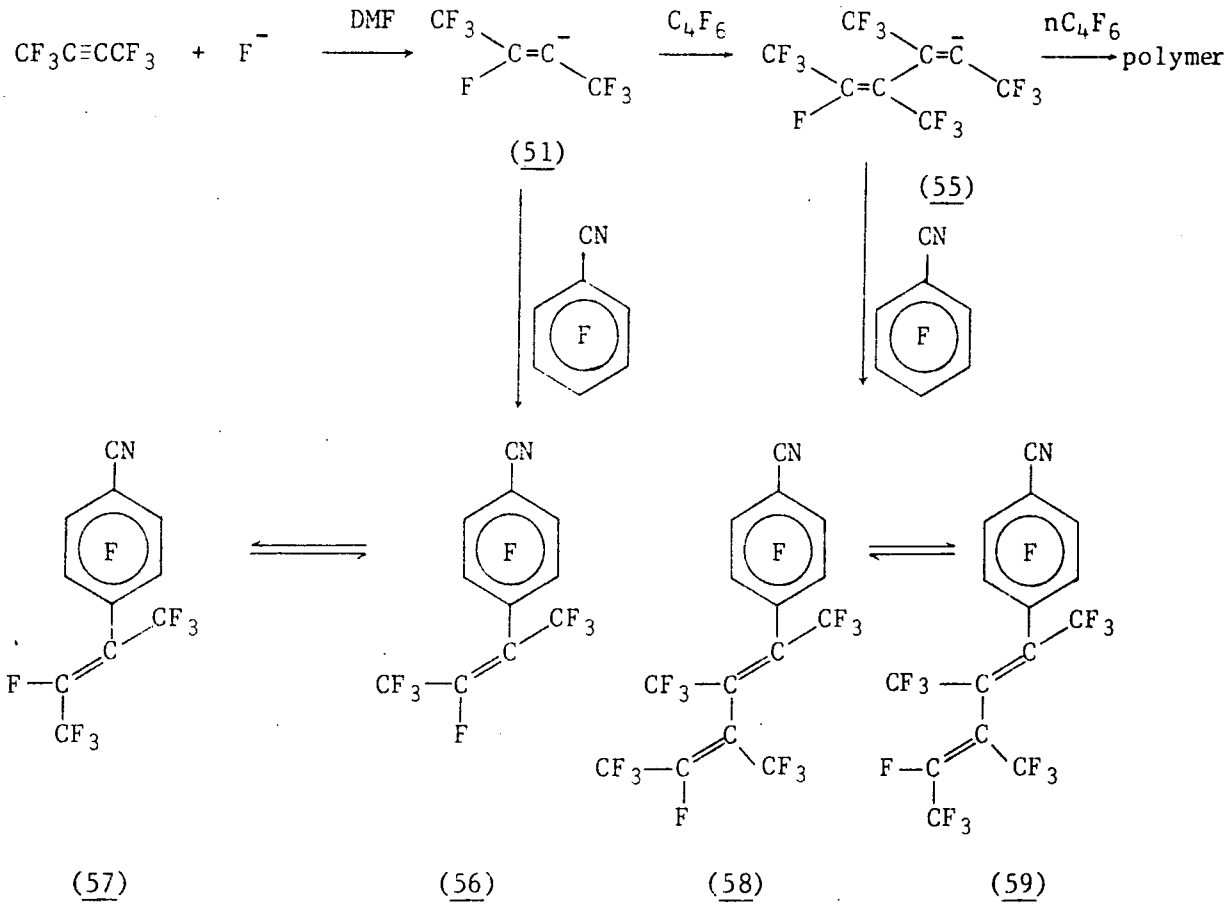
hydrides have been shown to catalyse *cis-trans* isomerisation in certain cases.[91] Cullen has suggested that the reactions of amines, phosphines, arsines and tin hydrides proceed by nucleophilic attack, the hydrogen atom on the tin being the nucleophile in the latter case. He made this assumption on the basis of observations that the rates of reactions of phosphines and arsines decrease as more electronegative groups are attached to the central atom and that the rates of reaction with hexafluorobut-2-yne are generally faster than with the less electrophilic trifluoropropyne. It is possible, however, that the addition reactions of some of these hydrides (e.g. the silanes and germanes) are free radical processes.

II.D.7 Reactions with Fluoride Ion

Hexafluorobut-2-yne polymerises in the presence of fluoride ion generated from caesium fluoride in various aprotic solvents.[92-95] The polymerisation appears to go via nucleophilic attack of fluoride ion on the triple bond to give the heptafluorobutenide anion (51). This then reacts with further molecules of acetylene to give a series of anions, each of which can abstract a proton from the solvent. A series of oligomers of the type $H-(C_4F_6)_n-F$ is thus produced and the dimer (53) and trimer (54) have been isolated.[95] The properties of the polymer are discussed in Chapter V.

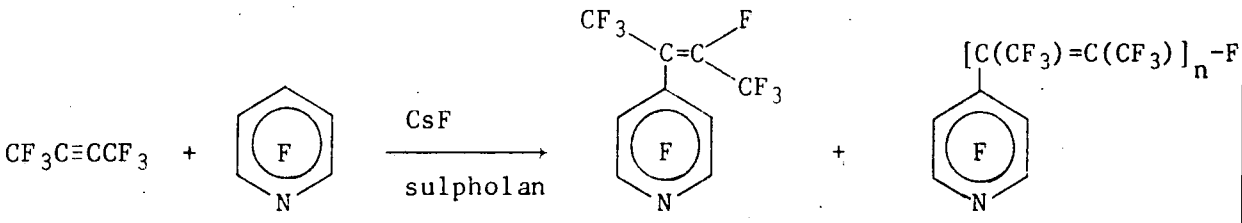


In the presence of suitable electrophilic reagents the intermediate carbanions can be trapped. Thus when hexafluorobut-2-yne is added to perfluorobenzonitrile and caesium fluoride in DMF, products (56)-(59) are obtained along with some polymer.[93] Under the reaction conditions (56) is in equilibrium with (57) (5:1) and (58) is in equilibrium with (59) (5:1).



(57) (56) (58) (59)

Similarly using pentafluoropyridine as a trapping agent products (60)-(62) were produced.

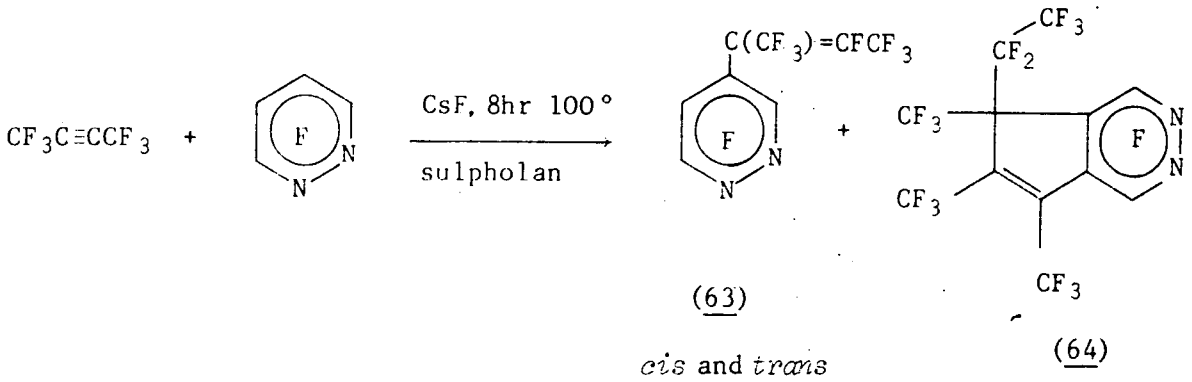


(60) 10% *cis* and *trans*

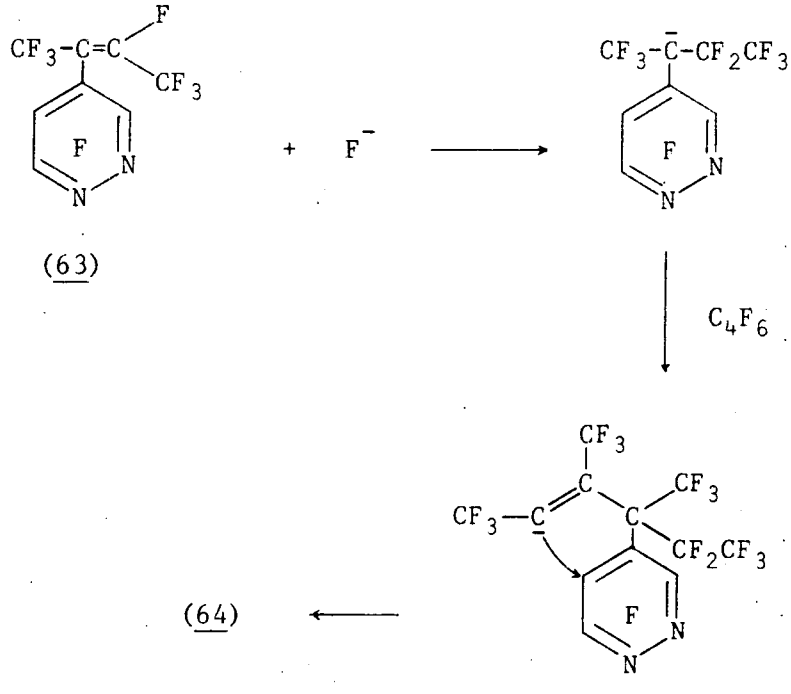
(61) n=2 18%

(62) n=3 10%

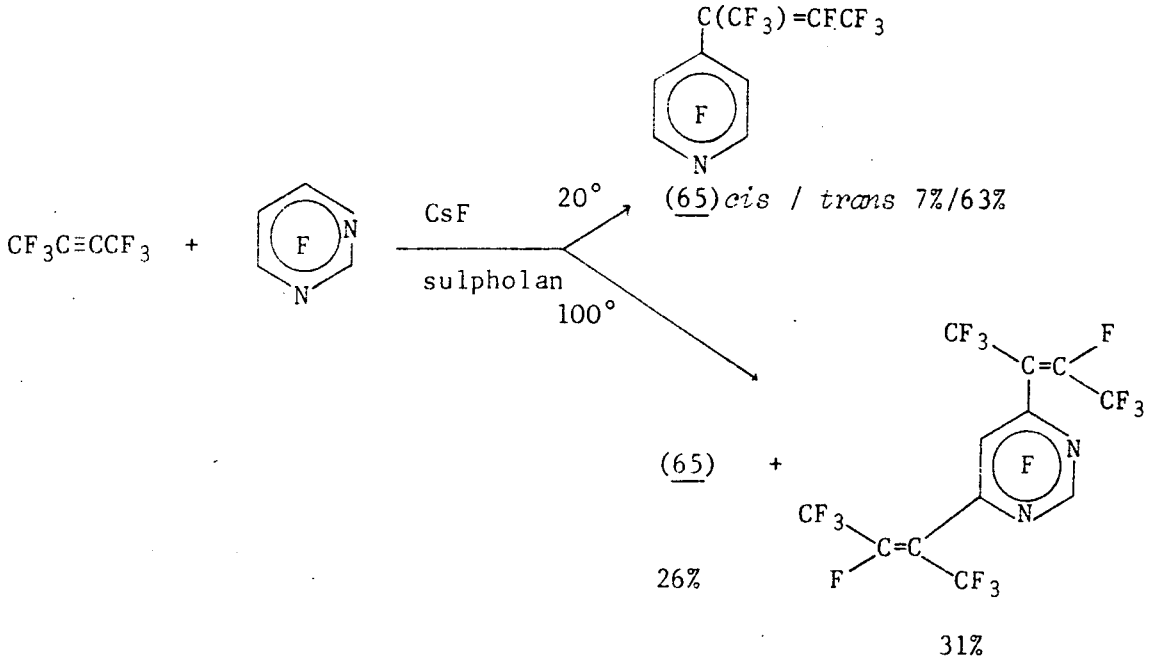
Trapping agents more susceptible to nucleophilic attack, such as tetrafluoropyridazine give better yields of substitution products and less polymer.[92,96] However, in this case the 2:1 adduct does not have a structure analogous to (58) or (61) but has been shown to be a diazaindene.



Of the several possible ways in which (64) may be formed, the following seems most probable.



A similar reaction with tetrafluoropyrimidine at 20° gave a high yield of a mixture of *cis* and *trans* isomers of the 1:1 adduct (65).[96] At 100° some disubstituted compound was also isolated.



Miller has reported an interesting fluoride ion promoted telomerisation of hexafluorobut-2-yne with the bromobutenes (66) and (67).[97] Telomers of the type $F\text{-}(CCF_3{=}CCF_3)_n\,Br$, where $2 \leqslant n \leqslant 6$, are obtained together with some fully fluorinated products. The amounts of the various telomers produced are dependent on the ratio of butyne to bromobutene used.

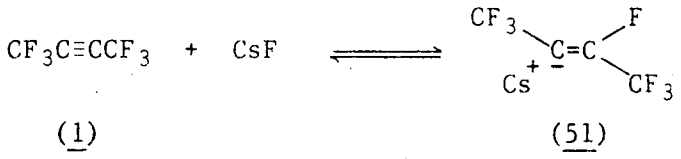
When (67) is used, the initial step is the formation of the monobromo compound (66).

$$\underset{(67)}{CF_3CBr{=}CBrCF_3} + CsF \xrightarrow{CH_3CN} \underset{(66)}{CF_3CF{=}CBrCF_3} + CsBr \qquad (1)$$

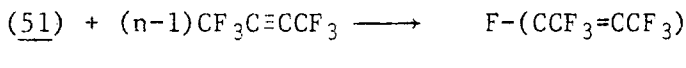
$$CF_3CF{=}CBrCF_3 + (n-1)\,CF_3C{\equiv}CCF_3 \xrightarrow[CH_3CN]{CsF} F\text{-}(CCF_3{=}CCF_3)_n\,Br \qquad (2)$$

The telomerisation, summarised by equation (2), is believed to take place in several steps analogous to the initiation, propagation and termination steps of a conventional free radical reaction. Reaction of hexafluorobut-2-yne with caesium fluoride gives the anion (51),

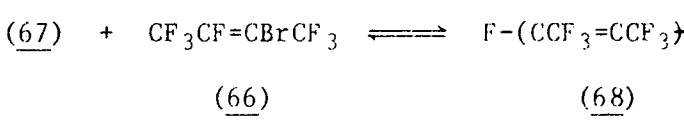
which reacts further to give a series of anions of progressively higher molecular weight. These can react with (66) by nucleophilic attack on bromine, giving the telomers (68) and regenerating (51). A slow vinylic substitution by fluoride ion gives small yields of fully fluorinated polyenes (69).



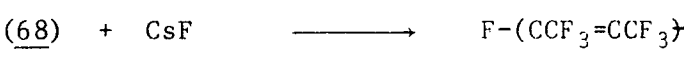
(1) (51) (3)



(51) (67) (4)



(67) (66) (68) (51) (5)



(68) (69) (6)

Table II.3 shows the yields of the various telomers obtained in two experiments using different ratios of butyne (1) to butene (66).

It is interesting that all the double bonds in the products (68) and (69) have *trans* configurations. This is consistent with exclusive *anti* addition of caesium fluoride and of the intermediate alkylcaesiums to hexafluorobut-2-yne and with retention of configuration during bromine transfer.

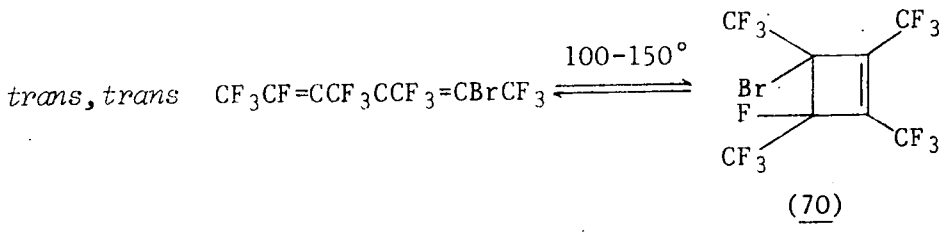
This reaction is of great interest as it is the basis for the synthesis of a range of novel perfluorinated compounds. For example, when the hexadiene (68), n=2, is heated at 100-150° it gives the cyclobutene (70); treatment with methyllithium generates tetrakis-

Table II.3

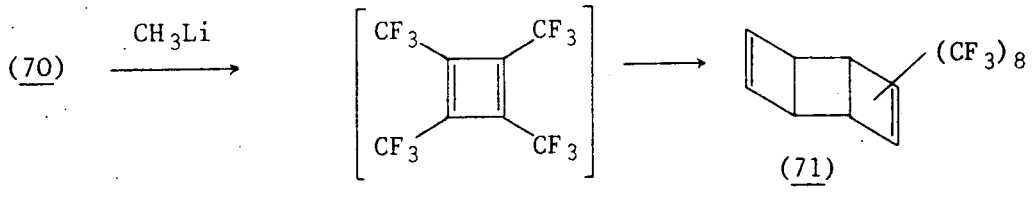
Yields of Products Obtained by Anionic Telomerisation of Hexafluorobut-2-yne[97]

mmol of (61)	mmol of (66)	Conditions	Products
176	208	30° 2hr.	(69) n=2 5%
			(68) n=2 87%
			(68) n=3 3%
15	5.3	30° 3.5hr.	(68) n=2 7%
			(68) n=3 23%
			(68) n=4 38%
			(68) n=5 20%
			(68) n=6 11%

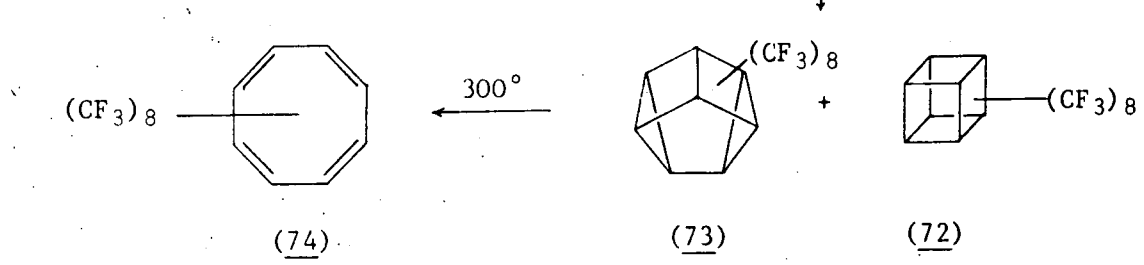
trifluoromethyl cyclobutadiene (18), which is the precursor of compounds (72)-(74).[98]



(70)

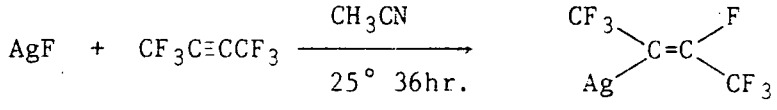


(18) (71)



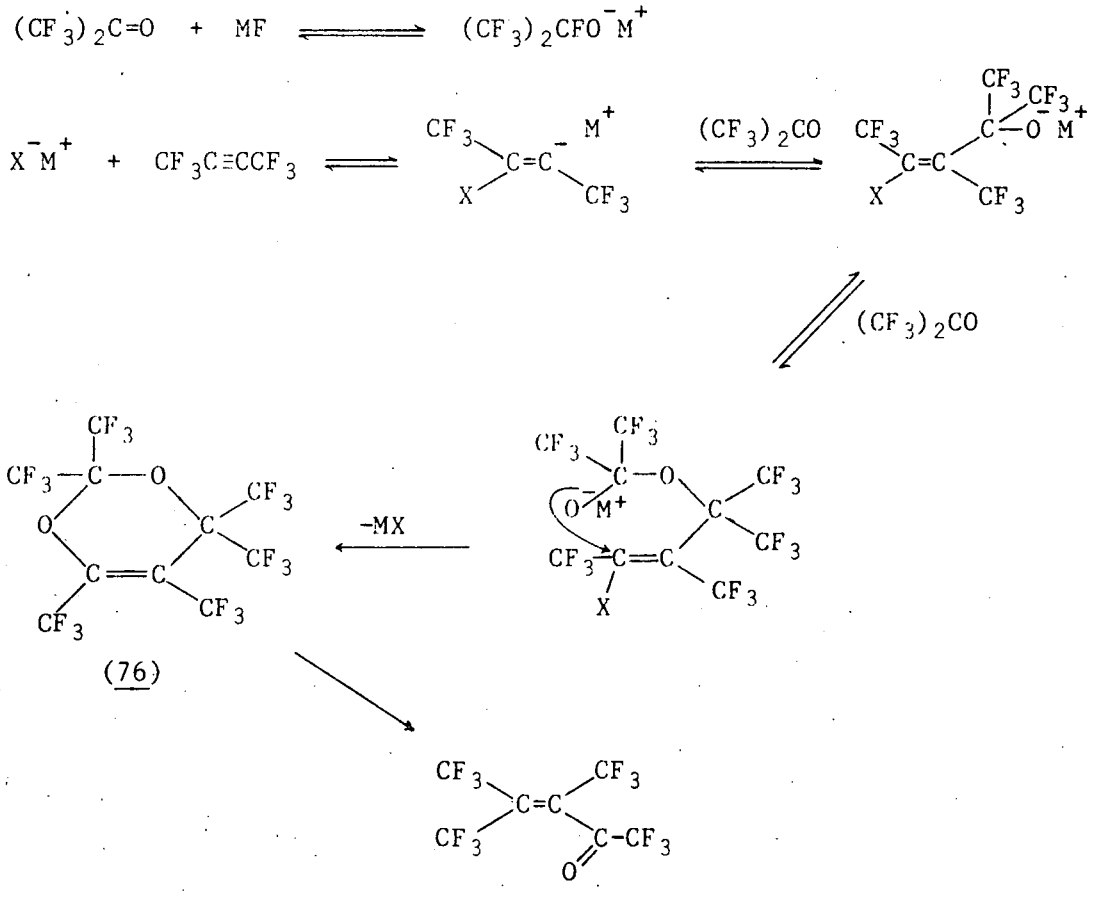
(74) (73) (72)

Silver fluoride, unlike caesium fluoride, does not cause hexafluorobut-2-yne to polymerise but instead gives a stable *trans* adduct (75).



(75)

In the presence of metal fluorides, hexafluorobut-2-yne reacts with two molecules of hexafluoroacetone to give a cyclic product (76), which slowly converts to the enone (77).[100] It is not certain whether the mechanism involves initial attack on the acetylene by fluoride or by perfluoroisopropoxide.

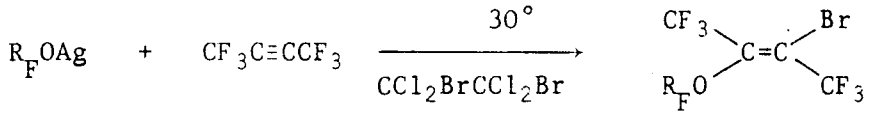


(76)

(77)

M = Cs or Ag X = F or $(CF_3)_2CFO$

Similarly silver perfluoroalkoxides react with hexafluorobut-2-yne in the presence of a bromine transfer agent to give the corresponding 2-bromo-3-(perfluoroalkoxy)-but-2-ene.[100]

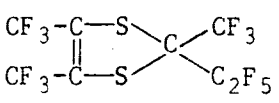
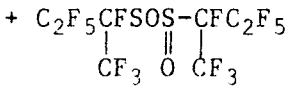
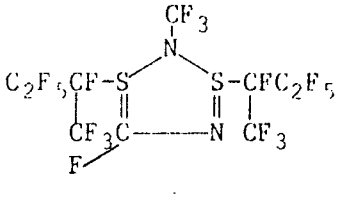
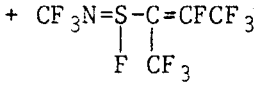
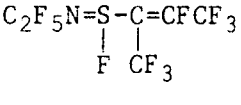
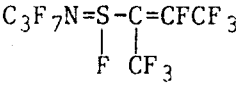


R_F = CF_3-, CF_3CF_2-, $(CF_3)_2FC$-, $(CF_3)_3C$-, C_6F_5, $CF_3C(=O)$-.

Several miscellaneous fluoride ion induced reactions of hexafluorobut-2-yne are summarised in Table II.4. No details of mechanisms or stereochemistry of the products were given.

Table II.4

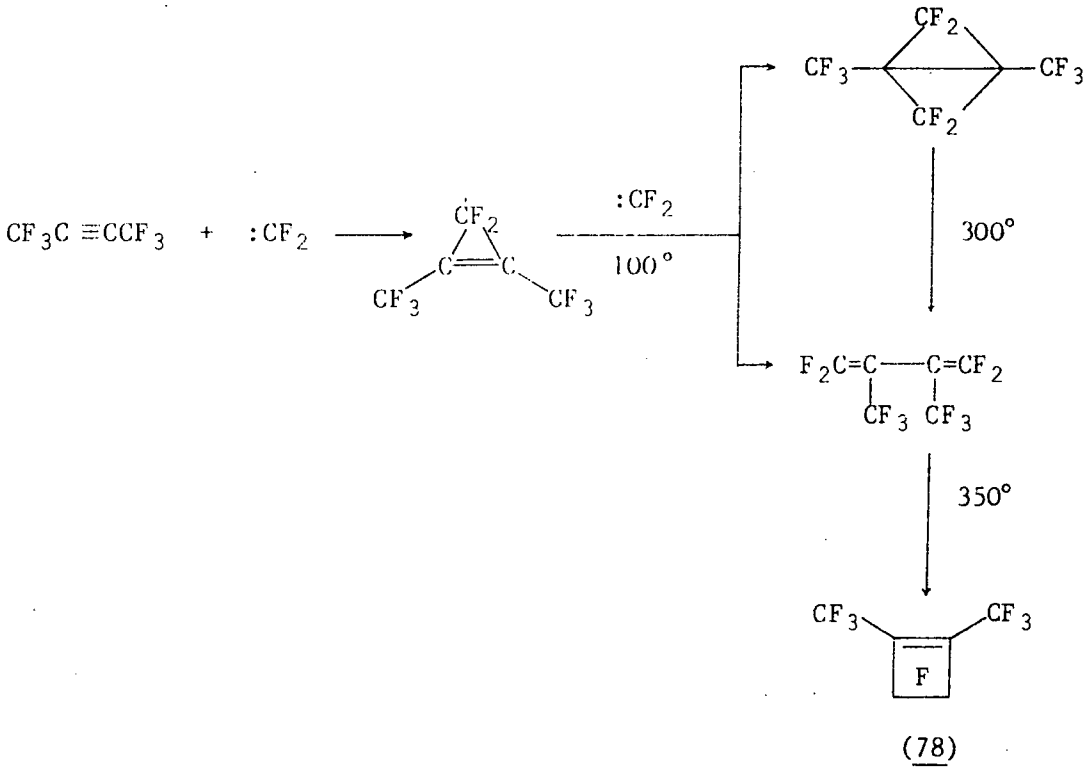
Miscellaneous Caesium Fluoride Catalysed Reactions of Hexafluorobut-2-yne

Reactants	Conditions	Products	Reference
$CF_3HgOOCCF_3$		$Hg[C(CF_3)=CFCF_3]_2$	101
$SOF_2 + SF_4$	80° 24 hrs.	 + 	102
$CF_3N=SF_2$	70° 10 hrs.	 + 	102
$C_2F_5N=SF_2$	124° 54 hrs.		102
$C_3F_7N=SF_2$	150° 72 hrs.		102

II.E Cycloadditions

II.E.1 1,1 Cycloadditions

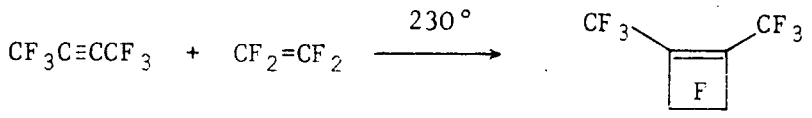
Difluorocarbene, generated by pyrolysis of $(CF_3)_3PF_2$, adds to hexafluorobut-2-yne[104] in the gas phase to give a cyclopropene derivative; further addition gives a bicyclobutene together with some perfluoro-(2,3-dimethylbuta-1,3-diene).



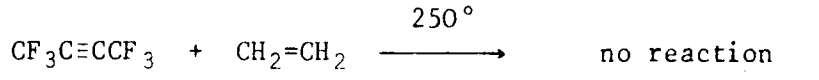
(78)

II.E.2 1,2 Cycloadditions

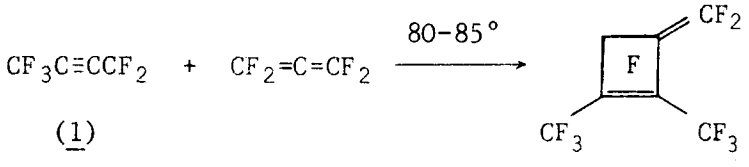
Hexafluorobut-2-yne has been reported to undergo [2+2] cycloaddition with a variety of alkenes and allenes to give 1,2 bistrifluoromethyl cyclobutenes. For example, tetrafluoroethylene gives a small yield of (78)[104] although no similar reaction has been detected between ethylene and hexafluorobut-2-yne.[105]

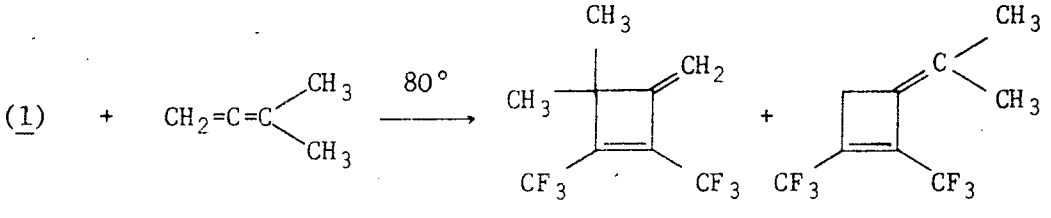


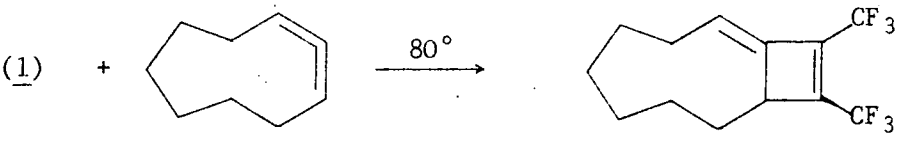
(78) 3%



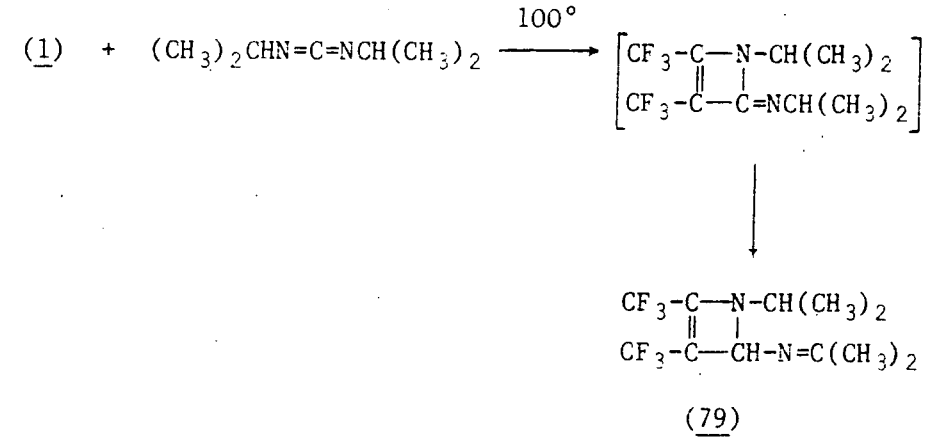
Hexafluorobut-2-yne adds to certain allenes giving cyclobutenes with exocyclic double bonds. With unsymmetrical allenes, addition can take place across either double bond to give a mixture of products.







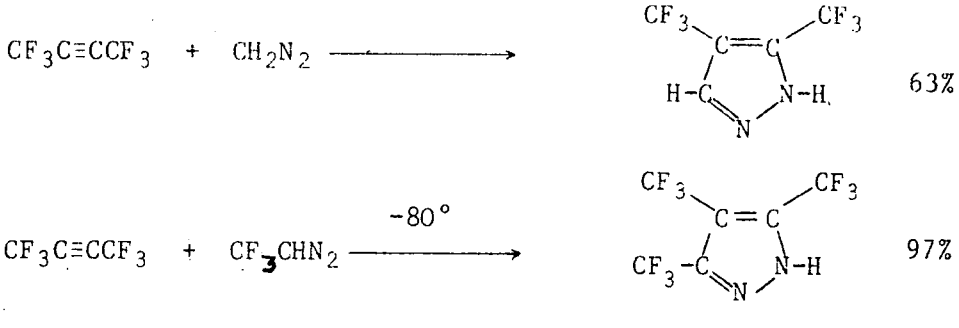
The [2+2] cycloadduct between hexafluorobut-2-yne and diisopropylcarbodiimide is unstable and rearranges to give the isomeric azetine (79).[82]



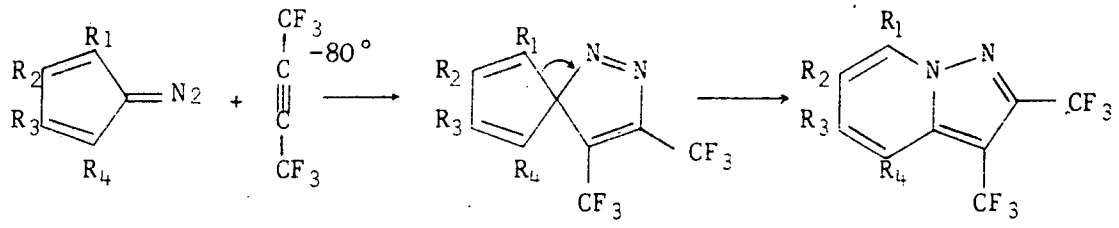
(79)

II.E.3 1,3 Cycloadditions

Various 1,3 dipolar species have been added to hexafluorobut-2-yne to give a range of heterocyclic compounds. Diazomethane and 2,2,2-trifluorodiazoethane add to give the corresponding pyrazoles.[109]



Similarly, diazocyclopentadienes yield as primary products the spiro-pyrazoles (80) but only compound (80a) has been isolated.[110] Compounds (80b) and (80c) undergo spontaneous |1,5|-sigmatropic shifts giving pyrazolo pyridines (81b) and (81c). A similar rearrangement occurs for (80a) on refluxing in toluene.



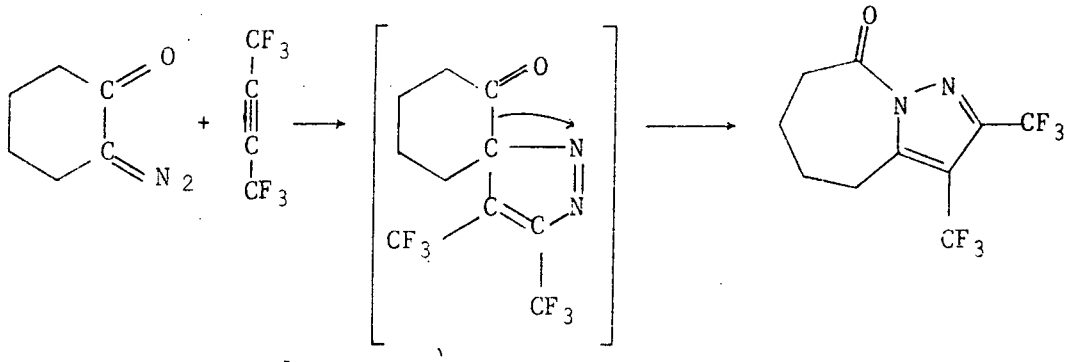
(80) (81)

a R_1, R_2 = annelated benzene ring R_3, R_4 = annelated benzene

b R_1, R_2, R_3, R_4 = C_6H_5

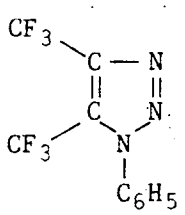
c R_1, R_2 = annelated benzene ring R_3, R_4 = C_6H_5

The same type of behaviour has been observed for other cyclic azides.[115]

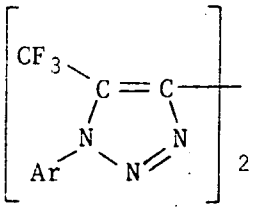


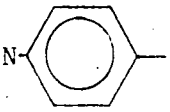
A few triazoles have been prepared form perfluoroacetylenes by reaction with aromatic azides.

$$CF_3C{\equiv}CCF_3 + C_6H_5\text{-}N{=}\overset{+}{N}{=}\overset{-}{N} \longrightarrow \quad [111]$$

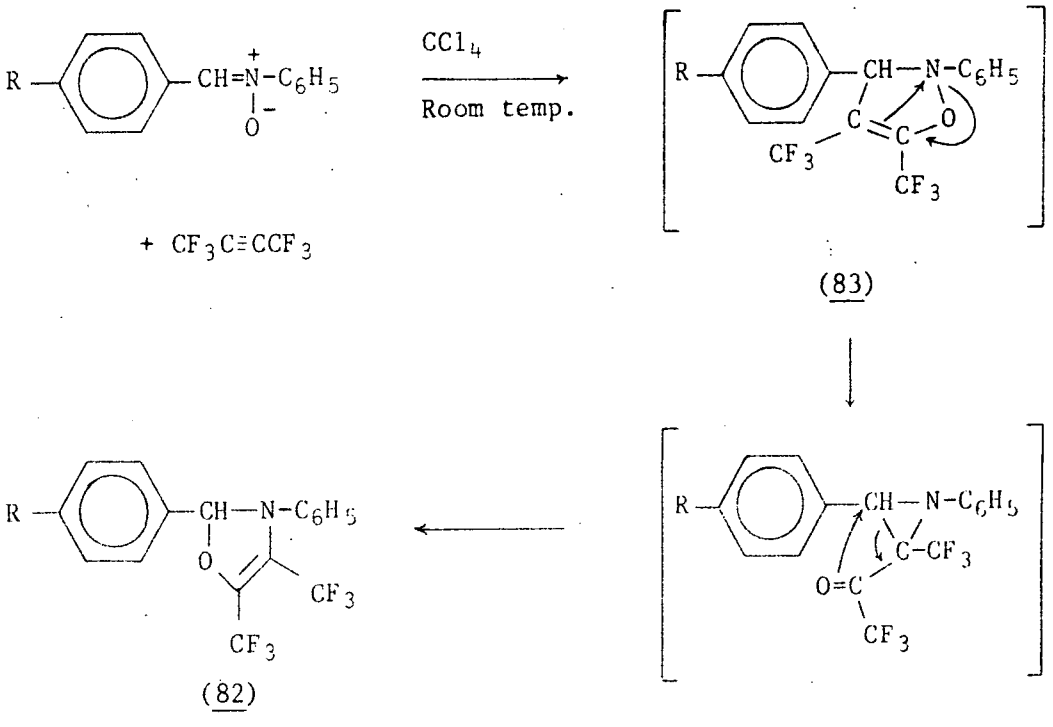


$$CF_3C{\equiv}C\text{-}C{\equiv}CCF_3 + 2ArN_3 \longrightarrow \quad [42]$$



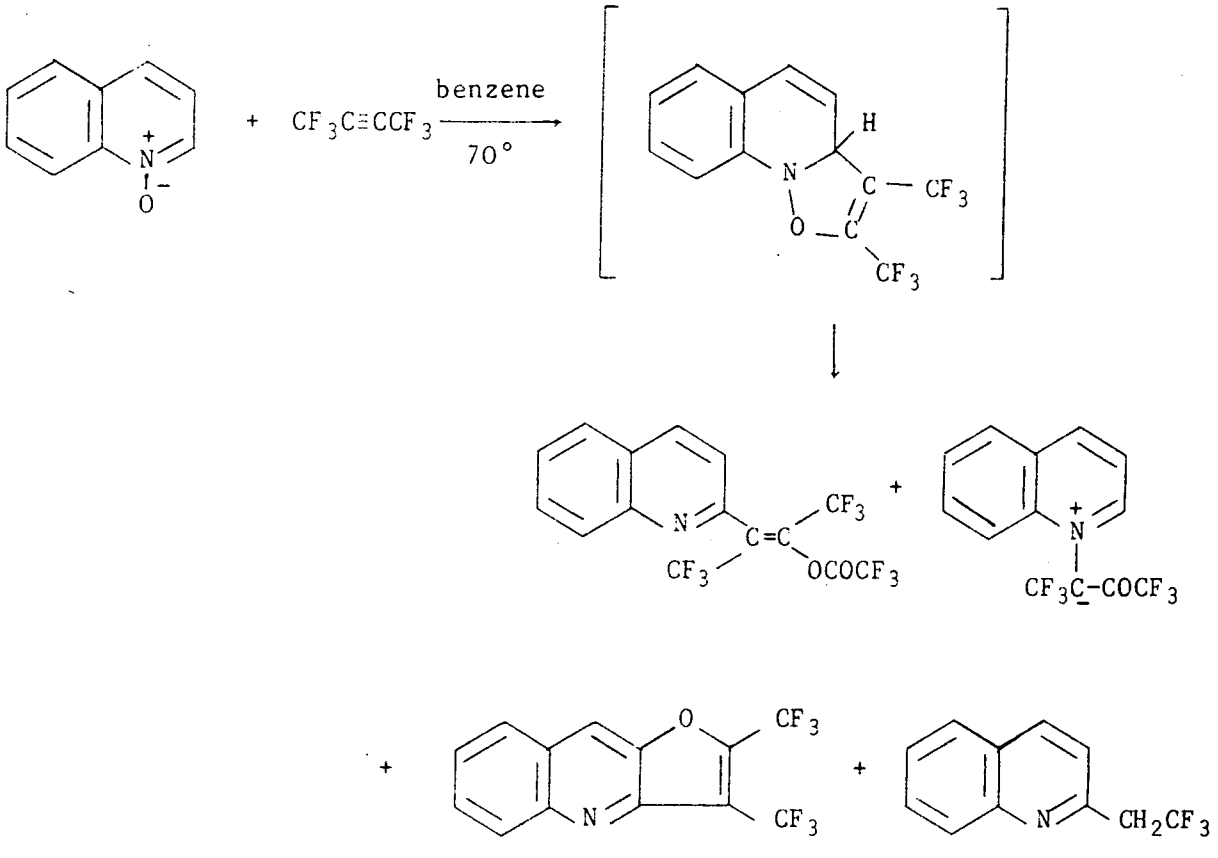
Ar = $(CH_3)_2N$- 

Aromatic nitrones add to hexafluorobut-2-yne[112] to give oxazolines (82) instead of the expected isoxazolines (83). The following mechanism is proposed for the rearrangement of the simple 1,3 dipolar adducts (83) to the products (82).



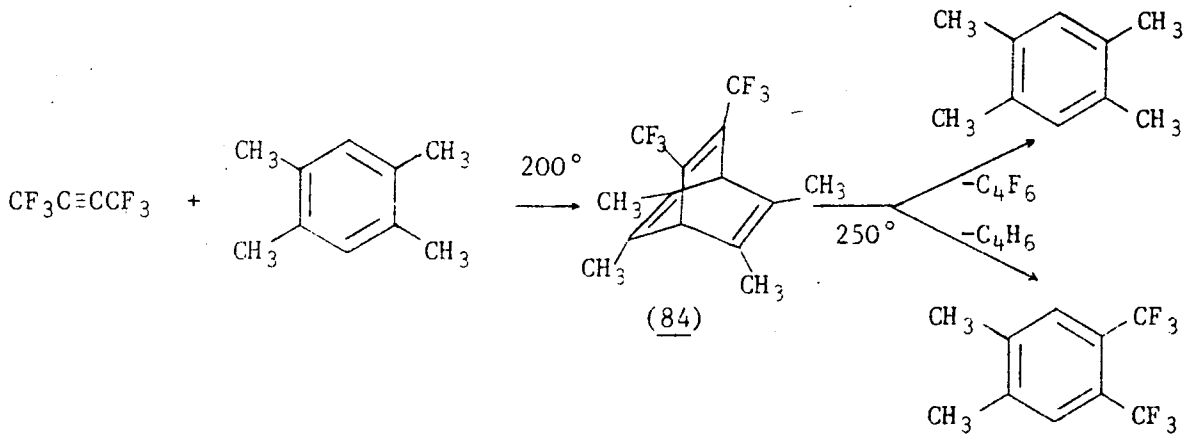
R = H, OCH_3, NO_2

Similarly, the 1,3 dipolar adducts formed from the reaction of aromatic N-oxides with hexafluorobut-2-yne have not been isolated. Instead complex mixtures of rearranged products are obtained and the mechanism of these reactions is far from clear.[113]



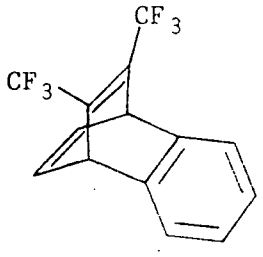
II.E.4 1,4 Cycloadditions

Bisperfluoroalkyl acetylenes are very powerful dienophiles and undergo Diels-Alder reactions with a wide range of dienes. In fact, hexafluorobut-2-yne is so dienophilic that it adds to compounds which are not normally considered as dienes. For example, it adds to durene at 200° to give the bicyclooctatriene (84) and this was the first reported Diels-Alder addition to a simply substituted benzene ring.[105]

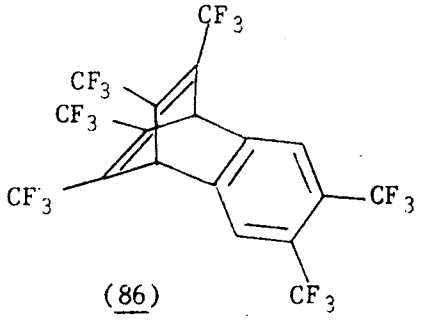


On heating the adduct (84) to 250° a retro Diels-Alder reaction takes place giving a mixture of durene and 1,2-dimethyl-4,5-bistrifluoromethyl benzene. Similarly $H\text{-}(CF_2)_5\text{-}C{\equiv}C\text{-}(CF_2)_5H$ adds to durene but no adduct was formed with less active acetylenes such as trifluoropropyne or acetylene itself.[105]

Hexafluorobut-2-yne adds across the 9 and 10 positions of anthracene and reacts with naphthalene to give adduct (85). Even the considerably deactivated 2,3,6,7-tetrakistrifluoromethyl naphthalene reacts to give adduct (86) in good yield.[105]



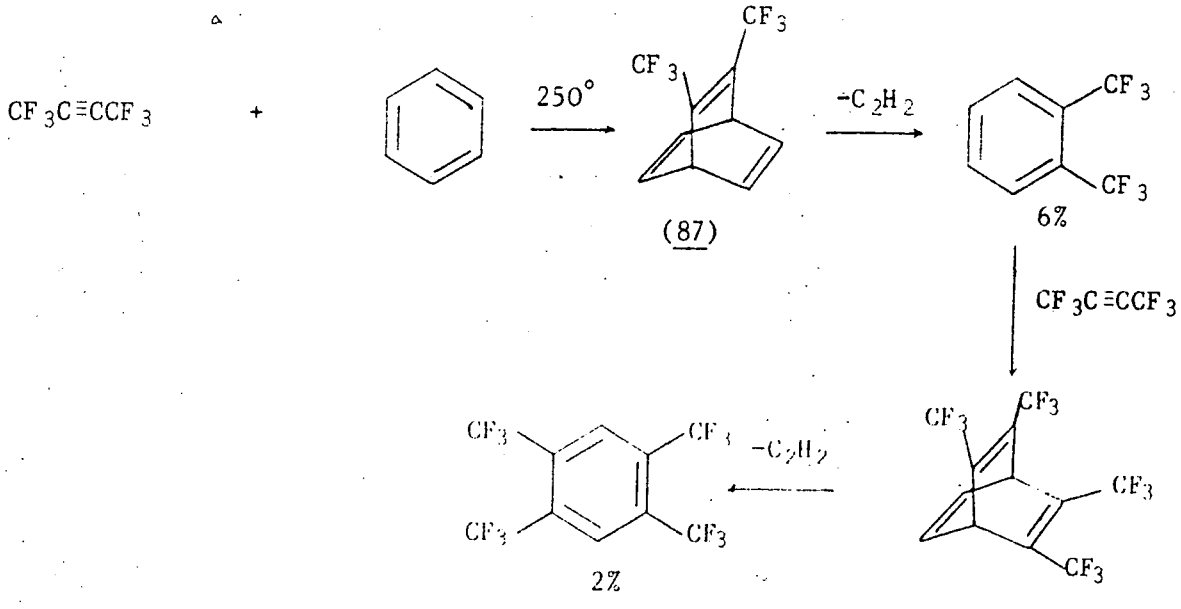
(85)

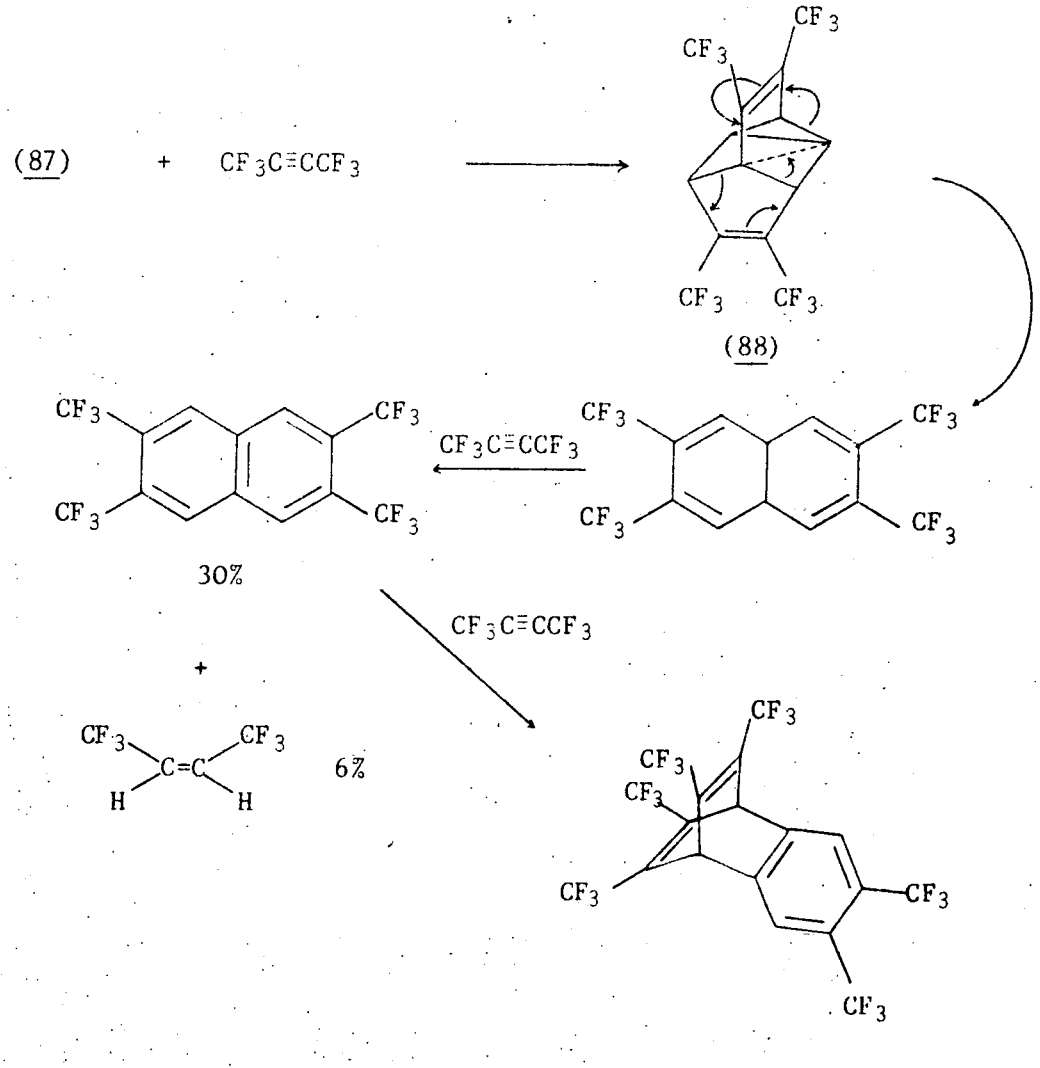


(86)

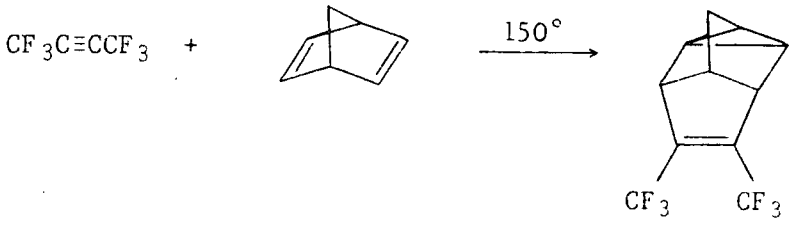
At 250°, hexafluorobut-2-yne reacts with benzene[105,115] giving 7 products, which are formed by a series of Diels-Alder / retro Diels-Alder

additions. Small quantities of 1,2,4-tristrifluoromethyl benzene (2%) and 1,4,6,7-tetrakistrifluoromethyl naphthalene (6%) are also produced.





The 1:1 adduct (87) was not isolated as it readily undergoes a retro Diels-Alder reaction under these conditions. However, it can be isolated in yields of 7 - 10% if the reaction is carried out at lower temperatures (180 - 200°). Besides the retro Diels-Alder reaction, the 1:1 adduct can also add a further molecule of butyne to give the intermediate (88). This type of behaviour has also been observed in the reaction of hexafluorobut-2-yne with bicycloheptadiene.[105]

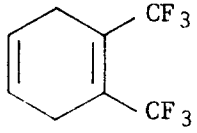
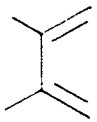
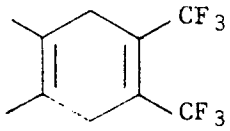
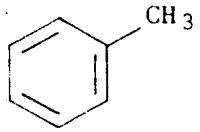
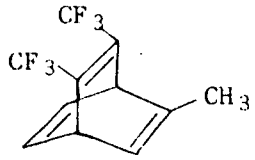
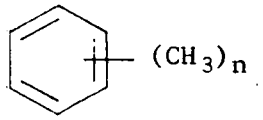
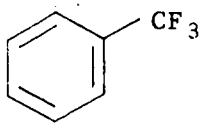
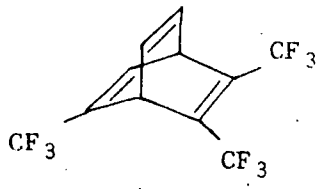
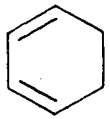
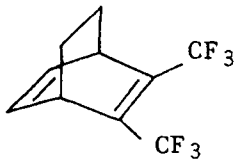


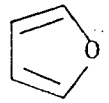
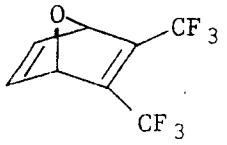
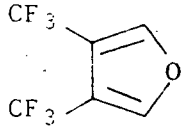
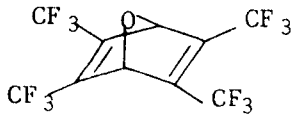
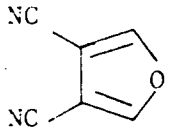
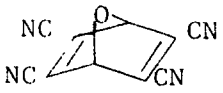
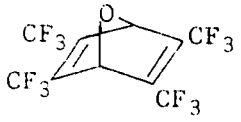
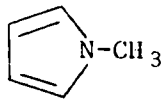
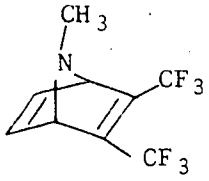
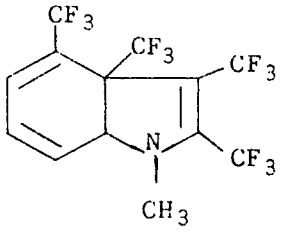
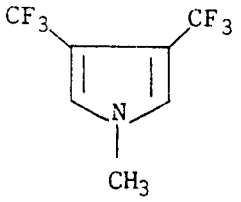
In recent years a large number of Diels-Alder adducts with both cyclic and acyclic dienes have been reported and these are summarised in Table II.5. Often the 1:1 adduct is unstable under the conditions of its formation and only products resulting from retro Diels-Alder reactions are observed.

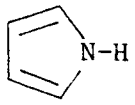
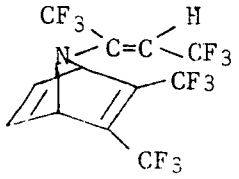
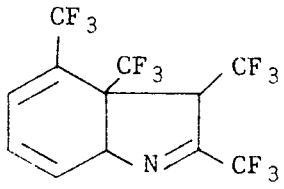
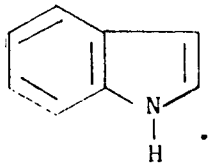
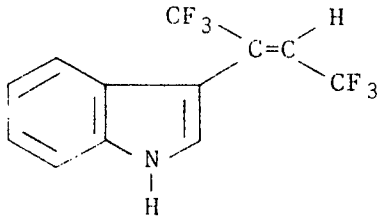
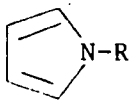
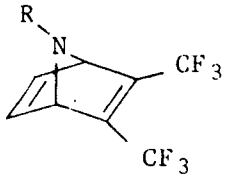
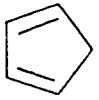
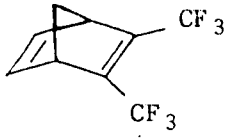
This table gives an idea of the large variety of dienes which will add to hexafluorobut-2-yne and indicates the synthetic possibilities of the Diels-Alder reaction for preparing trifluoromethyl substituted compounds. Another important use of the dienophilic properties of hexafluorobut-2-yne is the trapping of unstable species which cannot be observed directly. For example, attempts to generate bismabenzene give only polymeric material but when hexafluorobut-2-yne is present the Diels-Alder adduct can be isolated.[124]

Table II.5

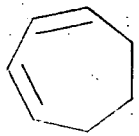
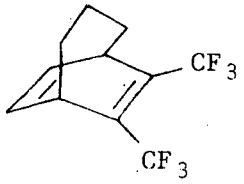
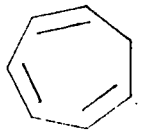
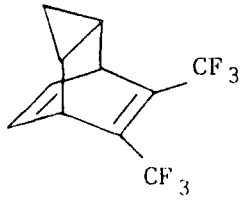
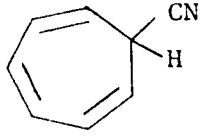
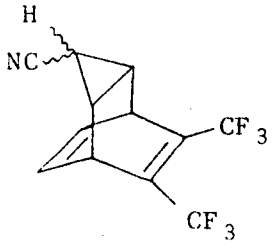
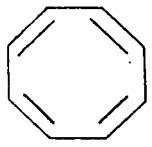
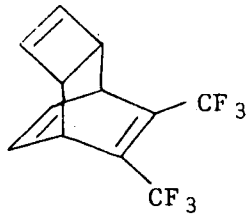
Summary of Diels-Alder Reactions with Hexafluorobut-2-yne

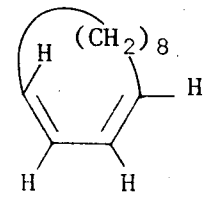
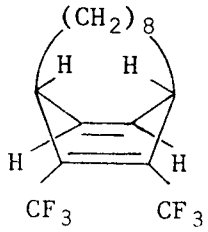
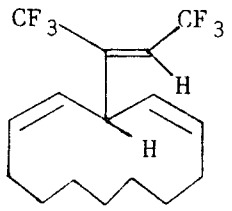
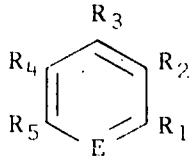
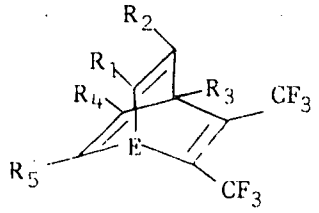
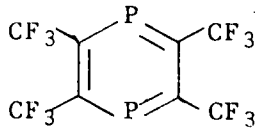
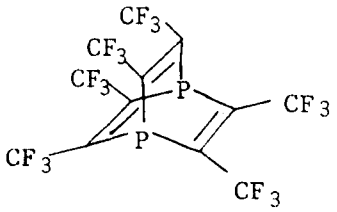
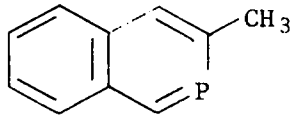
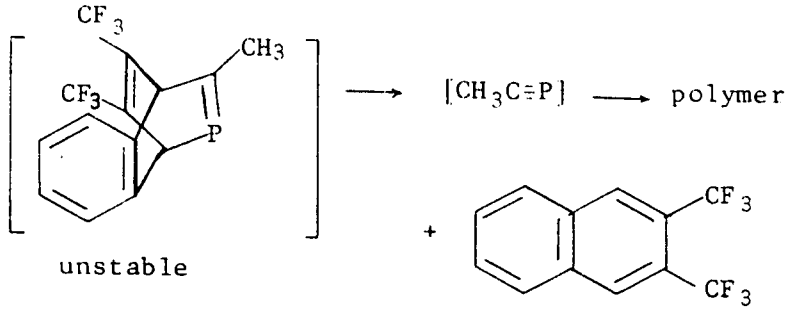
Diene	Diels-Alder Adduct	Other Products	Conditions	Ref.
			28° 48 hrs.	114
			100° 6 hrs.	114
		not identified	180° 12 hrs.	115, 117
 n = 2,3				115, 117
			250° 10 hrs.	139
			100° 6 hrs.	117

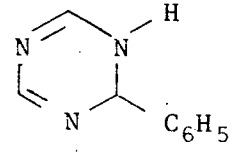
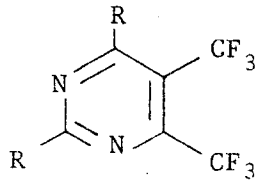
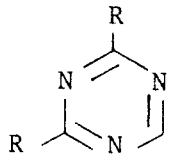
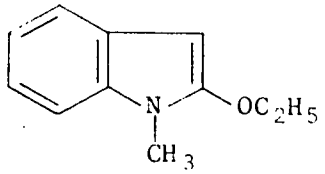
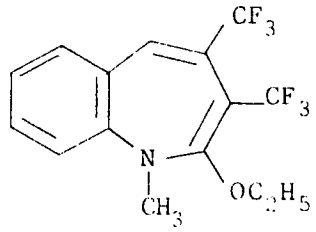
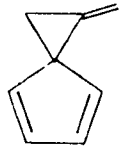
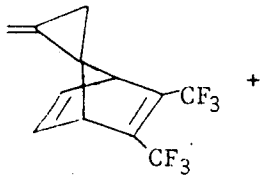
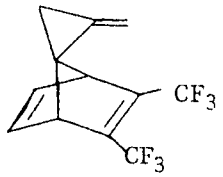
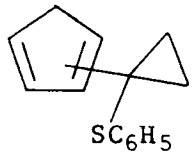
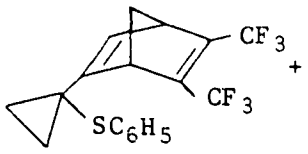
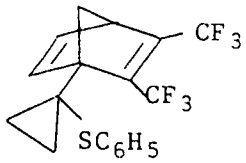
Diene	Diels-Alder Adduct (where isolable)	Other Products	Conditions	Ref.
			100° 6 hrs.	118
			140° 24 hrs.	118
	not isolated	 + 	160° 24 hrs.	118
		 + 	75° 16 hrs.	119

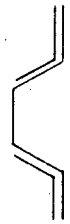
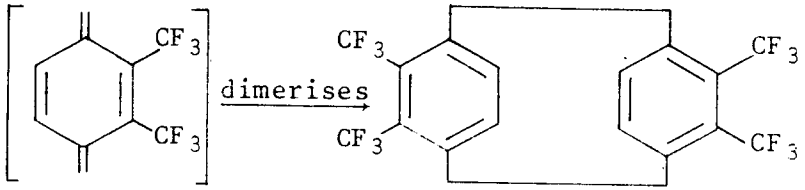
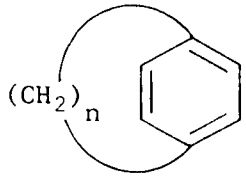
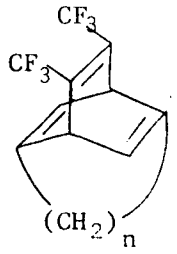
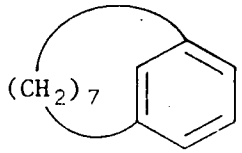
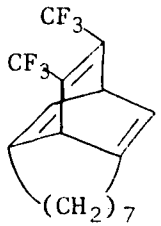
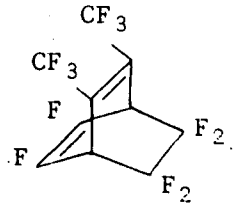
Diene	Diels-Alder Adduct (where isolable)	Other Products	Conditions	Ref.
	 a		75° 16 hrs.	119
	not isolated		100° 48 hrs.	119
 I R=p-tosyl II R=$COOCH_3$			I CH_2Cl_2 140° 27 hrs. II 120° 2 hrs.	120
			100° 24 hrs.	121

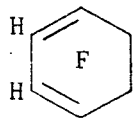
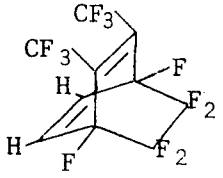
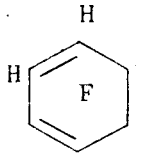
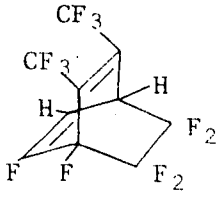
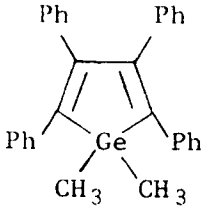
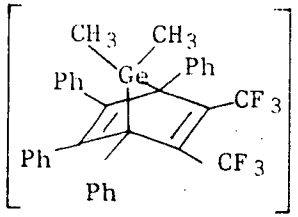
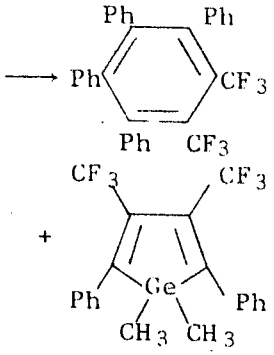
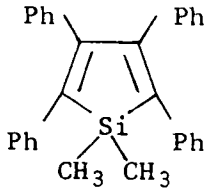
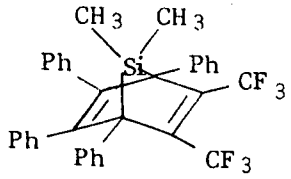
a Formed by nucleophilic addition of the 1:1 adduct to hexafluorobut-2-yne

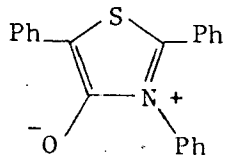
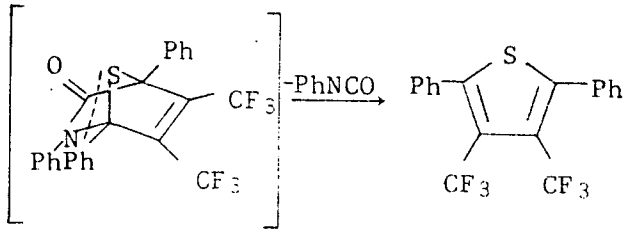
Diene	Diels-Alder Adduct (where isolable)	Other Products	Conditions	Ref.
			100° 40 hrs.	122
			150° 24 hrs.	121
			120° 18 hrs.	123
			120° 6 hrs. 150°100 hrs.	117 121

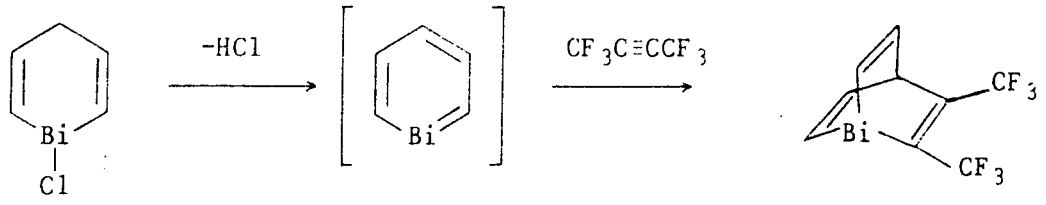
Diene	Diels-Alder Adduct (where isolable)	Other Products	Conditions	Ref.
			150° 42 hrs	130-131
 E=P, As, Sb, Bi				124-127
				128
	 unstable	[CH$_3$C≡P] ⟶ polymer	250° 50 mins.	129

Diene	Diels-Alder Adduct (where isolable)	Other Products	Conditions	Ref.
			80-90° 3 hrs.	132
				
	 + 		0°	135
	 + 		10° 6 hrs.	134

Diene	Diels-Alder Adduct (where isolable)	Other Products	Conditions	Ref.
	 unstable		65° 9 hrs.	136
 n=7,8				137
				137
			225° 18 hrs.	138

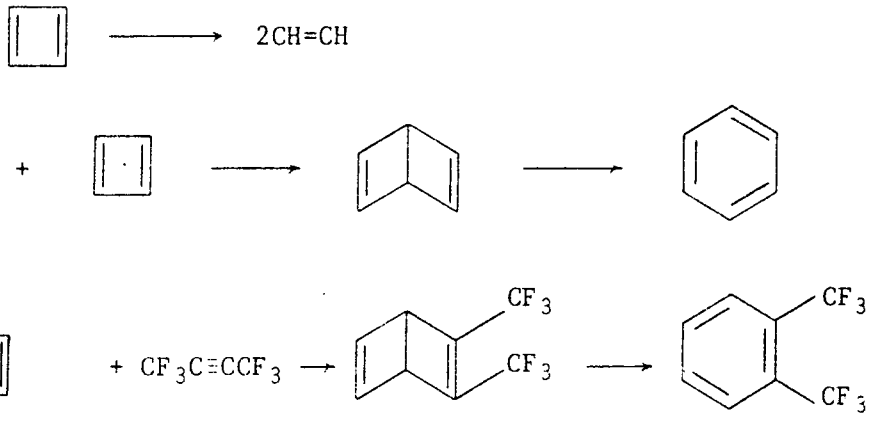
Diene	Diels-Alder Adduct (where isolable)	Other Products	Conditions	Ref.
			200° 14.5 hrs.	140
			200° 23 hrs.	141
	 not isolated	 + + $(CH_3)_2Ge$ + $PhC{\equiv}CPh$	190° 5 hrs.	142
			115° 24 hrs.	143

Diene	Diels-Alder Adduct (where isolable)	Other Products	Conditions	Ref.
				144



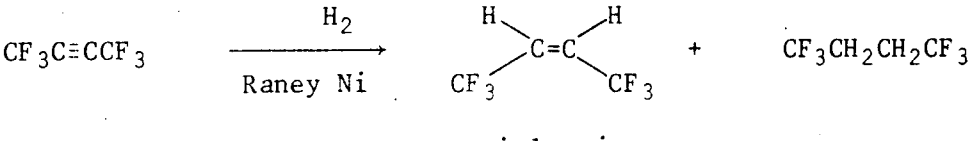
Similarly, 1-methylsilabenzene, which is too unstable to be isolated, has been trapped as a Diels-Alder adduct.[146] Also cyclobutadiene, generated by u.v. photolysis of tricarbonylcyclobutadiene iron, has been reacted with hexafluorobut-2-yne to give 1,2-bistrifluoromethyl benzene.[147]

$$C_4H_4Fe(CO)_3 + h\nu \longrightarrow C_4H_4 + Fe(CO)_3$$



II.F Miscellaneous Reactions

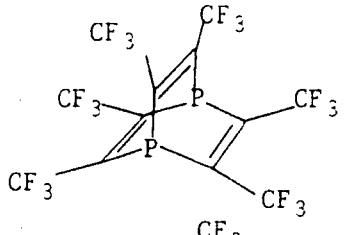
Hexafluorobut-2-yne undergoes many of the standard reactions characteristic of unsaturated compounds; thus it can be hydrogenated using a Raney nickel catalyst[8,27] and it is oxidised to trifluoroacetic acid by potassium permanganate.[8,148]



mainly *cis*

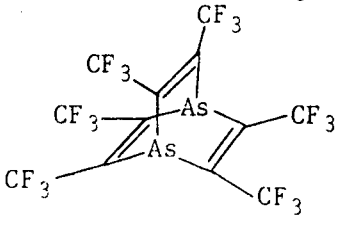
Several non-metallic elements react with hexafluorobut-2-yne to give cyclic products. These reactions are catalysed by iodine and it is possible that the process involves 2,3-diiodohexafluorobut-2-ene as an intermediate.

$$P + 3CF_3C{\equiv}CCF_3 \xrightarrow[200^\circ]{I_2}$$



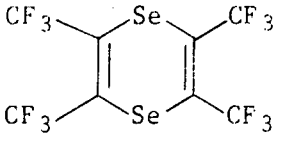
[56]

$$As + CF_3CI{=}CICF_3 \xrightarrow{200^\circ}$$



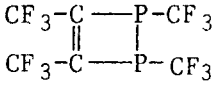
[56]

$$Se + CF_3CI{=}CICF_3 \xrightarrow{180^\circ}$$

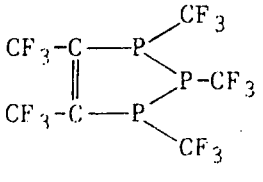


[58]

$(CF_3P)_4$ and $(CF_3P)_5$ react with hexafluorobut-2-yne giving cyclic products (89) and (90) respectively.[149]

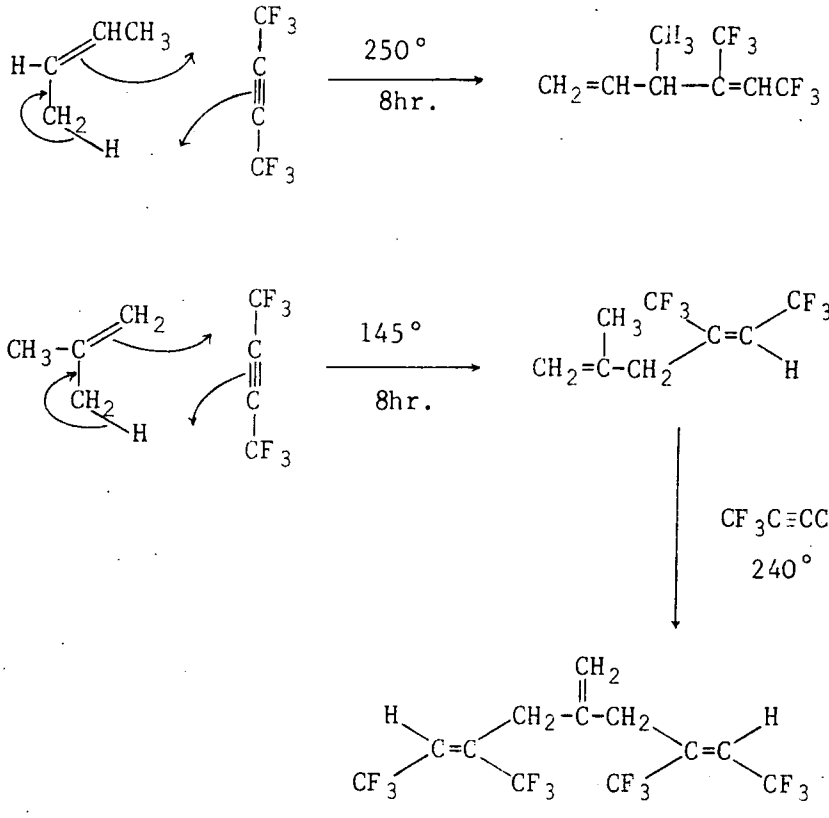


(89)

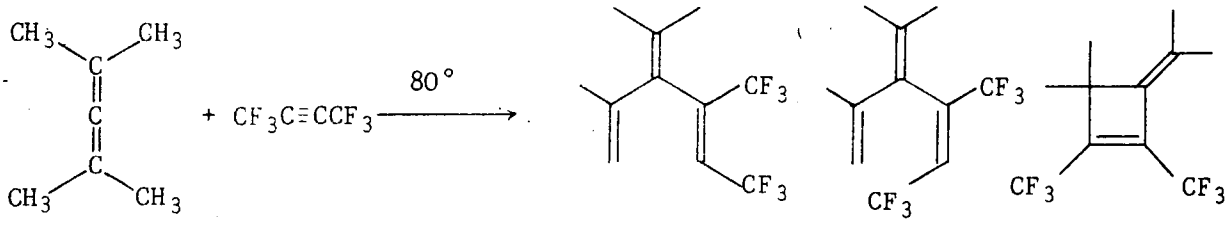


(90)

A few examples of the ene reaction have been reported using hexafluorobut-2-yne as the enophile.[150] Diadducts are sometimes formed when the olefin has more than one allylic hydrogen.



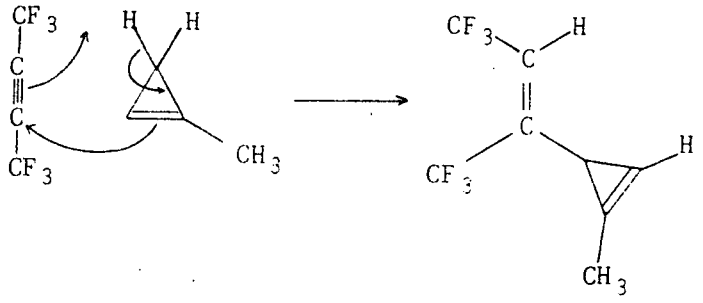
Several allenes have also been reacted with hexafluorobut-2-yne.[151] 2,4-Dimethylpenta-2,3-diene gives two ene insertion products together with a [2+2] cycloaddition product.



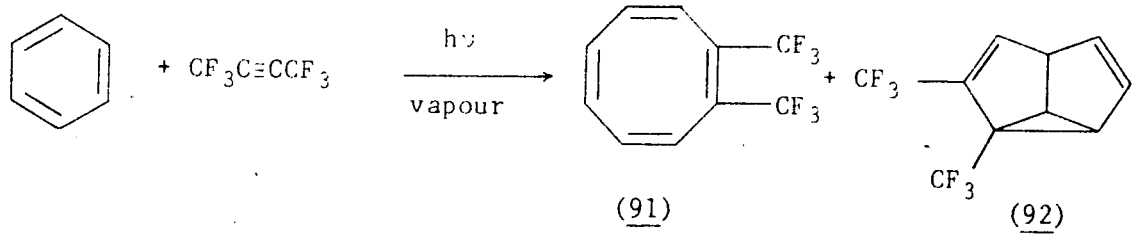
Ratio 78 8 11

Other allenes (e.g. 3-methylbuta-1,2-diene and cyclonona-1,2-diene) give exclusively [2+2] cycloaddition products (see section II.E.2).

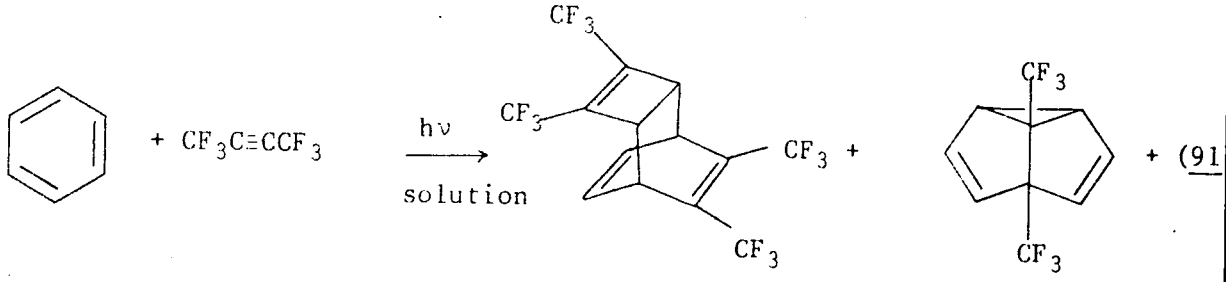
Hexafluorobut-2-yne and 1-methylcyclopropene undergo an ene reaction at 30°.[152]



The photochemical addition of hexafluorobut-2-yne to benzene gives different products from those obtained in the thermal reaction. Vapour phase photolysis gives (91) and (92), whereas carrying out the reaction in solution the products (91), (93) and (94) are obtained.



(91) (92)



(93) (94)

DISCUSSION

CHAPTER III

PREPARATION OF HEXAFLUOROBUT-2-YNE

III.A Introduction

Prior to this work, the best method available for preparing hexafluorobut-2-yne (1) was the two stage route starting from hexachlorobuta-1,3-diene first reported by Henne and Finnegan in 1949.[8]

$$CCl_2{=}CCl{-}CCl{=}CCl_2 \xrightarrow[135^\circ]{SbF_3,\ SbF_3Cl_2} \underset{(95)}{CF_3CCl{=}CClCF_3} \xrightarrow{Zn\ /\ solvent} \underset{(1)}{CF_3C{\equiv}CCF_3}$$

Although it is obtainable from commercial sources, hexafluorobut-2-yne is too expensive to purchase in the large quantities necessary for its chemistry to be studied in depth. This chapter describes attempts to find new convenient methods of synthesising this acetylene from readily available starting materials.

III.B Dechlorinations of 2,3-Dichlorohexafluorobut-2-ene

III.B.1 In Flow Systems

The literature methods for dechlorinating 2,3-dichlorohexafluorobut-2-ene (95) suffer from the following disadvantages:

1) Large quantities of reduction products are formed (mainly 2-chlorohexafluorobut-2-ene and hexafluorobutane).
2) Long reaction times are needed.
3) Low conversion of starting material.

It was reasoned that if the reaction could be carried out without a solvent, no reduction products would be formed and better conversions to hexafluorobut-2-yne would be possible. Therefore, methods for carrying out the dechlorination in the gas phase using both flow and static systems were investigated.

The flow reactions described in this section were carried out by passing the dichlorobutene through a heated silica tube packed with a suitable dechlorinating agent (e.g. iron filings, zinc dust).

III.B.1.a Over Iron Filings

Dechlorinations over iron filings were attempted at various temperatures between 300 and 610° and the results of these experiments are summarised in Table III.1.

Table III.1

Dechlorination of (95) Over Iron Filings

Max. col. temp. °C	Contact time (s)	Mass of (95) (g)	Mass of (95) recovered (g)	Mass of gas collected (g)	% mass recovered
300	30	2.02	1.05	0.00	52
368	15	2.01	0.74	0.00	37
450	15	2.02	0.78	0.00	39
456	15	5.05	1.95	0.21	43
520	15	1.96	0.00	0.00	0
565	15	2.05	0.00	0.11	5
610	10	2.01	0.00	0.09	4
20	15	3.06	2.56	-	84

At temperatures up to 456° no hexafluorobut-2-yne was collected and less than half of the butene was recovered. At higher temperatures all the starting material was consumed but only very small quantities of gaseous products were obtained.

Gas collected from the reaction at 456° appeared on g.l.c. as one peak with identical retention time as hexafluorobut-2-yne but the infrared spectrum revealed the presence of a contaminant. The hexafluorobut-2-yne produced at 565° contained a different impurity which was the only product obtained at 610°. This gas could not be identified by infrared or mass spectrometry.

Low mass recoveries were observed in all these reactions and this may be due to either or both of the following explanations:

1) Inefficient trapping of unreacted starting material and products.
2) Decomposition of hexafluorobut-2-yne on the surface of the iron.

Control experiments were run to see whether the trapping was at fault. Hexafluorobut-2-yne (1) and 2,3-dichlorohexafluorobut-2-ene (95) were passed through the apparatus at 20° with recoveries of 80% and 84% respectively. Therefore, although a little material is lost due to incomplete trapping, this can only be partly responsible for the low mass balances obtained in these reactions.

When (1) was passed through the tube at 450°, 54% was recovered and the iron filings gained in weight by an amount equivalent to 36% of the mass of the acetylene passed. A similar reaction at 500° gave only 13% recovery. These results imply that hexafluorobut-2-yne reacts on the surface of the iron and is retained there. A sample of these filings was submitted for mass spectroscopic analysis but no spectrum was obtained even with a probe temperature of 300°. These observations can

be accounted for by any of the following reactions:

1) Polymerisation of hexafluorobut-2-yne on the surface of the metal
2) Formation of a thermally stable involatile iron complex
3) Dechlorination and defluorination to give carbonaceous material.

In order to obtain more information, the reaction of hexafluorobut-2-yne with iron filings was investigated in a static system. No reaction occurred at 200° but at 400° a black solid, a little liquid and some gaseous products were obtained. The gas contained a trace of (1) together with three other components of higher molecular weight. After washing with acid to remove unreacted iron, the black solid was shown to contain 70% carbon. These results show that (1) is substantially defluorinated by iron at high temperatures and it is therefore not surprising that very little was obtained in the flow dechlorination reactions described above.

III.B.1.b Over Zinc Dust

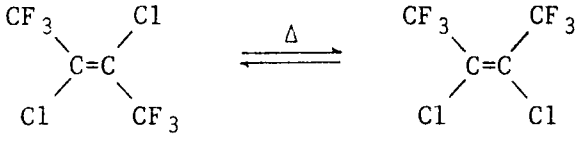
When hexafluorobut-2-yne was passed over zinc dust at 410° 70% was recovered unchanged and the zinc gained weight by an amount equivalent to 12% of the alkyne.

Passing (95) through the tube under the same conditions, 85% was recovered unchanged and only a trace of hexafluorobut-2-yne was produced. The temperature could not be raised further because zinc melts at 419°.

III.B.1.c Over Platinum Foil

For comparison, (95) was passed through a tube packed with platinum foil in order to determine whether gaseous products would be formed, similar to those obtained in the reactions over iron.

At 450°, 75% recovery of butene was obtained and no trace of gaseous products was detected. However, g.l.c. and ^{19}F n.m.r. indicated that isomerisation of the starting material had taken place. The commercial 2,3-dichlorohexafluorobut-2-ene used for all these experiments was a mixture of 90% *trans* and 10% *cis* isomers. However, the product from the reaction at 450° was a mixture of 63% *trans* and 37% *cis* iosmers. At 656°, 52% of the butene was recovered as a mixture of 54% *trans* and 46% *cis* isomers.



A trace of gas was also produced in this reaction, but i.r. spectroscopy showed it to be neither hexafluorobut-2-yne nor any of the products obtained in the reactions over iron filings.

Determination of *cis-trans* isomer ratios

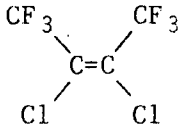
Approximate ratios were obtained by comparing g.l.c. peak areas but as the relative retention times of the two isomers were not known it was not possible to tell which was the major component of the mixture.

A more satisfactory method was to measure the intensities of the

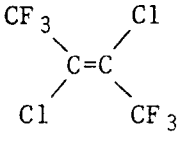
CF_3 resonances in the ^{19}F n.m.r. spectrum. The low field resonance was assigned to the *cis* isomer in agreement with the literature values shown in Table III.2.

Table III.2

^{19}F n.m.r. Data for *cis* and *trans*-2,3-Dichlorohexafluorobut-2-ene[153]



60.4



63.7

III.B.2 Reactions in a Sealed System

Dechlorinations of (95) were attempted in an autoclave using zinc dust as the dehalogenating agent. It was hoped that by using a longer contact time and lower temperatures than those used in the flow reactions the dechlorination would proceed smoothly without any defluorination. At 200°, 91% of the starting material was recovered unchanged and no gaseous products were detected. However, at 270° a good yield of gas was obtained but unfortunately this was found to be an 8 component mixture containing only a small percentage of hexafluorobut-2-yne.

A reaction was attempted using zinc dust activated by washing with glacial acetic acid. When a sample of this zinc dust was heated

with (95) at 270°, a black carbon rich solid was formed together with a little gas. Similar results were obtained using unactivated zinc at 325°. The black solid is involatile, does not dissolve in organic solvents or mineral acids and shows no absorption in the infrared. These reactions again demonstrate the susceptibility of hexafluorobut-2-yne towards defluorination by hot metals.

III.B.3 Reactions in Solution

After the unsuccessful attempts to dechlorinate 2,3-dichlorohexafluorobut-2-ene (95) in the gas phase, attention was turned to improving the conventional reactions employing a solvent. The reaction was carried out using zinc dust in dioxan, dioxan / sulpholan (40:60) and acetic anhydride; of these solvents the latter gave the best yield of hexafluorobut-2-yne (65%) although it was contaminated with considerable amounts of reduction products. Careful low temperature distillation gave the butyne in approximately 99% purity.

A reaction using magnesium turnings in tetrahydrofuran gave a small yield of hexafluorobut-2-yne together with a large quantity of tarry material from which no starting material was recovered.

III.C Isomerisation of Hexafluorocyclobutene

III.C.1 Introduction

While the work described above was in progress, another worker in this laboratory showed that good yields of hexafluorobut-2-yne were produced when hexafluorocyclobutene (96) was passed over caesium fluoride at high temperatures.[154] The best results were obtained at 590°, when the product gas consisted of 90% hexafluorobut-2-yne and

10% starting material and the total recovery of material was 72%.

(96)

$$\xrightarrow[\text{Flow system}]{\text{CsF}\quad\Delta} CF_3C{\equiv}CCF_3$$

(1)

These experiments were only carried out using small quantities of (96) (4 - 6g), so it was important to see whether the reaction could be scaled up to provide a preparative route to hexafluorobut-2-yne.

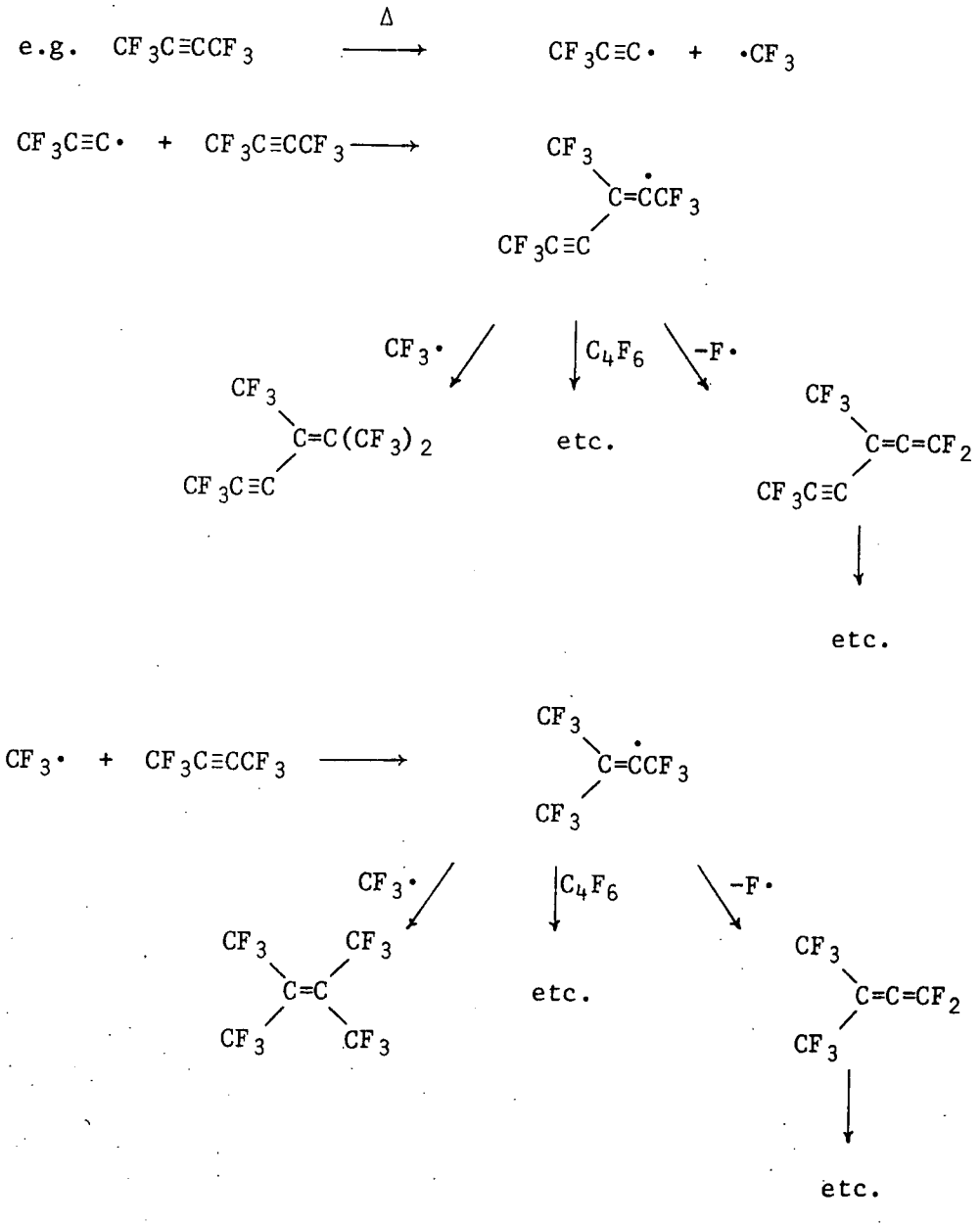
III.C.2 Reaction Conditions

Hexafluorocyclobutene was passed over caesium or potassium fluoride at several temperatures between 540 and 690° using a range of contact times. The results are summarised in the experimental section.

No significant differences were observed between the caesium fluoride and potassium fluoride catalysed reactions; both gave good conversions to hexafluorobut-2-yne at 590 - 600° with contact times of 20 - 30 seconds. Using higher temperatures or longer contact times significant amounts of complex liquid products (ca. 10 components) were obtained and the overall mass recovery was lower. At lower temperatures large amounts of hexafluorocyclobutene were recovered.

The liquid products were analysed by m.s. / g.l.c. and shown to have molecular weights in the region of 340 - 800 but they do not appear to be simple multiples of C_4F_6. Similar products were obtained on passing hexafluorobut-2-yne over potassium fluoride under the same conditions, indicating that these complex mixtures are derived from the butyne and not the cyclobutene. They can be thought of as being

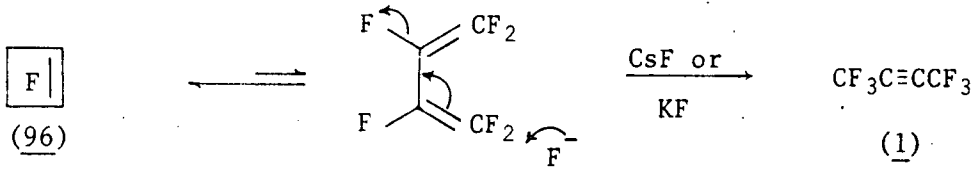
produced by free radical processes involving the initial homolytic fission of the C-C bond.



III.C.3 Discussion

The fluoride ion induced rearrangement of hexafluorocyclobutene (96) to give hexafluorobut-2-yne (1) can be conveniently considered as occurring in two stages. First, the cyclobutene ring opens to give hexafluorobuta-1,3,-diene (97), which is then isomerised under the

influence of fluoride ion to (1). Both of these reactions are well established and it is somewhat surprising that they had not previously been related.

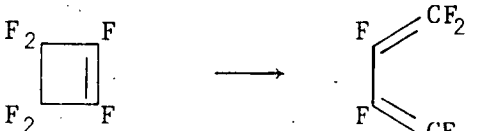
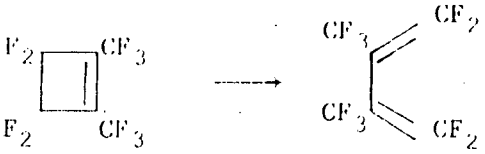


(96) (97) (1)

The thermal ring opening of cyclobutenes to give dienes is a well known reaction in hydrocarbon chemistry. At high temperatures the two isomeric forms often exist in equilibrium and in the case of cyclobutene itself the ring opening goes virtually to completion.[155] However, the position of equilibrium is dramatically changed on going from a hydrocarbon to a fluorocarbon system. Hexafluorobuta-1,3-diene (97) readily undergoes ring closure to give the cyclobutene (96)[156] and this difference in behaviour is clearly demonstrated by the ΔH values shown in Table III.3.

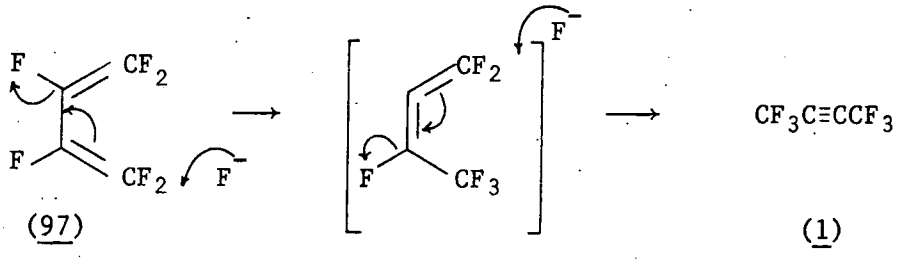
Table III.3

ΔH Values for Cyclobutene Ring Opening Reactions

	Reaction	ΔH (kJ/mol)
1)	 (98) → (99)	-33
2)	 (96) → (97)	+49
3)	 (78) → (100)	+ 1.7

These effects have been attributed to (a) destabilisation of the π system on substitution with fluorine,[156,157] similar to that invoked to account for the instability of 1-fluoroacetylenes (see Chapter I) and (b) the fact that the C-F bond strength increases in the change from sp^2 to sp^3 hybridisation.[158-160] Either of these considerations could explain the anomalous behaviour of hexafluorocyclobutene, as the number of fluorines attached to sp^2 hybridised carbon decreases from 6 to 2 on cyclisation..However, as there is the same net change in the number of sp^2 C-F bonds in both reactions (2) and (3) the fact that their enthalpies are different implies that the destabilisation introduced by fluorine attached to unsaturated carbon is additive in nature, i.e. (97) which has 6 sp^2 C-F bonds is destabilised to a greater extent than (100) which has only 4.

It is well established that terminal difluoromethylene groups are susceptible to attack by fluoride ion giving trifluoromethyl substituted compounds. In particular, the isomerisation of hexafluorobuta-1,3-diene (97) proceeds very readily at 100° to give a good yield of hexafluorobut-2-yne.[33] The reaction mechanism involves two S_N2' displacements by fluoride ion.



(97) (1)

Comparison of the total bond enthalpies of the carbon skeletons in but-2-yne and buta-1,3-diene indicates that the latter is the more stable molecule and this is the case for the hydrocarbon system.

Average bond enthalpies at 298K (kJ/mol)[162]:

C-C	348
C=C	612
C≡C	837

C-C≡C-C	C=C-C=C
2 C-C = 696	2 C=C = 1224
1 C≡C = 837	1 C-C = 348
Total 1533	Total 1572

However, the order of stability is reversed for the fluorocarbon analogues, i.e. hexafluorobut-2-yne is more stable than hexafluorobuta-1,3-diene and this is a further example of the instability of fluorine attached to unsaturated carbon.

In view of these considerations it is not surprising that the ring opening and isomerisation reactions can be carried out in one step by passing hexafluorocyclobutene over metal fluorides. A high temperature is necessary to drive the cyclobutene - butadiene equilibrium over to the right. The butadiene is then quantitatively converted to hexafluorobut-2-yne which can react further to give liquid products if the temperature is too high or the contact time too long. A temperature of 600° with a contact time of 30 seconds appears to be the best compromise as the ring opening goes to ca. 94% completion and only 3% of the butyne is converted to liquid products under these conditions.

CHAPTER IV

FREE RADICAL REACTIONS OF HEXAFLUOROBUT-2-YNE

IV.A Polymerisation and Attempted Copolymerisations of Hexafluorobut-2-yne

IV.A.1 Preparation and Properties of Polyhexafluorobut-2-yne

Irradiation of hexafluorobut-2-yne with high energy particles from a ^{60}Co source gives a white solid polymer[51,52] which is not attacked by boiling concentrated acids or bases and is insoluble in all common solvents.[51] Clearly such a material is of great interest particularly now that an efficient route to hexafluorobut-2-yne has been developed. Therefore it was decided to investigate some of the properties of this potentially useful polymer.

IV.A.1.a Introduction

Most of the reported structural investigations of polyhexafluorobut-2-yne have been carried out on the polymer which is produced from the reaction of the acetylene with fluoride ion. However, since the i.r. spectra are identical for both the fluoride ion and the gamma ray polymers (see Appendix II), it seems reasonable to assume that they have similar structures. A discussion of the structure of these polymers is given in Chapter V.

IV.A.1.b Preparation

Irradiation of commercial hexafluorobut-2-yne gave high yields (75-85%) of polymer and similar results were found using a sample of

the acetylene which had been prepared from perfluorocyclobutene by the method described in the previous chapter. However, poor yields of polymer were obtained from hexafluorobut-2-yne made by dechlorination of 2,3-dichlorohexafluorobut-2-ene. This is presumably due to the presence of traces of by-products which inhibit the polymerisation process. A similar phenomenon was observed in many of the attempted gamma ray induced addition reactions which are discussed later in this chapter. Even when no addition to the acetylene occurred, little or no polyhexafluorobut-2-yne was obtained. This apparent inhibition could be due to the operation of efficient chain termination processes when certain types of contaminants are present in the acetylene.

IV.A.1.c Thermal Behaviour

It is well known that polytetrafluoroethylene breaks down to the monomer on pyrolysis in vacuo and mass spectral data[89,90] indicated that polyhexafluorobut-2-yne might behave similarly. When a sample of the polymer, prepared by the method described in the previous section, was heated in vacuo at approximately 600° for 4 hours, a great deal of discolouration and a 10% loss in weight was observed. A little brown solid sublimed but no gaseous products were obtained. This aspect of the thermal behaviour of polyhexafluorobut-2-yne is therefore completely different to that of polytetrafluoroethylene.

Considerable differences between the thermal properties of the two polymers were also observed by thermogravimetric analysis (T.G.A.).[164] Isothermal experiments were carried out at 502, 550 and 600° in air and showed polyhexafluorobut-2-yne to be remarkably stable; e.g. at 502° polytetrafluoroethylene completely degraded after 4.5 hours whereas polyhexafluorobut-2-yne had only lost 7% of its mass (see Figure 1).

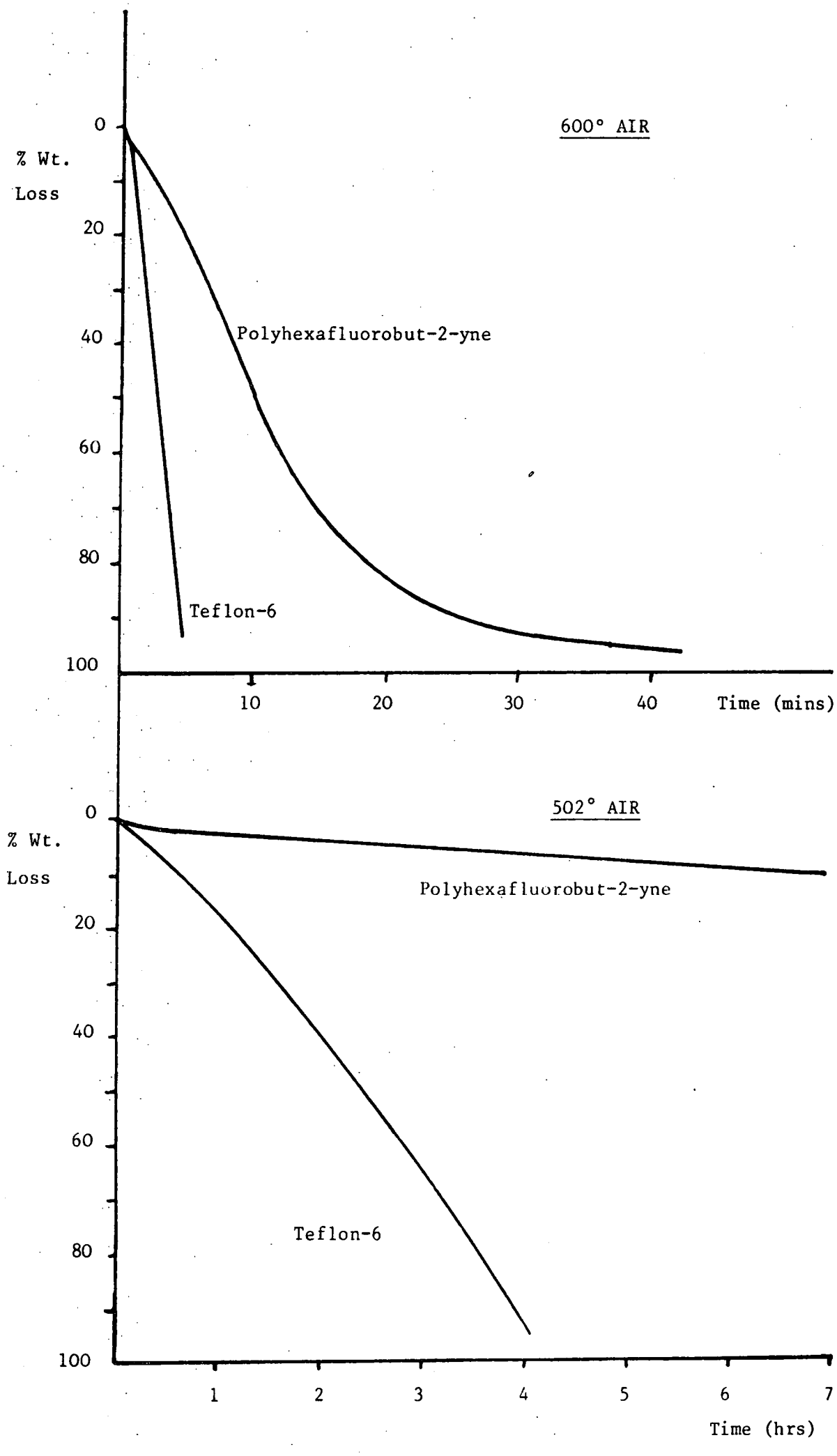

600° AIR
% Wt. Loss
0
20
40
60
80
100
Polyhexafluorobut-2-yne
Teflon-6
10
20
30
40
Time (mins)
502° AIR
% Wt. Loss
0
20
40
60
80
100
Polyhexafluorobut-2-yne
Teflon-6
1
2
3
4
5
6
7
Time (hrs)

Figure 1

When the temperature of the polymer was steadily increased decomposition suddenly set in at approximately 608° and was 50% complete by 644° and 687°, in air and nitrogen respectively.

IV.A.1.d Reaction with Aqueous Potassium Hydroxide Solution

Stirring the polymer with refluxing potassium hydroxide solution in glass apparatus gave a large quantity of silica like solid as the only product and no gas was evolved. Using a teflon reaction vessel, most of the polymer was recovered unchanged but a small fraction had evidently dissolved and could not be recovered from the brown reaction mixture. It would appear that hydrolysis does not occur readily because of difficulty in wetting the polymer, but its use in strongly caustic environments is clearly going to be limited.

IV.A.1.e Reaction with Fluorine and Bromine

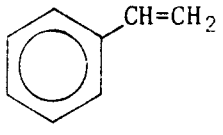
No significant uptake of fluorine was observed when the polymer was exposed to the neat gas at various temperatures up to 90°. However, in one experiment where the polymer was heated more strongly, it spontaneously combusted leaving a little black ash. The polymer is also resistant to attack by bromine, both in ordinary light and on exposure to u.v. radiation.

IV.B Attempted Copolymerisation Reactions

Several gamma ray induced reactions to prepare copolymers from hexafluorobut-2-yne have been attempted. With dimethyl acetylenedicarboxylate and styrene, quantitative recoveries of both the fluorocarbon and the

hydrocarbon were obtained. Methyl methacrylate, however, readily homopolymerised and the hexafluorobut-2-yne was recovered unchanged.

$CF_3C{\equiv}CCF_3 + CH_3OOCC{\equiv}CCOOCH_3 \xrightarrow{\gamma}$ no reaction

$CF_3C{\equiv}CCF_3 +$  $\xrightarrow{\gamma}$ no reaction

$CF_3C{\equiv}CCF_3 + CH_2{=}C(CH_3)(COOCH_3) \xrightarrow{\gamma}$ poly(methyl methacrylate)

This is an example of how the presence of other compounds can inhibit the polymerisation of hexafluorobut-2-yne. Even more surprisingly, hexafluorobut-2-yne prevents the homopolymerisation of styrene. The acetylenic diester did not form a homopolymer when irradiated by itself.

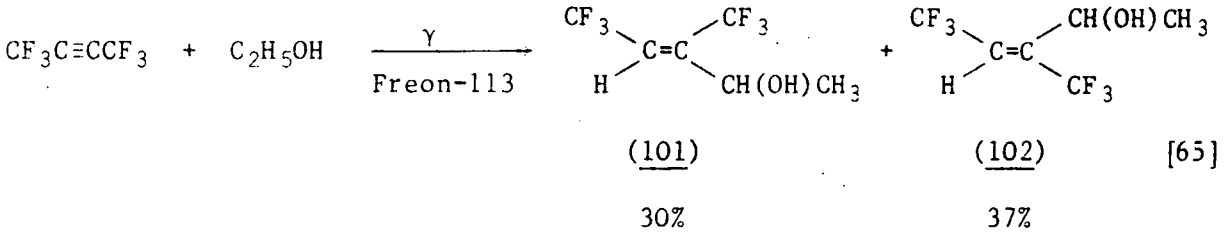
$CH_3OOCC{\equiv}CCOOCH_3 \xrightarrow{\gamma}$ no reaction

IV.C Free Radical Additions to Hexafluorobut-2-yne

IV.C.1 Introduction

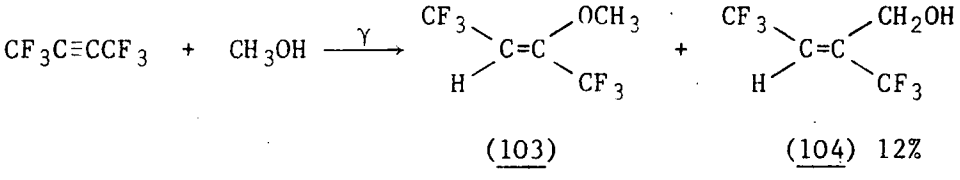
Several examples of free radical additions to hexafluorobut-2-yne have been reported and these were discussed in Chapter II. Most of these reactions involved compounds containing a relatively weak bond; for example halogens, hydrogen halides, perfluoroalkyl iodides and hydrogen sulphide all readily add in the presence of a suitable initiator. Only one report of a radical addition of a C-H bond across the triple bond of hexafluorobut-2-yne has appeared in the literature.[65] The radiation induced addition of ethanol using Freon-113 (1,1,2-trichloro-

trifluoroethane) as a solvent gave approximately equal amounts of the *cis* and *trans* adducts (101) and (102).



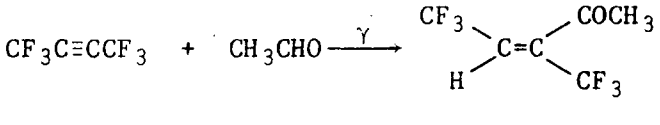
(101) 30% (102) 37% [65]

Work carried out in this laboratory has shown that a low yield of the *trans* adduct (104) was obtained from a similar reaction of hexafluorobut-2-yne with methanol in the absence of a solvent.[165] In this case however, the major product was (103), formed by nucleophilic attack by the alcohol.



(103) (104) 12%

Acetaldehyde was also found to add to hexafluorobut-2-yne, giving a low yield of the enone (105).[165]



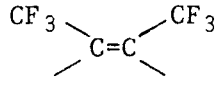
(105) 19%

Assignments of the stereochemistry were made for adducts (101)-(105) on the basis of well established n.m.r. coupling constants.[166-168] Typical values of CF_3 coupling constants are given in Table IV.1 and using this information it is an easy matter to distinguish between

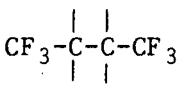
cis and *trans* isomers. Some of the smaller couplings (e.g. $J_{CF_3,CF_3,trans}$ and $J_{CF_3,H,vicinal}$) are often not properly resolved but the strong couplings (e.g. $J_{CF_3,CF_3,cis}$ and $J_{CF_3,H,geminal}$) are usually clearly defined and allow unambiguous assignments to be made.

Table IV.1

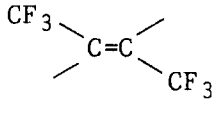
Characteristic CF_3 Coupling Constants



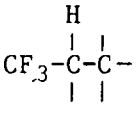
J = 11 - 13 Hz



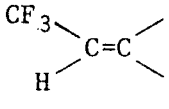
J = 0 - 18 Hz



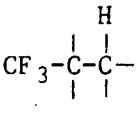
J = 1 - 2 Hz



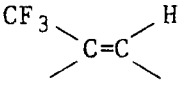
J = 2 - 29 Hz



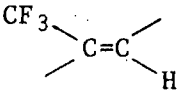
J = 7 - 9 Hz



J = 0 - 1.6 Hz



J = 0 - 2 Hz



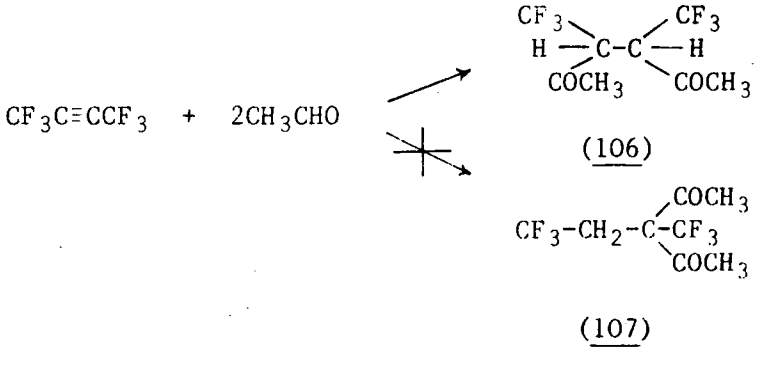
J = 0 - 1Hz

In this chapter free radical additions of various hydrocarbon and halocarbon derivatives to hexafluorobut-2-yne are discussed. Both gamma irradiation and peroxides were used to initiate the reactions.

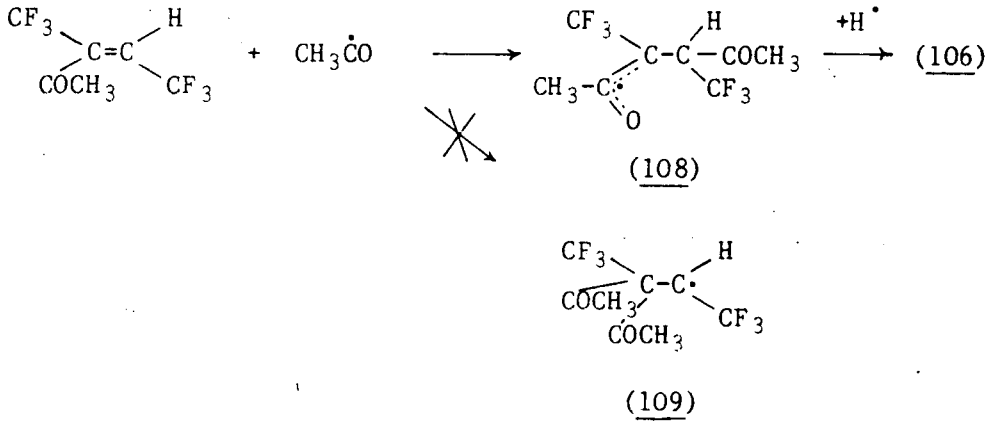
IV.C.2 Reactions with Aldehydes

IV.C.2.a Acetaldehyde

The reaction of hexafluorobut-2-yne with acetaldehyde was repeated using a longer dose of radiation than had previously been used and the yield of enone (105) was increased to 30%. A similar yield was obtained using benzoyl peroxide as the initiator and some solid product was also formed. After recrystallisation this gave a 17% yield of a compound which was shown to be a 2:1 adduct by mass spectroscopy and elemental analysis. The product was assigned the symmetrical structure (106) rather than the unsymmetrical structure (107) on the basis of the ^{19}F n.m.r. spectrum, which showed just one singlet in the CF_3 region.



Compound (106) is the product expected on steric grounds because addition of a $CH_3\dot{C}O$ radical to the 1:1 adduct would take place at the least crowded end of the double bond. Also the intermediate (108) is presumably lower in energy than (109) due to the stabilising effect of the carbonyl group adjacent to the radical centre.



(108)

(109)

A higher yield of 2:1 adduct was obtained using an excess of acetaldehyde.

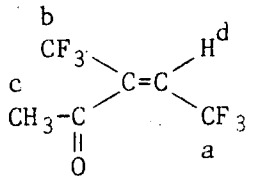
$CF_3C{\equiv}CCF_3$	+	CH_3CHO	⟶	(105)	+	(106)
1		2.5		18%		45%

Photolysis of (E)-3-Trifluoromethyl-1,1,1-trifluoropent-2-en-4-one (105)

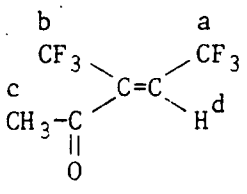
A slow reaction was observed when the 1:1 acetaldehyde adduct (105) was photolysed at 300 nm. G.l.c. of the product mixture showed the presence of (105) plus two other major components and m.s./g.l.c. demonstrated that these all had the same molecular weight. Three fractions were separated by preparative scale g.l.c. and two were identified as (105) and the *cis* isomer (110). The other component decomposed on the detector of the g.l.c. machine to give a mixture of (105) and (110). Attempts to isolate this unstable compound by using a low g.l.c. detector temperature gave similar results. Fortunately this third component could be identified from n.m.r. data on the mixture. After subtracting the signals due to (105) and (110) the remaining resonances could be assigned to the oxetene (111). These data are summarised in Table IV.2.

Table IV.2

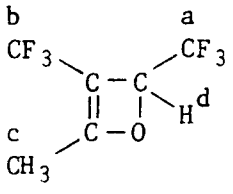
N.m.r. Data for $C_6H_4F_6O$ Isomers



(105)



(110)

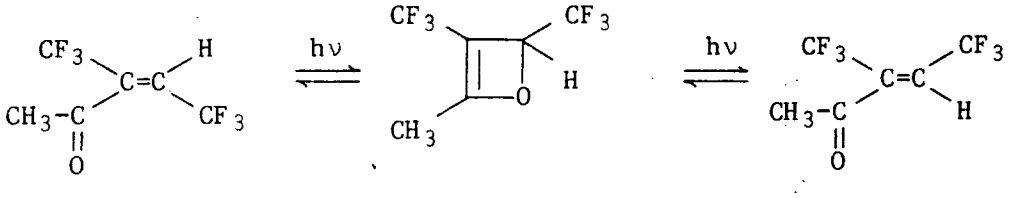


(111)

	Resonance	δ		Resonance	δ		Resonance	δ	
F	a	63.1	D, J_{ad}=7.5	a	62.1	M	a	81.2	S
	b	67.5	S	b	60.9	Q, J_{ba}=10	b	62.4	S
H	c	2.50	S(broad)	c	2.50	S(broad)	c	2.18	S
	d	6.45	Q, J_{da}=7.5	d	6.93	Q, J_{da}=8	d	5.58	S

S = singlet D = doublet Q = quartet M = multiplet

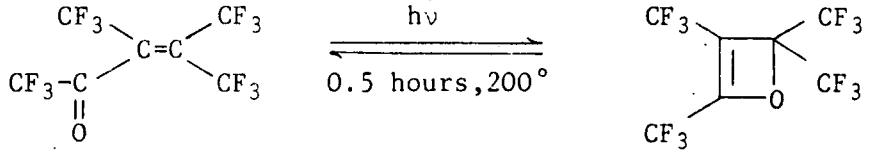
Although the yield of oxetene (111) increased with irradiation dose, a maximum of 72% conversion was observed after 94 hours. No further reaction had occurred by 352 hours and this suggests that a photo-equilibrium is set up as follows:



(105) (111) (110)

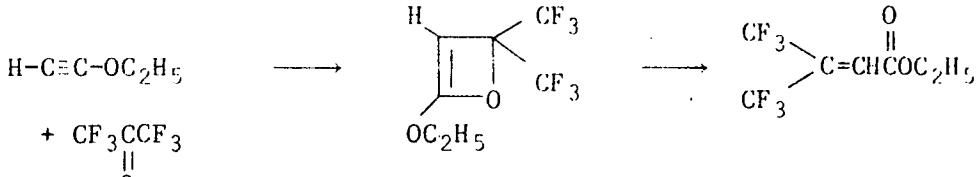
A number of related reactions have been discussed in the literature, giving oxetenes of varying degrees of stability. A few of these are mentioned here for the purpose of comparison. Miller has reported a photochemical cyclisation reaction giving an oxetene (116) which is

converted back to the enone (115) on heating.[100]



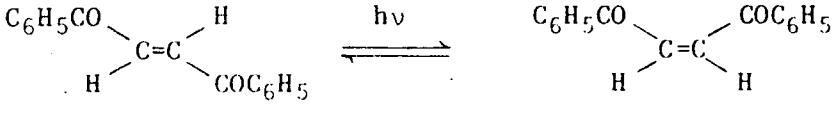
(115) (116)

The oxetene produced from the uncatalysed reaction of hexafluoroacetone and ethoxyacetylene slowly isomerises at room temperature to give the enone (117).[169]

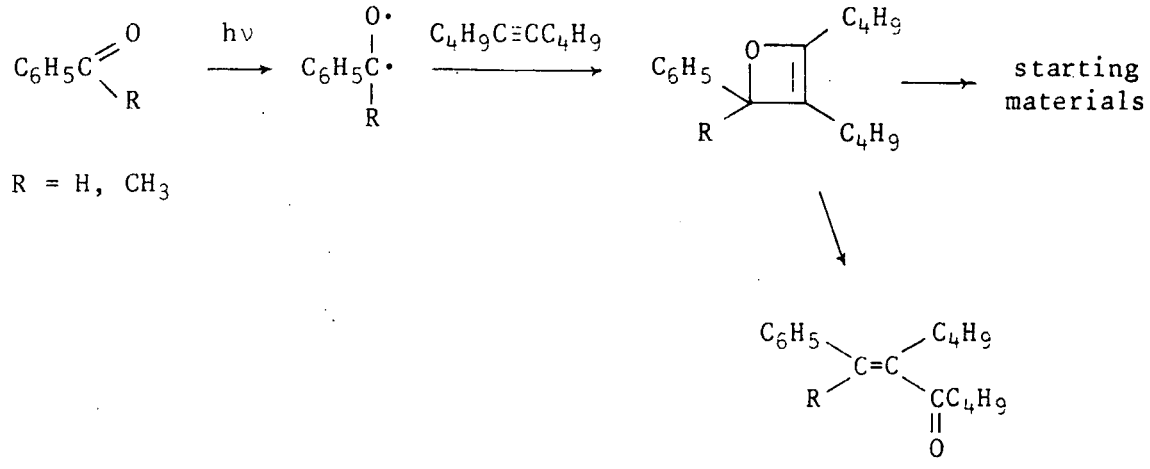


(117)

Relatively little has been reported on the photosensitised reactions of non-fluorinated acyclic enones. However, *trans*-dibenzoylethylene does undergo isomerisation on irradiation.[170]

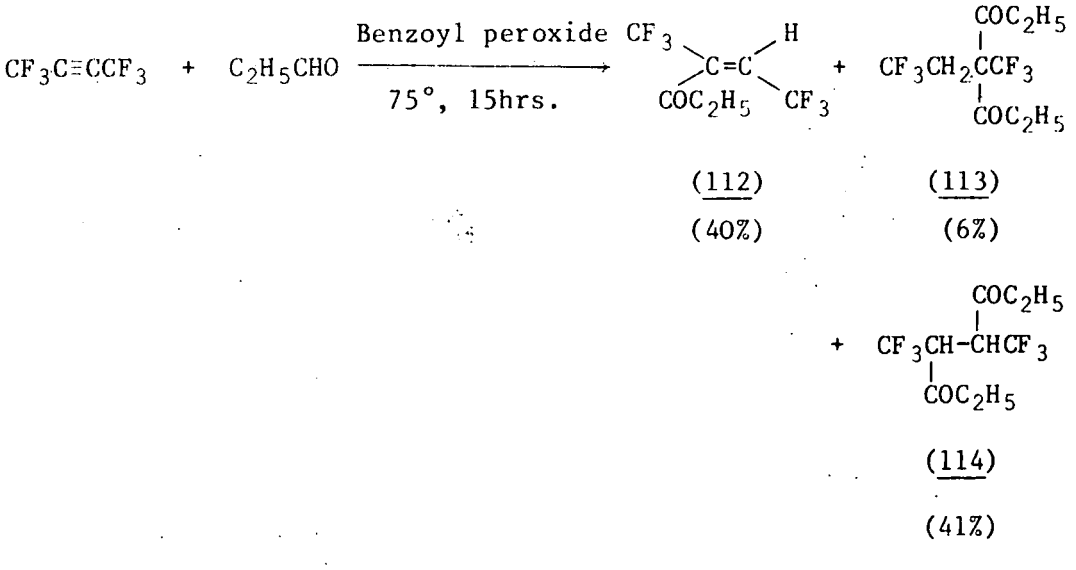


Photosensitised reactions of benzaldehyde and acetophenone with dibutylacetylene give unisolable oxetenes which decompose either back to starting materials or ring open to give enones.[171]



IV.C.2.b Propanal

Propanal and a small excess of hexafluorobut-2-yne reacted under benzoyl peroxide initiation to give both liquid and solid products. The liquid was a single component, identified by mass spectroscopy and n.m.r. as (E)-3-trifluoromethyl-1,1,1-trifluorohex-2-en-4-one (112) and the solid was a mixture of 12% unsymmetrical and 88% symmetrical 2:1 adducts (113) and (114).



Structural Assignments

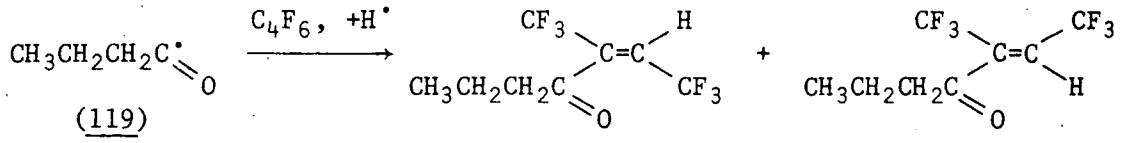
A *trans* structure was assigned to (112) by comparing coupling constants with those given in Table IV.1. The ^{19}F n.m.r. spectrum of (112) consists of two CF_3 resonances and the largest coupling constant was J = 7.5 Hz, arising from geminal H-CF_3 coupling. This rules out a *cis* configuration of the CF_3 groups leaving the structure (112) as the only possibility.

The mass spectrum of the solid showed a weak parent peak corresponding to an adduct formed by reaction of two molecules of propanal with one of hexafluorobut-2-yne and the ^{19}F n.m.r. spectrum indicated the presence of two different species. Three CF_3 resonances were observed, the strongest being a singlet arising from the symmetrical isomer (114) and two smaller singlets of lower intensity were assigned to the unsymmetrical isomer (113). These data are summarised in Table IV.3.

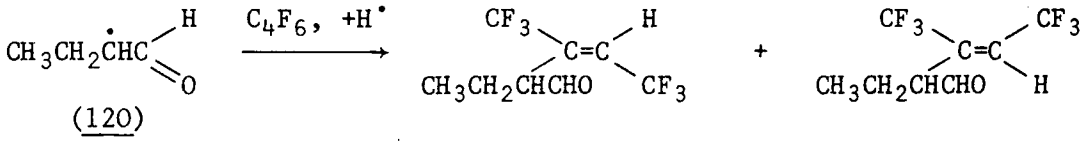
The formation of a mixture of 2:1 adducts is in contrast with the acetaldehyde reaction, as even on reexamining the products from the latter, only the symmetrical adduct (106) could be detected. The reason for this difference is not understood.

IV.C.2.c Butanal

Under benzoyl peroxide initiation, butanal reacted with a small excess of hexafluorobut-2-yne to give a liquid containing seven components. Three major and one of the minor components were identified as 1:1 adducts by m.s./g.l.c. and the expected product (118) was isolated by preparative scale g.l.c. Since attack by radical (119) can only produce two 1:1 adducts, it seems likely that the other two arise from a radical of type (120).

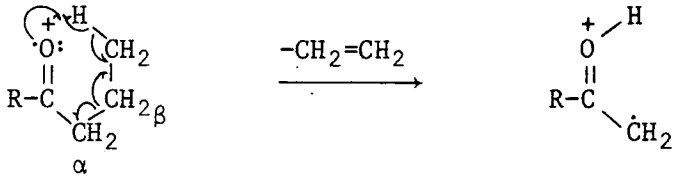


(119) (118)



(120)

Two of the other minor components showed high mass peaks which can be derived from 2:1 adducts by simple, well precedented fragmentations.[172]

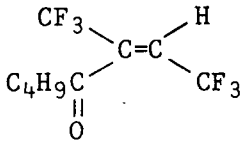


m/e = 306 m/e = 278

R = $CF_3CH_2C(CF_3)(COC_3H_7)$— or $CF_3CH(COC_3H_7)$———$CH(CF_3)$-

IV.C.2.d Pentanal

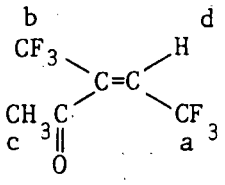
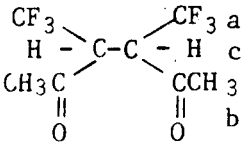
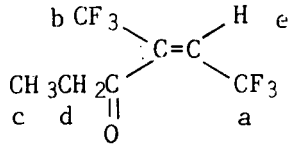
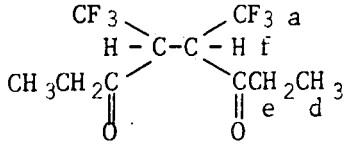
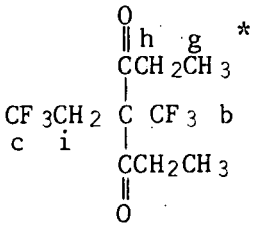
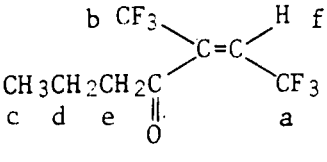
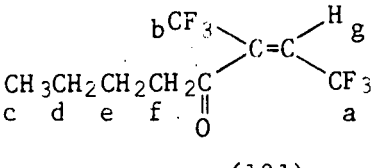
Pentanal reacted with hexafluorobut-2-yne using benzoyl peroxide as the initiator to give a complicated mixture of products from which two fractions were separable by preparative scale g.l.c. The first fraction was readily assigned the structure (121) by examination of the n.m.r. spectrum (see Table IV.3). Identification of the second fraction was not possible as it evidently contained two components which could not be separated.



(121)

Table IV.3

N.m.r. Data for Aldehyde Adducts

	Signal	^{19}F Chemical Shift	Multiplicity (J values in Hz)
 (105)	a	63.1	D, J_{ad} = 7.5
	b	67.5	
 (106)	a	63.9	S
 (112)	a	63.0	D, J_{ae} = 7 of Q, J_{ab} = 1.6
	b	67.3	Broad S
 (114) *	a	64.2	Broad M
 (113)	b	60.2	S
	c	69.6	S
 (118)	a	62.7	D, J_{af} = 7.5
	b	67.0	S
 (121)	a	57.5	D, J_{ag} = 7
	b	61.5	S

^1H

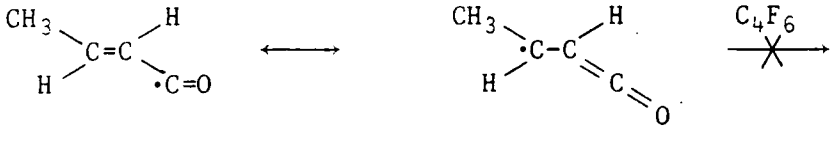
	Signal	Chemical shift	Multiplicity (J values in Hz)
(105)	c	2.50	S
	d	6.45	D, J_{da} = 7.5
(106)	b	2.4	S
	c	4.1	S
(112)	c	1.08	T, J_{cd} = 7
	d	2.69	Q, J_{dc} = 7
	e	6.40	Q, J_{ea} = 7 of Q, J_{eb} = 1.3
(114)*	d,g	1.13	
(113)*	e,h,i	2.68	Broad
	f	4.08	
(118)	c	0.95	T, J_{cd} = 7
	d	1.71	Sx, J_{dc} = J_{de} = 7
	e	2.72	T, J_{ed} = 7
	f	6.42	Q, J_{fa} = 7.5
(121)	c	0.86	T, J_{cd} = 7
	d,e	1.37	Broad M
	f	2.60	T, J_{fe} = 7
	g	6.23	Q, J_{ge} = 7

* run as a mixture of (113) and (114)

S = singlet, D = doublet, T = triplet, Q = quartet, Sx = sextet

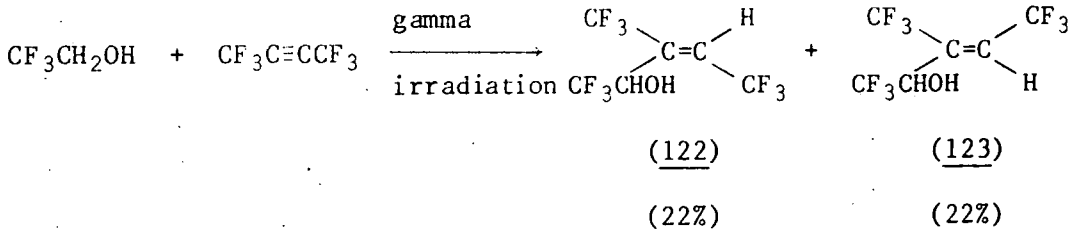
IV.C.2.e Attempted Reaction with (E)-But-2-enal (Crotonaldehyde)

No reaction occurred between (E)-but-2-enal and hexafluorobut-2-yne using benzoyl peroxide initiation and this is probably due to stabilisation of the intermediate radical by delocalisation of the unpaired electron.



IV.C.3 Reaction with 2,2,2-Trifluoroethanol

Irradiation of hexafluorobut-2-yne with an excess of trifluoroethanol gave a mixture of three products, from which the two major components were isolated in equal quantities. Spectral data showed these products to be (E)- and (Z)-3-trifluoromethyl-1,1,1,5,5,5-hexafluoropent-2-en-4-ol. The stereochemistry of these adducts followed from the ^{19}F n.m.r. coupling constants of the vinylic CF_3 groups.



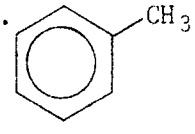
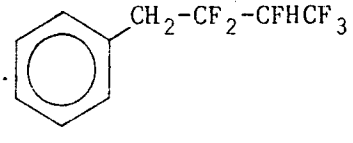
(122) (22%) (123) (22%)

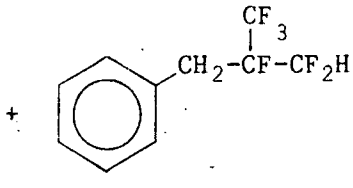
IV.C.4 Reactions Attempted with Other Compounds Containing C-H Bonds

Since aldehydes react quite readily with hexafluorobut-2-yne a series of free radical reactions was undertaken using a variety of functional hydrocarbons to determine which other types of C-H bond would add across the triple bond. Gamma irradiation, benzoyl peroxide and di-*tertiary*-butyl peroxide were used as initiators. Most of the compounds used failed to react with hexafluorobut-2-yne but small quantities of products were detectable from the reactions with aromatic hydrocarbons. The results are summarised in Table IV.4.

Discussion

Most of the hydrocarbons listed in Table IV.4 have been reported to react with fluoroalkenes under gamma ray or peroxide initiation.

e.g.  + $CF_2=CF-CF_3$ $\xrightarrow[\text{peroxide}]{\gamma \text{ or}}$ 



[173]

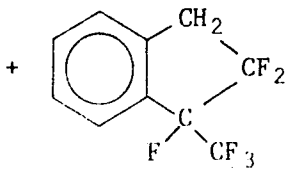
+ 

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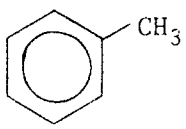
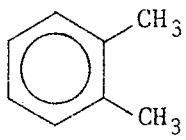
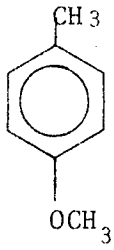
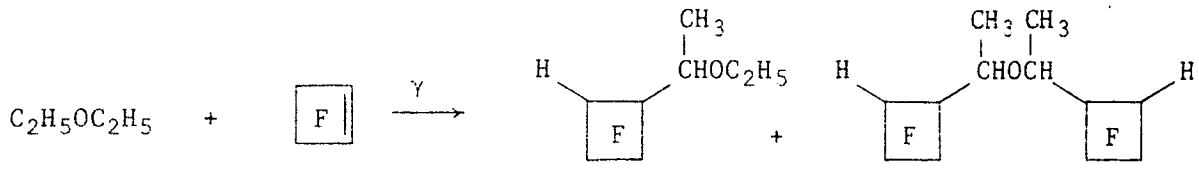
Table IV.4

Attempted Free Radical Additions to Hexafluorobut-2-yne

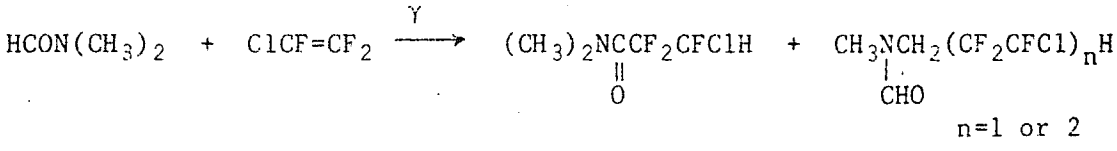
Reactant	Initiator	Results
$HCON(CH_3)_2$	A	No reaction
	γ	No reaction
CH_3OCH_3	A	No reaction
	γ	No reaction
	γ, 80°	No reaction
$CH_3CH_2OCH_2CH_3$	A	No reaction
$CF_3\overset{\overset{O}{\|}}{C}CF_2H$	γ	Some polymer
	γ	Some polymer + 3 products in trace amounts
	A	3 products in trace amounts
	B	Small yield of complex mixture of liquid products
	γ	Some polymer
	γ	Some polymer
	B	Small yield of complex mixture of liquid products

A benzoyl peroxide 75-85°

B di-*t*-butyl peroxide 125-135°

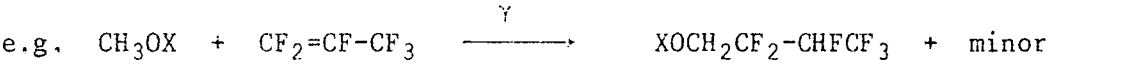


[174]



[175]

Recent work carried out in these laboratories has shown that a wide variety of ethers of the type CH_3OX add to fluoroalkenes in free radical processes to give products resulting from fission of a C-H bond α to the oxygen atoms.[165]

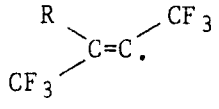


$X = CH_3$, CH_2OCH_3, $CH_2CH_2OCH_3$

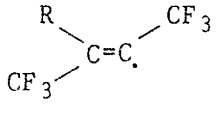
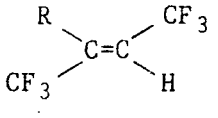
It is therefore somewhat surprising that analagous reactions with hexafluorobut-2-yne failed to give significant amounts of products. Almost quantitative recoveries of starting materials were observed in all the reactions using benzoyl peroxide and gamma irradiation as the initiator. A small amount of polyhexafluorobut-2-yne was formed in some cases but since ca. 80% polymerisation was observed when hexafluorobut-2-yne was irradiated alone, it must be concluded that these hydrocarbons have an inhibiting effect on the polymerisation reaction.

To underatand these observations it will be helpful to consider the mechanism of the free radical chain addition reaction. The process involves a series of steps summarised as follows.

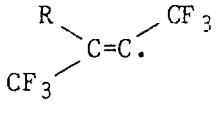
Initiation $R\text{-}H \xrightarrow{\text{Initiator}} R\cdot + H\cdot$ (1)

Propagation $R\cdot + CF_3C{\equiv}CCF_3 \longrightarrow$  (2)

(124)

Chain Transfer  + R-H ⟶  + R· (3)

Since hexafluorobut-2-yne is readily homopolymerised by gamma irradiation some degree of telomerisation might also be anticipated (Step 4) although no telomeric products were detected in any of the benzoyl peroxide or gamma ray initiated addition reactions. Chain termination occurs by radical-radical combination reactions.

Telomerisation  + $CF_3C{\equiv}CCF_3 \longrightarrow R\text{-}[C(CF_3)=C(CF_3)]_2^{\cdot}$ (4)

The ease with which the initiation step proceeds depends on the strength of the bond to be broken. Some dissociation energies of C-H bonds in different environments are given in Table IV.5.

Obviously the initiation step is not the determining factor in these reactions, since in view of the bond energies shown in Table IV.5, dimethyl ether would be expected to undergo homolytic C-H bond fission more readily than methanol. Also, the reactions with fluoroalkenes demonstrate that ethers form radicals quite readily. As mentioned above these radicals add to a wide range of fluoroalkenes and furthermore, radicals of the type $CH_3\dot{C}O$ and $CH_3\dot{C}HOH$ readily add to hexafluorobut-2-yne.

Table IV.5

Bond Dissociation Energies of C-H Bonds in Selected Compounds[176]

R-H	B.D.E. kJ mol^{-1}
CH_3-H	434
C_6H_5-H	431
C_2H_5-H	410
CCl_3-H	402
$HOCH_2$-H	389
CH_3OCH_2-H	385
CH_3CO-H	366
$C_6H_5CH_2$-H	356

It is therefore probable that the propagation step also occurs for the unsuccessful reactions shown in Table IV.4.

$$R\cdot + CF_3C{\equiv}CCF_3 \longrightarrow \underset{CF_3}{\overset{R}{\diagdown}}C{=}C\overset{CF_3}{\diagup} \qquad (124)$$

R = $CH_3O\dot{C}H_2$, $C_2H_5O\dot{C}HCH_3$ etc.

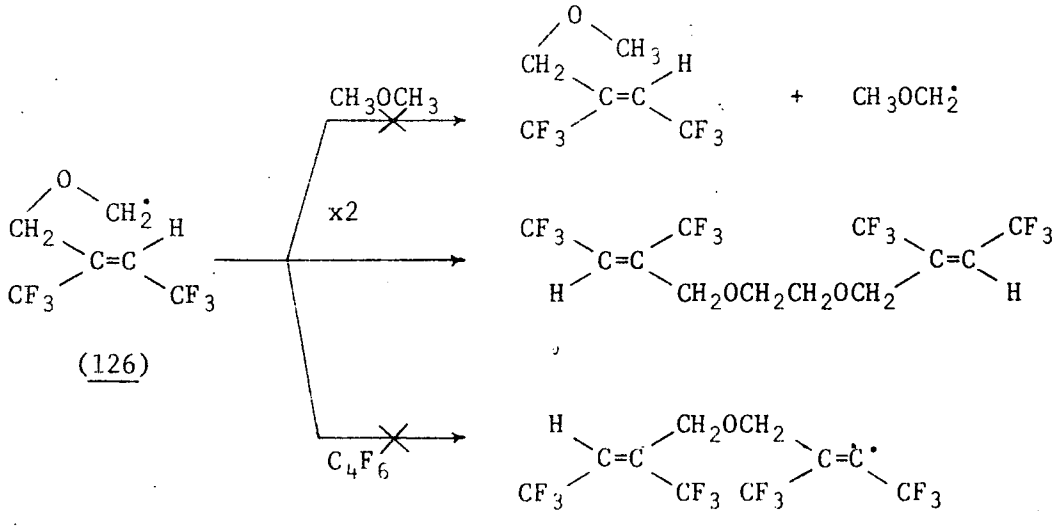
Thus it seems that there is some difference between the intermediate radicals (124) which allows the chain reaction to proceed when R· = $CH_3\dot{C}O$ and $CH_3\dot{C}HOH$ but favours chain termination when R = $CH_3O\dot{C}H_2$ etc. A difference of a factor of one hundred in the chain lengths of these processes would be sufficient to fit the observations.

In the case of the reaction with dimethyl ether, the intermediate radical (125) has the possibility of undergoing intramolecular hydrogen

atom transfer to give (126). This radical can abstract a hydrogen atom, react with a further molecule of butyne or dimerise.

(125) (126)

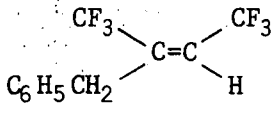
It has been found that dimethyl ether adducts of the type $HR_FCH_2OCH_3$ are less reactive towards fluoroalkenes than dimethyl ether itself[165] and therefore it is unlikely that radical (126) will attack another molecule of acetylene. It is also possible that radical (126) is too unreactive for it to abstract a hydrogen atom from dimethyl ether, leaving dimerisation as the most likely alternative. This would have the effect of terminating the chain reaction and would account for the failure to observe detectable quantities of products.



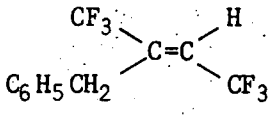
(126)

Traces of products formed from the benzoyl peroxide and γ ray initiated reactions with toluene were not isolable but m.s./g.l.c.

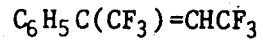
showed the presence of the two isomeric 1:1 adducts which are probably the *cis* and *trans* isomers (127) and (128). In addition the benzoyl peroxide initiated reaction gave a third component which corresponded to an adduct of type (129). This product presumably arises from reaction of hexafluorobut-2-yne with phenyl radicals generated from the initiator.



(127)

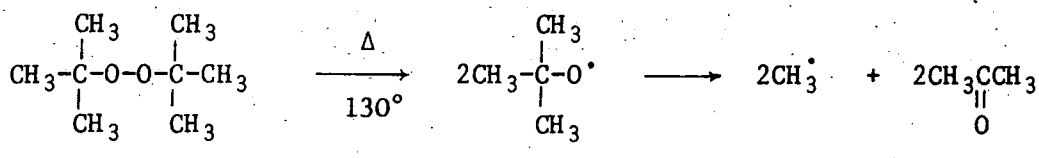


(128)

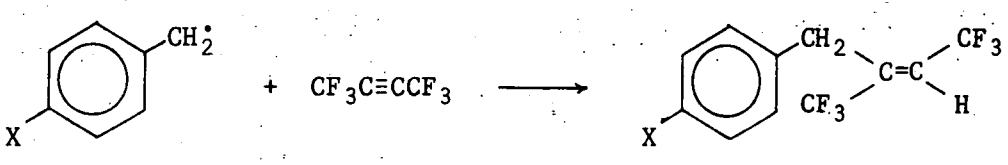


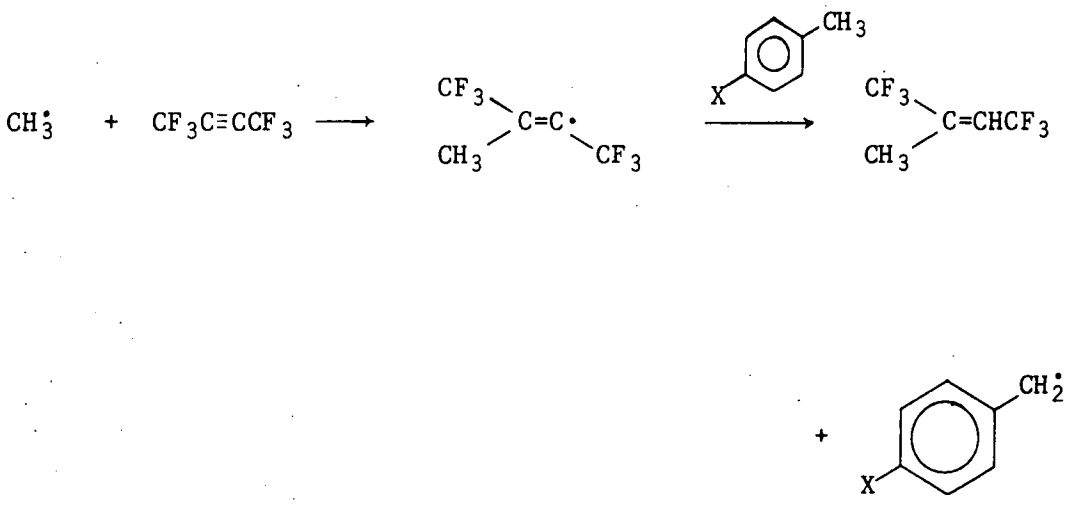
(129)

Better conversions of hexafluorobut-2-yne (ca. 10%) were obtained in the di-*tertiary*-butyl peroxide (DTBP) induced reactions, probably because of the higher temperature at which they were performed. The products from these reactions were very complicated mixtures but m.s./g.l.c. showed that some of the expected adducts were indeed formed together with products arising from the attack of methyl radicals (generated from the initiator) on hexafluorobut-2-yne.



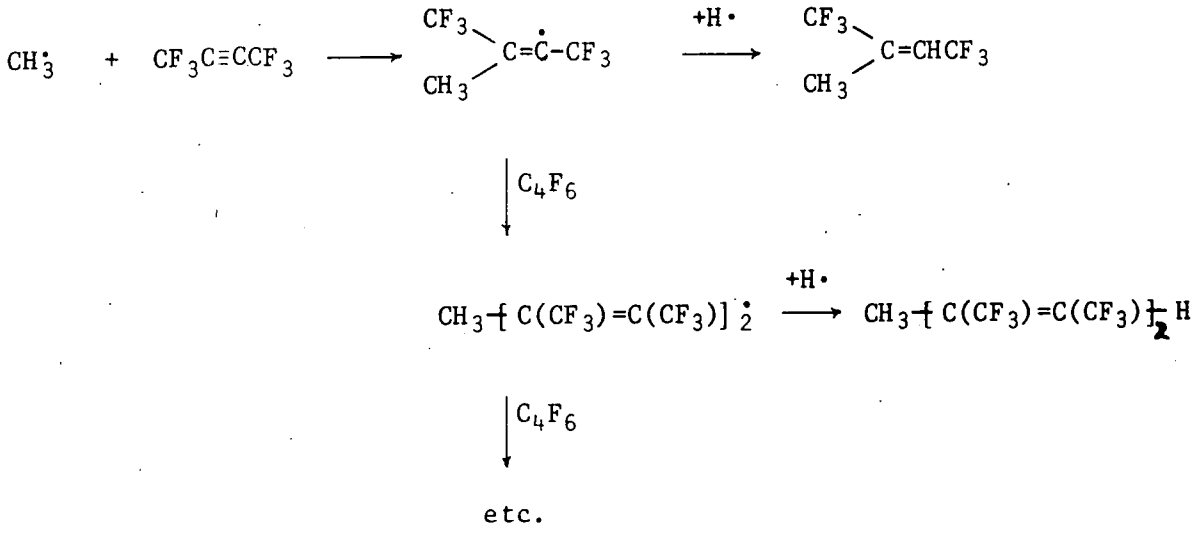
X = H or OCH_3





For comparison the reactions of hexafluorobut-2-yne with initiators were investigated. Benzoyl peroxide was recovered quantitatively on heating with hexafluorobut-2-yne at 70° for 16 hours. This result was very surprising, since under these conditions, substantial decomposition of the peroxide would have been anticipated (half life of benzoyl peroxide at 80° is ca. 3.5 hours[177]). However, the same results were obtained on repeating the experiment at 75°. In a control reaction a sample of the same peroxide was found to be an effective initiator for the addition of acetaldehyde to hexafluorobut-2-yne. No satisfactory explanation for these results has been found.

However, complex liquid products were obtained when hexafluorobut-2-yne was heated with DTBP. A series of oligomers of the type $CH_3-(C_4F_6)_n-H$, where n = 1 - 4, was detectable by m.s./g.l.c. and these are presumably produced by a methyl radical induced telomerisation process.



IV.C.5 Reactions Attempted with Compounds Containing C-X Bonds

A few free radical reactions of hexafluorobut-2-yne with compounds containing carbon-halogen bonds were attempted but no products were observed except for a little polymer. The results are summarised in Table IV.6.

Table IV.6

Attempted Reactions with Halogen Containing Compounds

Compound	Initiator	Results
$CHCl_3$	γ	No reaction
CCl_4	γ	Some polymerisation
$CFCl_3$	γ	Some polymerisation
CF_2Br_2	γ	Some polymerisation
$CH_3\overset{\overset{O}{\|}}{C}Cl$	γ	Some polymerisation

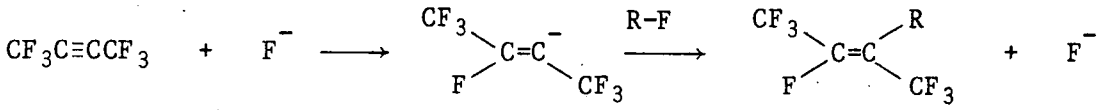
Similar arguments to those given in the previous section can be used to account for the failure of these halocarbon systems to add to hexafluorobut-2-yne. In view of the results given in the previous section it is perhaps not surprising that electrophilic radicals such as $CCl_3^{\bullet}$ and $CFCl_2^{\bullet}$ do not react with the very electrophilic acetylene.

CHAPTER V

REACTIONS INVOLVING FLUORIDE ION

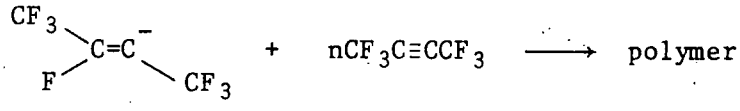
V.A Introduction

Several fluoride ion induced reactions of hexafluorobut-2-yne have been reported in the literature and these were discussed in Chapter II. Most of these reactions involved the initial formation of the heptafluorobutenide anion (51), which was then trapped by reagents susceptible to nucleophilic attack.



(51)

In the absence of a trapping agent, (51) reacts with further molecules of hexafluorobut-2-yne to give a homopolymer.



(51)

The work described in this chapter falls into three categories. Firstly, the fluoride ion induced polymerisation of hexafluorobut-2-yne was repeated and some of the properties of the polymer were investigated. Then copolymerisation of hexafluorobut-2-yne with other electrophilic acetylenes was studied and finally, a series of fluoride ion catalysed co-oligomerisations of hexafluorobut-2-yne with perfluoroalkenes is described.

V.B Polymerisation and Copolymerisation Reactions

V.B.1 Polyhexafluorobut-2-yne

V.B.1.a Introduction

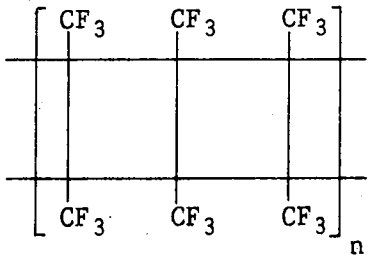
The gamma ray initiated polymerisation of hexafluorobut-2-yne was discussed in the previous chapter. This section deals with the fluoride ion induced polymerisation, which was first observed in the course of work involving the addition of the heptafluorobutenide anion (51) to polyfluoroaromatic systems.[92,93]

In the presence of a dipolar aprotic solvent and a source of fluoride ion, hexafluorobut-2-yne polymerises in good yield to give a chemically inert, off-white solid.[92-4] The most obvious structure which can be envisaged for the polymer is the linear polyene (130), arising from a simple anionic polymerisation process.

$$F^- + CF_3C{\equiv}CCF_3 \longrightarrow FC(CF_3){=}\bar{C}(CF_3) \xrightarrow{C_4F_6} F\!\left[C(CF_3){=}C(CF_3)\right]_n$$

(130)

However, a polymer with this type of structure might well be expected to be coloured and the fact that it is actually off-white appears to support a highly crosslinked ladder type structure such as (131).



(131)

A saturated structure is also indicated by the absence of a C=C stretch in the infrared spectrum,[92-4] although this could simply be a consequence of the symmetry of the double bonds in structure (130).

The mass spectrum of the volatile fractions of the polymer was repetitive every 162 mass units[92,93] and showed the presence of a series of oligomers of general formula $F-(C_4F_6)_n H$.[95] This is consistent with a polymerisation process initiated by fluoride ion and terminated by proton abstraction from the solvent but it does not provide a means of distinguishing between the two possible structures. The polymer was finally assigned the polyene structure following an ESCA investigation.[163]

V.B.1.b Preparation and Thermal Behaviour

Fluoride ion induced polymerisations of hexafluorobut-2-yne were carried out using sulpholan and tetraglyme as solvents and the resulting off-white solids were studied by thermogravimetric analysis (T.G.A.).[164] These samples were considerably less stable than the polymer obtained by gamma irradiation (see Chapter IV). The latter showed no significant weight loss until 608°, whereas the polymers prepared using caesium fluoride started to sublime at 200°. By 600°, the weight loss was approximately 50% and these results are as would be anticipated for a polymer consisting of a mixture of oligomers with a large range of molecular weights.

V.B.1.c Solubility

The fluoride ion polymer was partly soluble in acetone and methanol, again indicating the presence of low molecular weight material. It was observed that when these solutions were evaporated from a glass surface,

the residue rendered the surface water-repellent.[164]

V.B.2 Copolymerisation with Acetylenic Esters

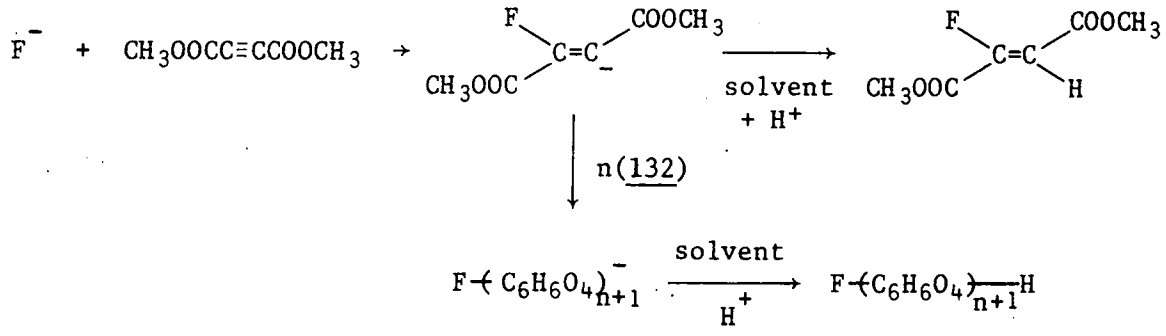
Reaction of hexafluorobut-2-yne (1) with the acetylenic diester (132) in the presence of caesium fluoride gave a tan coloured copolymer.

$$CF_3C{\equiv}CCF_3 \quad (1) \quad + \quad CH_3OOCC{\equiv}CCOOCH_3 \quad (132) \xrightarrow[\text{tetraglyme}]{\text{CsF}} \text{copolymer}$$

Only a few peaks at low mass number were seen in the mass spectrum. Peaks due to CF_3 and C_2F_5 were observed but those due to the molecular ions of (1) and (132) were very weak, indicating that the copolymer breaks down in a different manner to polyhexafluorobut-2-yne.

The ratio of (1) to (132) in the copolymer was dependent on how the reaction was performed. When the ester (132), caesium fluoride and tetraglyme were stirred together under an atmosphere of hexafluorobut-2-yne, the resulting copolymer was shown by elemental analysis to contain (1) and (132) in the ratio of 9.5:1. However, adding the two acetylenes simultaneously in small quantities gave a copolymer with a 2.1:1 ratio of monomer units.

These solids were shown to be genuine copolymers rather than mixtures of the two homopolymers since a reaction of the diester (132) with caesium fluoride in tetraglyme gave no solid products. Furthermore no starting material or liquid products were recovered by reduced pressure distillation and t.l.c. also indicated that all the diester had been consumed. The products from this reaction therefore probably consist of a series of involatile oligomers of the type $F\text{-}(C_6H_6O_4)_n\text{-}H$, by analogy with the fluoride ion initiated polymerisation of hexafluorobut-2-yne.



Polymerisation of dimethyl acetylenedicarboxylate has been reported by Russian workers using either neat amines[178-9] or various alkali metal salts in D.M.F.[180] as initiators and these observations lend support to the mechanism proposed above for the fluoride ion induced process. However, the oligomers of (132) were soluble in tetraglyme and could not be isolated from the reaction mixture.

This result allows for a better understanding of the copolymerisation reactions observed above. In the first reaction most of the diester probably homo-oligomerised before it had chance to react with the fluorocarbon. The homo-oligomers were left in solution and therefore the residual polymer contained a large excess of hexafluorobut-2-yne units. However, in the second reaction the chance of copolymerisation was increased by adding the monomers simultaneously and therefore the ester content of the resulting polymer was increased.

The copolymer obtained from a similar reaction between hexafluorobut-2-yne and diethyl acetylenedicarboxylate (133) was a brown viscid material which was soluble in ether. Elemental analysis indicated that this material contained ester and fluorocarbon units in a ratio of approximately 6:1.

It was of considerable interest to determine whether these copolymers could be hydrolysed to give a polymer containing both trifluoromethyl and carboxylic acid groupings. Such a functionalised

fluorocarbon polymer might have potential applications as an ion-selective membrane in electrolytic cells, as have certain copolymers of tetrafluoroethylene.[189] However, all attempts to hydrolyse the copolymer of (1) and (132) gave only recovered starting material even under forcing conditions. It was believed that this apparent unreactivity was due to difficulties in wetting the surface of the polymer and therefore a series of experiments was attempted using various surfactants. Again no hydrolysed products were obtained and it was concluded that perhaps the copolymer exists in a conformation where the ester groups are shielded against attack by the fluorocarbon units.

V.C. Co-oligomerisation with Fluoroalkenes

V.C.1 Introduction

An interesting analogy has been drawn between the role of fluoride ion in fluorocarbon chemistry and that of the proton in hydrocarbon chemistry.[181] Just as alkenes rearrange, polymerise or act as alkylating agents under acidic conditions, in the presence of fluoride ion, fluoroalkenes:

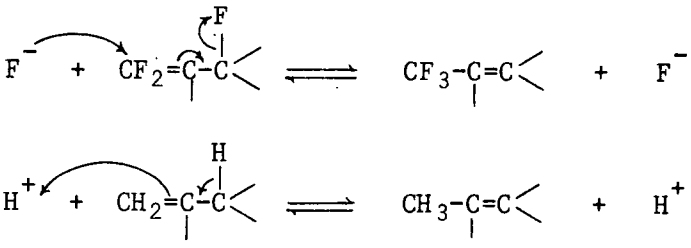
a) rearrange to give isomers containing the lowest possible number of vinylic fluorines,

b) oligomerise to give, usually, dimers, trimers and tetramers,

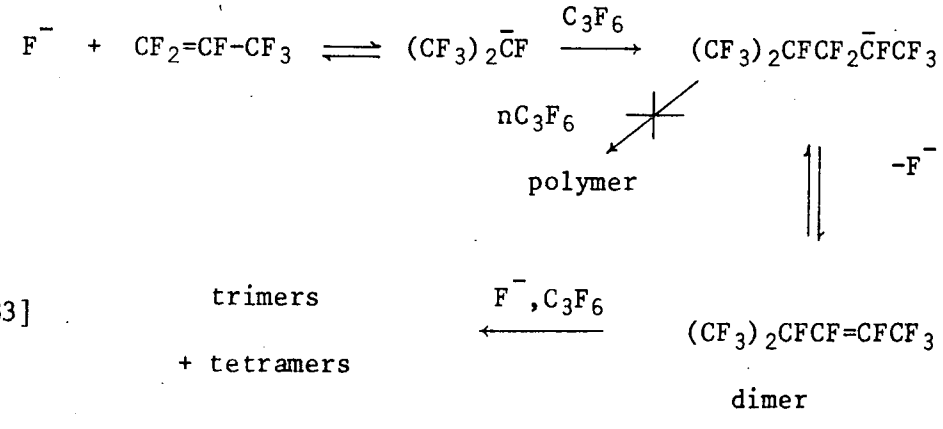
c) react with activated polyfluoroaromatic systems in what may be regarded as the nucleophilic equivalent of a Friedel-Crafts reaction.[182]

Examples of these processes are summarised below and, for comparison, the corresponding reactions in hydrocarbon chemistry are given.

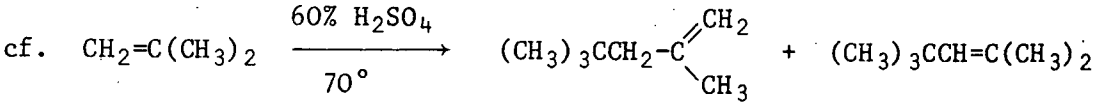
Rearrangement:

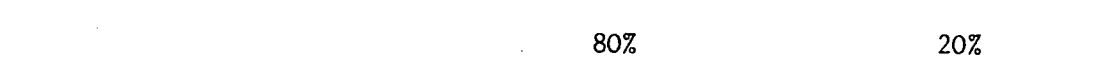


Oligomerisation:

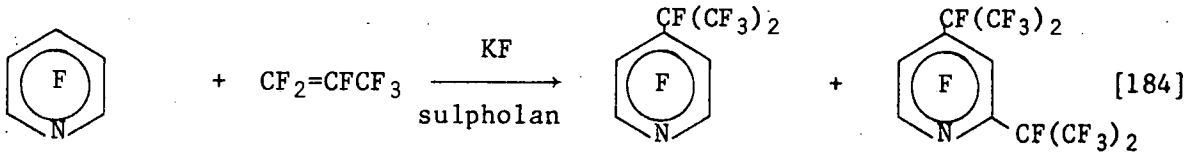


[183]

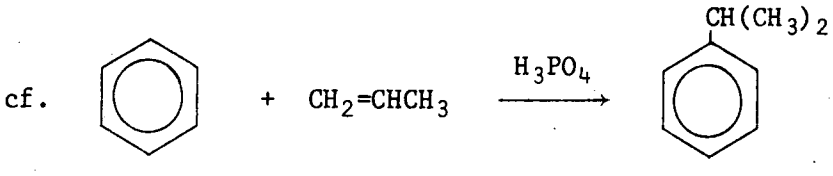




Alkylation Reactions:

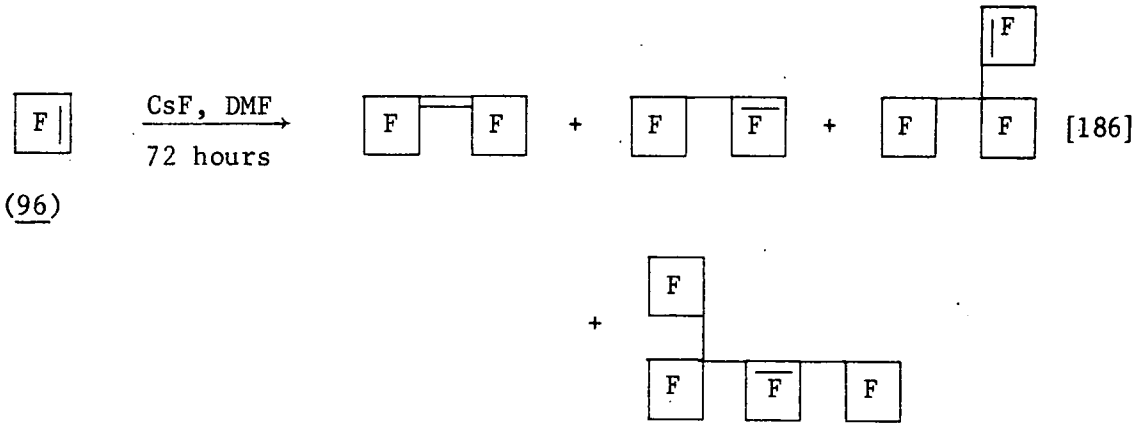


[184]



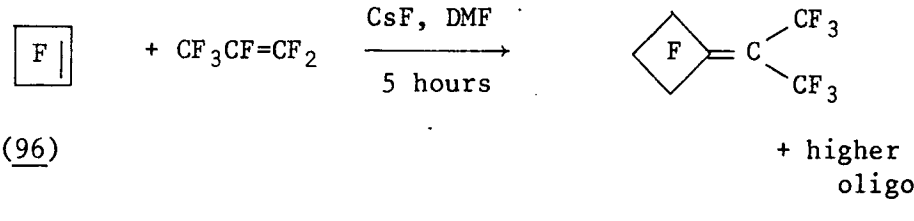
In recent years a wide range of novel perfluorinated compounds have been prepared by fluoride ion catalysed oligomerisations of fluoroalkenes.[195,154] The process has been extended to produce a series of co-oligomers incorporating two different fluoroalkene units.

e.g.



[186]

(96)

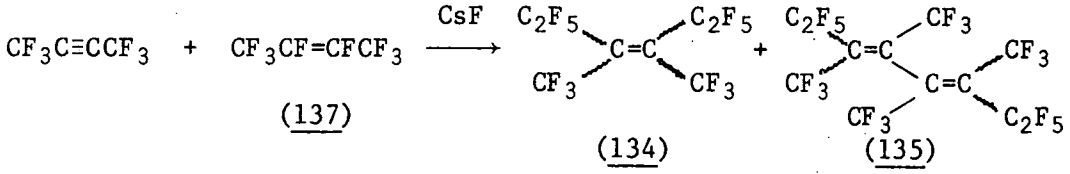


[187]

(96)

+ higher oligomers

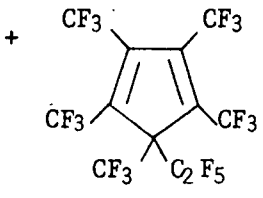
However, no similar reactions with hexafluorobut-2-yne have been reported in the literature, although previous work in this laboratory[185] indicated that oligomers (134)-(136) were produced from the reaction with octafluorobut-2-ene (137).



(137)

(134)

(135)

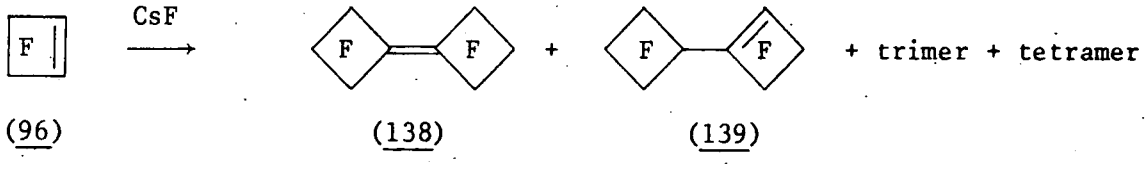


(136)

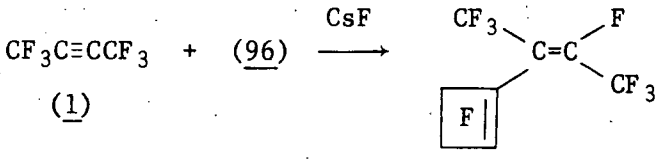
This section describes the preparation of co-oligomers from hexafluorobut-2-yne and the mechanism of these reactions is discussed.

V.C.2 Hexafluorocyclobutene

A rapid reaction occurred when a stirred suspension of caesium fluoride in tetraglyme was exposed to an atmosphere containing equal amounts of hexafluorobut-2-yne and hexafluorocyclobutene. Virtually all the gas had been consumed after 24 hours and three different procedures were attempted to work up the resulting reaction mixture. Flash distillation gave a very small recovery (5%) of a multicomponent liquid. Aqueous work-up gave a 26% recovery of a multicomponent liquid together with 53% of a tarry intractable material. A 25% recovery of a very complex mixture of liquid products was obtained by steam distillation. No products could be isolated from any of these mixtures but three dimeric species could be detected by m.s./g.l.c.. Since the fluoride ion initiated oligomerisation of (96) gives only two dimers,[186] (138) and (139), the third product is presumably a codimer of the type (140).



(96) (138) (139)

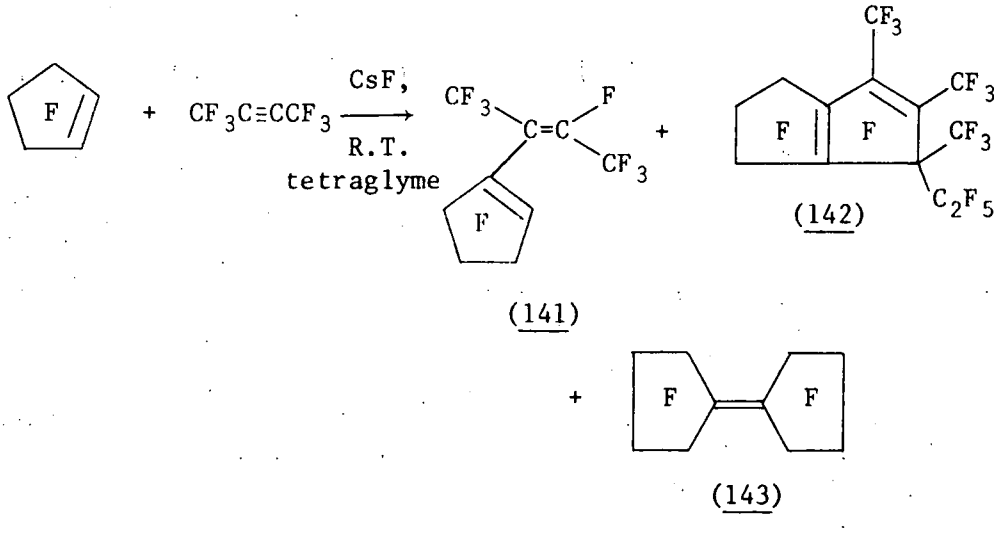


(1) (140)

V.C.3 Perfluorocyclopentene

This reaction proceeded rapidly, and virtually all the starting materials were consumed within 24 hours. Once again, however, low mass recoveries were obtained and the product mixtures were complex.

In a typical experiment with tetraglyme as the solvent, a 25% recovery of fluorocarbon was obtained using flash distillation to work up the reaction mixture. Steam distillation gave a better recovery (60%) but the product mixture contained ten components. However, small quantities of compounds (141) and (142) were isolated by preparative scale g.l.c. and m.s./g.l.c. revealed the presence of cyclopentene dimer (143).

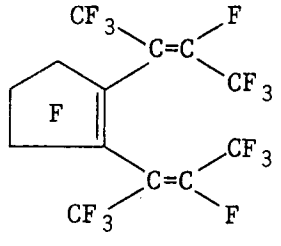


(141) (142)

(143)

Both (141) and (142) showed a parent peak in the mass spectrum and gave satisfactory elemental analyses. Structures were assigned on the basis of their ^{19}F n.m.r. spectra. Compound (141) showed two vinylic CF_3 groups, two vinylic fluorine atoms and three distinct CF_2 groups. The side chain was assigned a *trans* configuration by inspection of the CF_3 coupling constants as described in the previous chapter. The other co-oligomer was assigned the bicyclic structure (142) rather than the

isomeric 1,2-dibutenylcyclopentene structure (144) because the n.m.r. spectrum showed only CF_3 and CF_2 resonances. Also the weak C=C stretch in the infrared spectrum indicates the absence of vinylic fluorine atoms and is therefore consistent with structure (142).



(144)

A series of reactions using a variety of solvents was carried out in an attempt to improve the mass recovery but both sulpholan and dimethylformamide gave similar results to those described above. The use of a volatile solvent was then investigated as it was anticipated that it could be removed by distillation to leave the products behind. However, when the reaction was carried out in acetonitrile the majority of the product distilled over with the solvent and could not be isolated. The distillation residue was a complex intractable oil which was not investigated further. It therefore appears that the reaction in acetonitrile gives mainly volatile low oligomers, whereas the other solvents favour the formation of higher molecular weight compounds.

V.C.4 Perfluorocyclohexene

No reaction between hexafluorobut-2-yne and perfluorocyclohexene was observed either at room temperature or at 60°. Instead the acetylene homopolymerised and perfluorocyclohexene was recovered unchanged.

V.C.5 Hexafluoropropene

This reaction proceeded to virtual completion within 24 hours but again poor mass recoveries were obtained. However, a small quantity of liquid containing four major components was obtained and these were identified by m.s./g.l.c. as $C_{14}F_{24}$, $C_{11}F_{18}$ and two isomers of $C_{10}F_{18}$. Except for $C_{14}F_{24}$, these were isolated by preparative scale g.l.c. and the $C_{11}F_{18}$ component was identified as (145). This compound showed a parent peak in the mass spectrum and gave a satisfactory elemental analysis. The ^{19}F n.m.r. spectrum of (145) shows just two resonances in the CF_3 region with relative intensities of 2:1, implying a highly symmetrical structure for this compound. The structure was confirmed by comparing the spectral data for this compound with that of a closely related model compound (see section V.C.7.c.).

One of the $C_{10}F_{18}$ fractions could be assigned the cyclohexene structure (146), although the ^{19}F n.m.r. spectrum was complicated by the presence of several stereoisomers. Several of the resonances were either broadened or split but the two vinylic CF_3 groups and the two tertiary fluorines were clearly visible. (A tertiary fluorine is one attached to a saturated carbon on which all the other substituents are themselves carbon.)

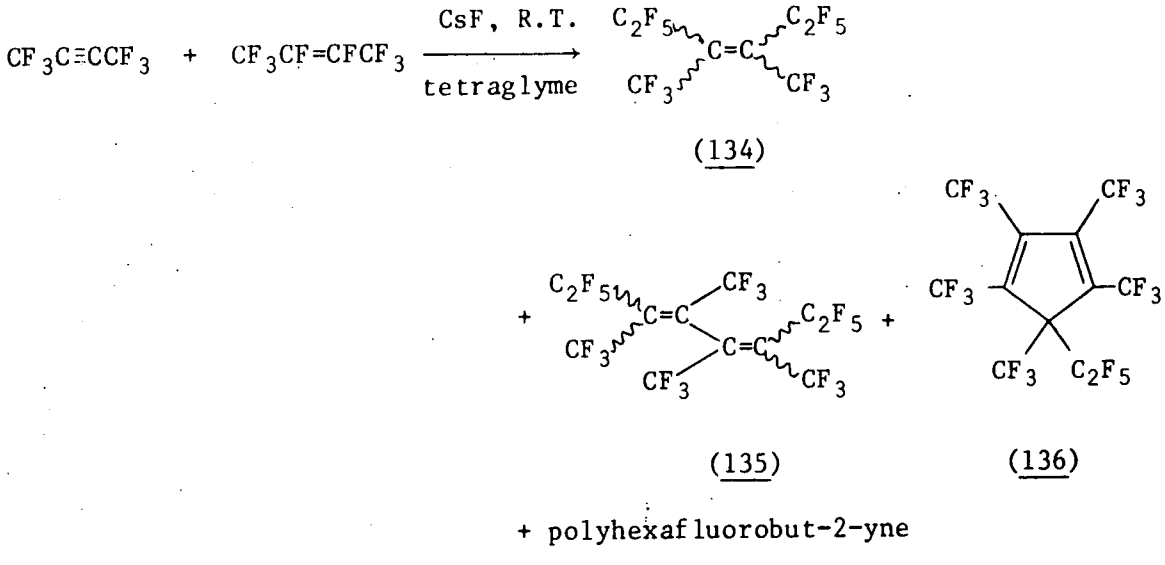
The other $C_{10}F_{18}$ fraction could not be assigned a structure, presumably because it was a mixture of isomers.

$$CF_3CF{=}CF_2 + CF_3C{\equiv}CCF_3 \xrightarrow[\text{tetraglyme}]{\text{CsF, R.T.}} C_{10}F_{18} + \text{(146)} + \text{(145)} + C_{14}F_{24}$$

Compound (145) is formed by reaction of two molecules of hexafluorobut-2-yne with one molecule of hexafluoropropene; however, attempts to improve the yield of this compound by using a 2:1 excess of the acetylene resulted in the formation of large quantities of polyhexafluorobut-2-yne. The same tendency for the butyne to polymerise was observed even using a slight excess of the propene and the course of the reaction is evidently critically dependent on such factors as how the gases are introduced into the reaction vessel etc.

V.C.6 Perfluorobut-2-ene

A better recovery of material was obtained for this reaction. Flash distillation gave a complex mixture of products from which compounds (134) and (135) were isolated and the presence of a little (136) was shown by m.s./g.l.c. A large quantity of polyhexafluorobut-2-yne was also formed in this reaction.



Compound (134) was identified by comparing g.l.c. retention times and ^{19}F n.m.r. spectra with those of a known sample.[185] Co-oligomer (135)

showed a broad vinylic CF_3 resonance (relative intensity 6), another CF_3 resonance at higher field (relative intensity 3) and two broad CF_2 resonances (total relative intensity 2). The broadness of these signals implies the presence of more than one isomer. Compound (136), which was not isolated, was shown to be one of the minor components of the product mixture by m.s./g.l.c. The mass spectrum of this component was identical to that of a sample of (136) prepared by a previous worker in this laboratory.[185]

V.C.7 Discussion

V.C.7.a General

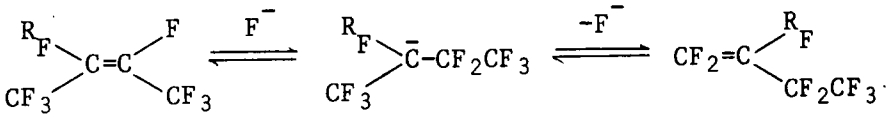
As mentioned in the previous sections, low mass recoveries were obtained in most of these experiments. Several work-up procedures were employed in an attempt to improve the mass balance. Flash distillation, which is a standard method for removing volatile material from involatile solvents, gave only small amounts of complex mixtures. This implies that the major part of the product consists of high molecular weight involatile oligomers which should therefore separate out on pouring into water. However, in most cases only a little intractable oil was obtained by this method. Solvent extraction also failed to separate the products from the reaction mixture.

Steam distillation gave a substantially improved recovery of material for the reaction with perfluorocyclopentene but unfortunately this method produced no significant improvements for the perfluorocyclobutene and perfluoropropene reactions.

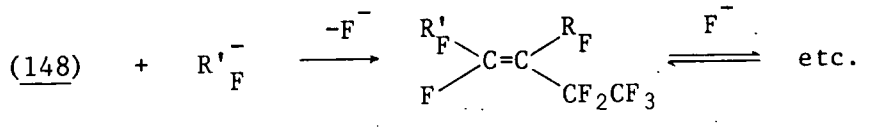
The cause of these isolation problems is not understood and is particularly mystifying considering that no similar difficulties were encountered in the co-oligomerisations of fluoroalkenes reported by a

previous worker in this laboratory.[154] Presumably the problem is associated with some complex reaction process which occurs when hexafluorobut-2-yne is used instead of one of the fluoroalkenes and which leads to mainly intractable products. One possibility for such a process is illustrated in Scheme V.1.

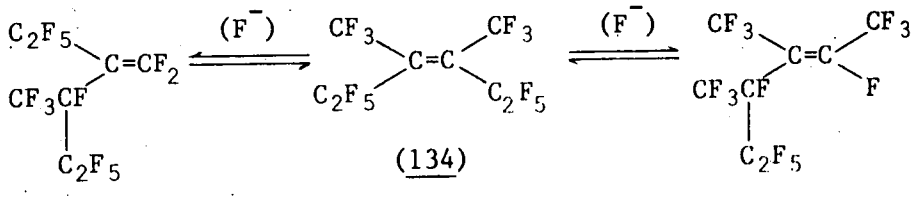
Scheme V.1



(147) (148)



In this way, simple oligomers of type (147) are converted into a complex mixture of compounds of higher molecular weight. The initial step of this process involves a fluoride ion induced isomerisation of (147) to give small concentrations of highly reactive compounds containing difluoromethylene groups (148). This type of isomerisation has been shown to occur for the internal alkene (134).[188]



(134)

Compounds of type (148) could then react with any anionic species present to give higher oligomers. In principle, this process may repeat

many times so that a very large number of products is possible. Another possible mechanism for the formation of complex mixtures of intractable products is discussed in the next section.

V.C.7.b Mechanism

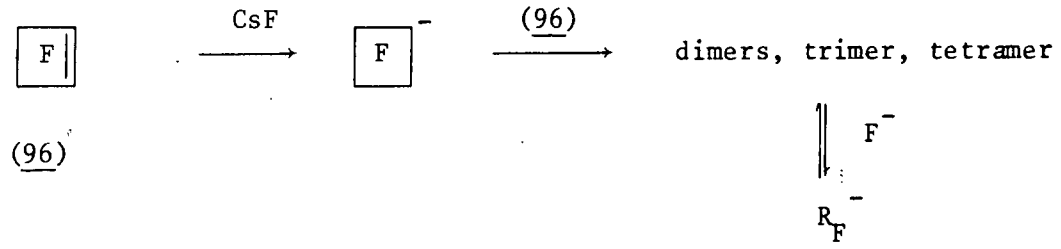
Previous work in this laboratory[154] has shown that in the presence of caesium fluoride and a dipolar aprotic solvent, hexafluorocyclobutene (96) readily oligomerises at room temperature to give a trimer as the major product together with smaller amounts of dimers and a tetramer. It is therefore probable that small amounts of these oligomers are formed in the co-oligomerisation reaction with hexafluorobut-2-yne; in addition it is likely that small concentrations of anions derived from these oligomers are also present in the reaction mixture. Therefore, in principle, a large number of reactions and products are possible (Scheme V.2) and this would account for the complex mixtures obtained in these experiments.

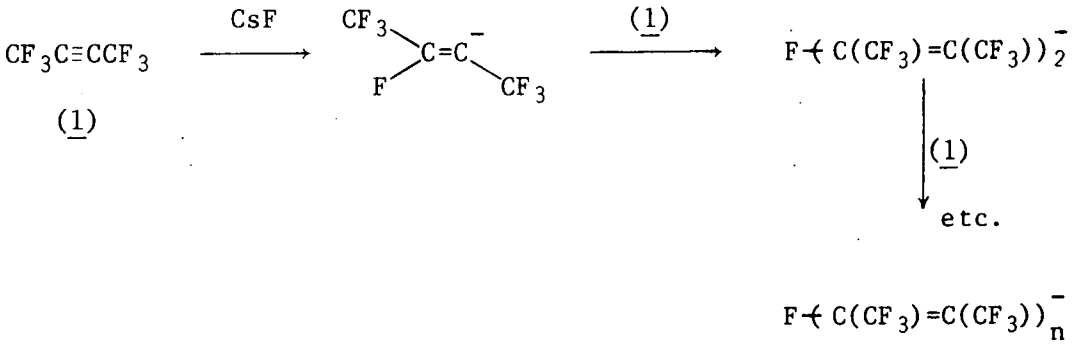
Compared with perfluorocyclobutene, perfluorocyclopentene is less susceptible to nucleophilic attack and does not oligomerise as readily.[190] The oligomerisation appears to be confined to the formation of dimers and only proceeds rapidly at elevated temperatures. It was therefore anticipated that the co-oligomerisation with hexafluorobut-2-yne would give fairly simple products. Unfortunately, however, although some low molecular weight compounds were isolated, the majority of the product apparently consisted of intractable higher oligomers when the reaction was performed in tetraglyme, sulpholan or dimethyl formamide. The situation was reversed using acetonitrile as solvent, mainly volatile products being produced in this case.

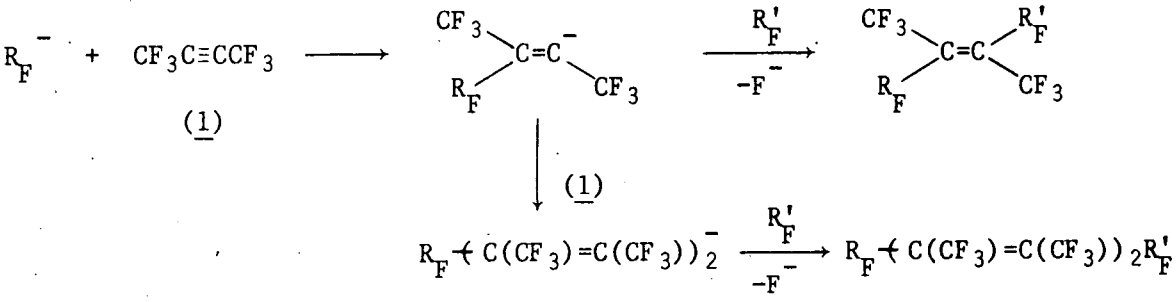
Compound (141) arises by nucleophilic attack of the heptafluorobutenide

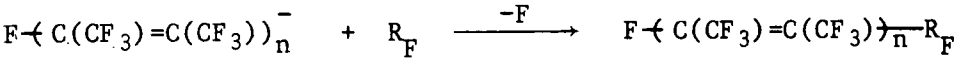
Scheme V.2

Co-oligomerisation of Hexafluorobut-2-yne with Hexafluorocyclobutene - Some Possible Reactions and Products







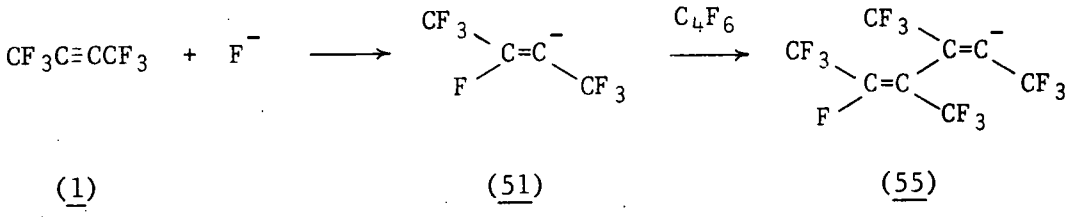


R_F, R'_F = (96) or its dimers, trimer or tetramer

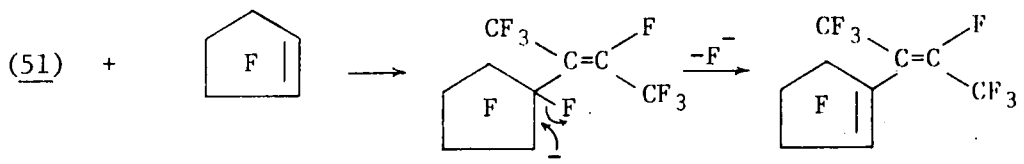
R_F^- = anion derived from R_F + F^-

Scheme V.3

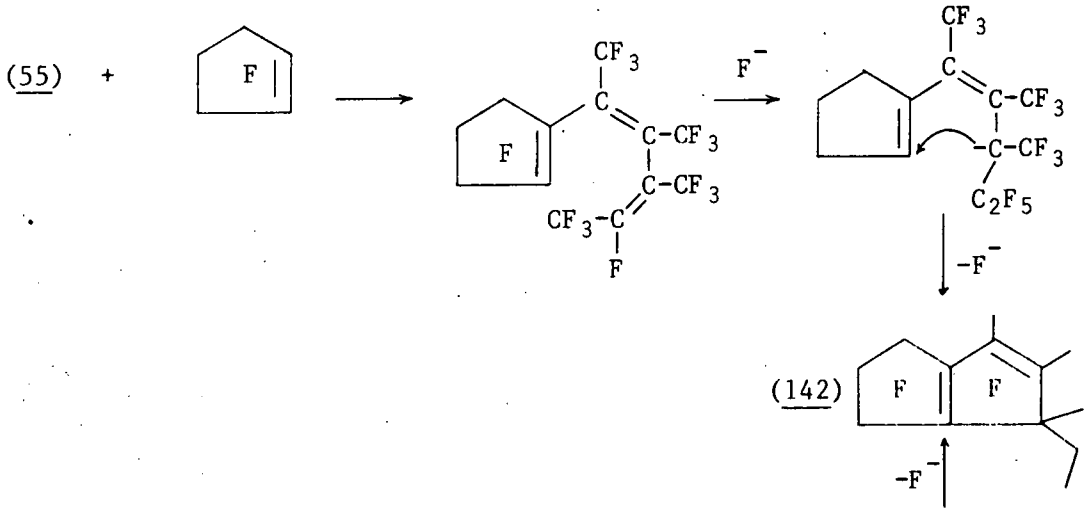
Co-oligomerisation of Hexafluorobut-2-yne with Perfluorocyclopentene



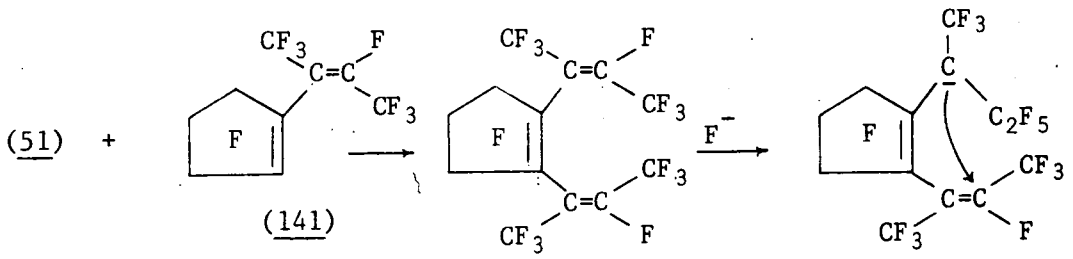
(1) (51) (55)



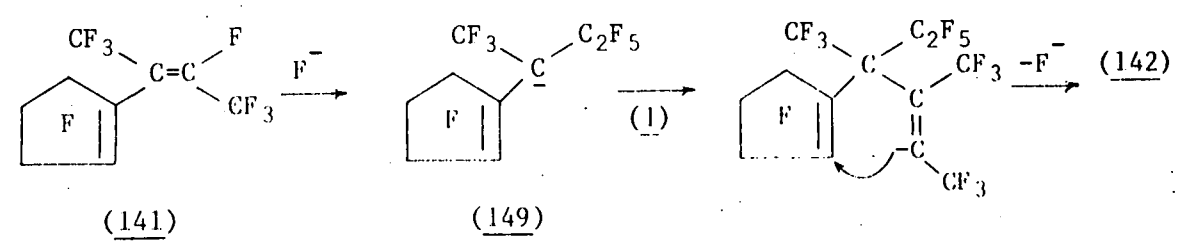
(141)



(142)



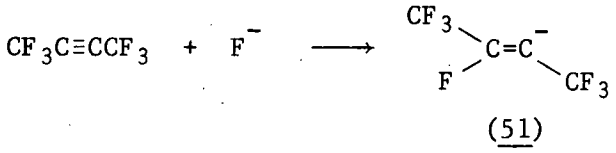
(141) (144)



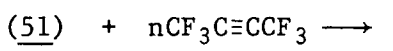
(141) (149) (142)

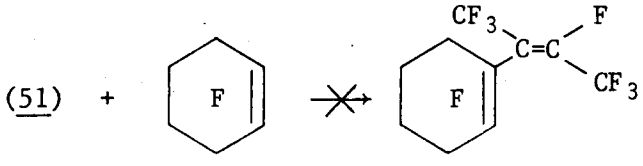
anion (51) on perfluorocyclopentene. There are several possible ways in which the 2:1 adduct (142) may be formed: (1) reaction of the dienide ion (55) with perfluorocyclopentene followed by a fluoride ion promoted cyclisation; (2) reaction of the 1:1 adduct (141) with a second heptafluorobutenide anion to give perfluoro-1,2-bis-(1-methylprop-1-enyl)-cyclopentene (144), followed by cyclisation; (3) reaction of the anion (149) with hexafluorobut-2-yne followed by cyclisation, or a corresponding concerted process. Although the last alternative seems most probable, there is insufficient evidence to allow a clear distinction between these processes. Products similar to (141) and (142) were obtained by previous workers in this laboratory from the fluoride ion initiated reaction of hexafluorobut-2-yne with tetrafluoropyridazine[96] (see II.D.7).

Perfluorocyclohexene (150) is less reactive than perfluorocyclopentene towards nucleophiles and presumably the failure to form co-oligomers such as (151) between (150) and hexafluorobut-2-yne is due to the far greater reactivity of the acetylene. The heptafluorobutenide anion (51) reacts preferentially with more acetylene rather than with the cycloalkene, thus giving polymer as the sole product.



(51)

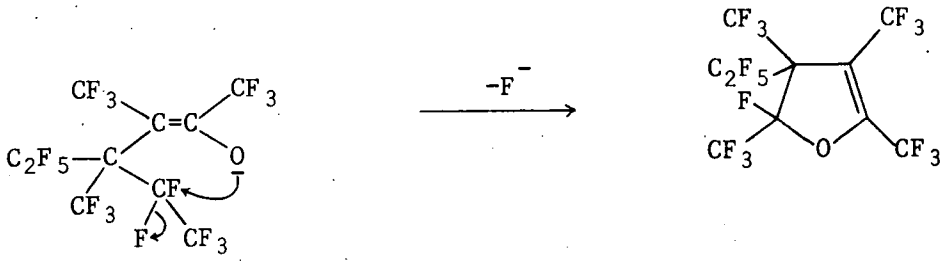




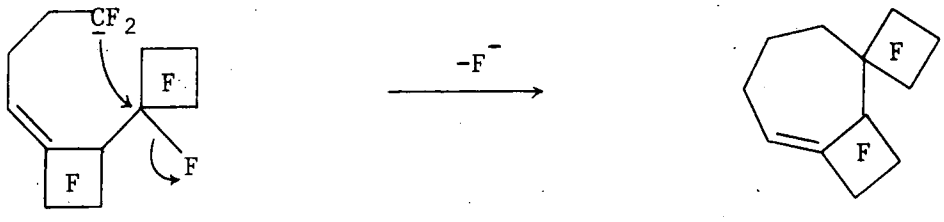
(150) (151)

In contrast to (150), hexafluoropropene is very susceptible to nucleophilic attack and readily oligomerises at room temperature in the presence of fluoride ion. A mechanism similar to that proposed for the cyclobutene reaction (Scheme V.2) may also be operating here and again this would account for the observed complexity of the product mixtures. The mechanisms proposed to account for the formation of compounds (145) and (146) are shown in Scheme V.4. Both the heptafluorobutenide anion (51) and the carbanion (153) generated from the propene (152) must take part in the reaction, since the major product, $C_{11}F_{18}$ (145) can only be formed by initial attack of (153) on hexafluorobut-2-yne, whereas the $C_{10}F_{18}$ isomer (146) can only arise from the reaction of (51) with (152).

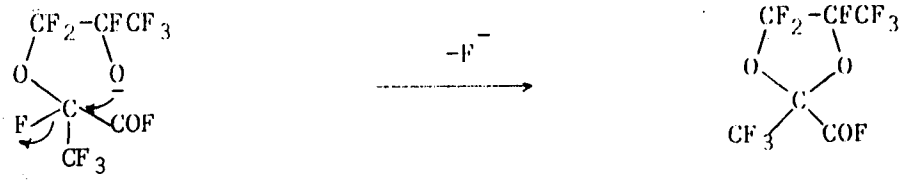
The cyclisation of the intermediate dienide anion (154) can be thought of as involving intramolecular nucleophilic displacement of fluoride ion from a saturated carbon atom and this unusual type of process, although not common, has been reported on other occasions, e.g:



[191]



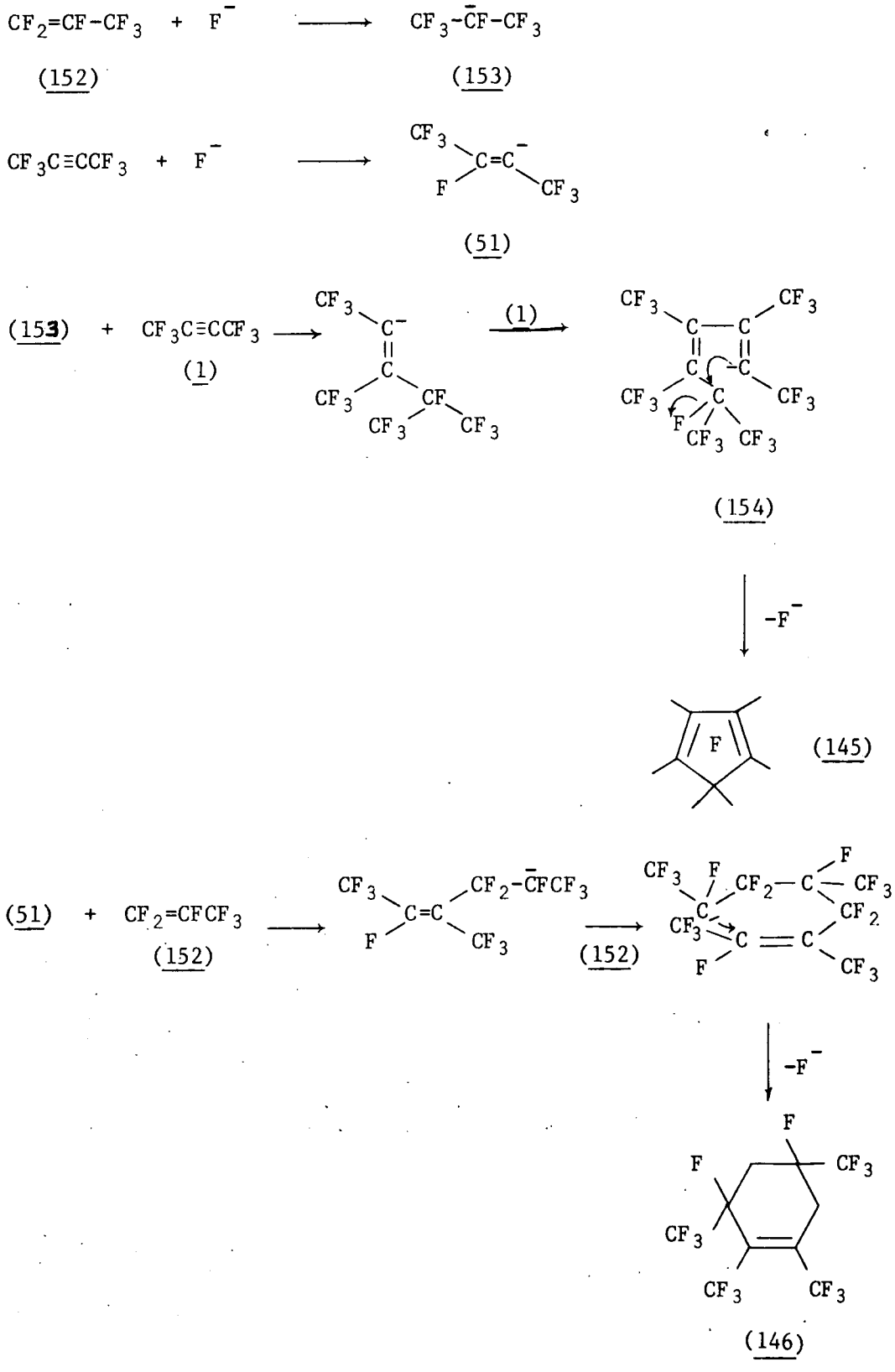
[154]



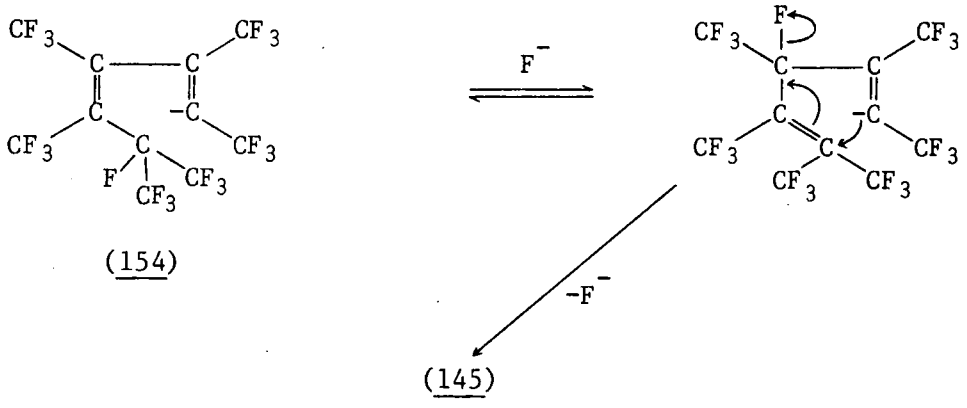
[192]

Scheme V.4

Co-oligomerisation of Hexafluorobut-2-yne with Hexafluoropropene



However, a mechanism involving a fluoride ion induced isomerisation of the dienide anion (154) cannot be ruled out. This alternative seems less likely as it calls for an attack by fluoride ion on an already negatively charged species.



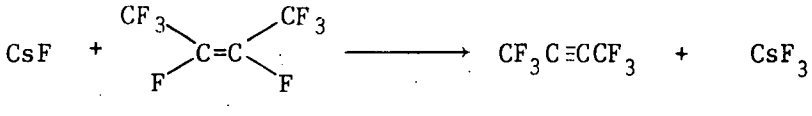
(154)

(145)

Perfluoro-(3,4-dimethylhex-3-ene) (134), the major product from the reaction of perfluorobut-2-ene with hexafluorobut-2-yne, is formed by the fluoride ion induced dimerisation of the alkene. Several mechanisms can be proposed for the formation of the co-oligomers (135) and (136) (Scheme V.5). However, the cyclic product (136) is probably formed by cyclisation of (156) by analogy with the mechanism which was shown to account for the formation of (145).

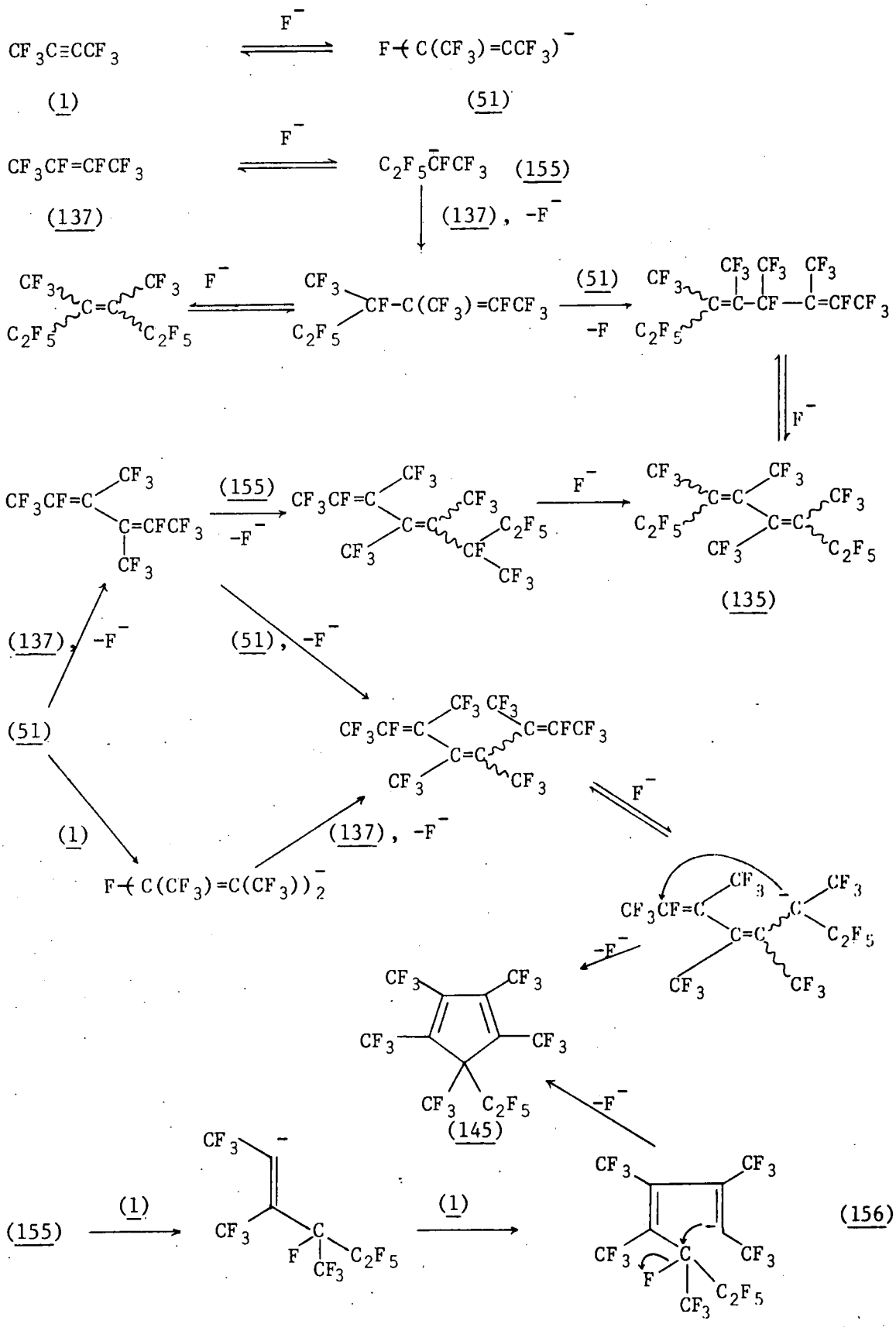
Somewhat surprisingly, the same products (134) - (136) were obtained by a previous worker in this laboratory[185] from the oligomerisation of perfluorobut-2-ene even in the absence of hexafluorobut-2-yne. Defluorination of the butene was proposed to account for the formation of the co-oligomers (135) and (136). Two possible mechanisms were suggested for this process:

i) defluorination by caesium fluoride, forming complex fluorides, i.e:



Scheme V.5

Co-oligomerisation of Hexafluorobut-2-yne with Perfluorobut-2-ene



ii) electron transfer

i.e:

$$R_F^- \overset{\frown}{\quad} C_4F_8 \longrightarrow R_F^{\bullet} + C_4F_8^{\bullet-} \xrightarrow[ii)-F^-]{i)-F^{\bullet}} C_4F_6$$

The hexafluorobut-2-yne thus formed can then react as in Scheme V.5 to give co-oligomers (135) and (136). As might be anticipated, this reaction gave a higher yield of perfluorobutene dimer (134) and correspondingly smaller quantities of (135) and (136) than the co-oligomerisation reaction described above.

V.C.7.c Structural Assignments

The structures of most of the co-oligomers described in this chapter followed simply from their ^{19}F n.m.r. spectra and assignments were made with reference to the data listed in Table V.1. These typical ranges for fluorine chemical shifts are applicable to most compounds containing only carbon and fluorine.

Structures were confirmed by comparing spectra with those of suitable model compounds (Table V.2), and infra-red spectroscopy was also useful as a confirmatory tool. It is known that the intensity and frequency of the C=C stretch increases with increasing number of vinylic fluorines. Double bonds attached only to carbon substituents tend to show very weak absorptions and are sometimes not detectable.

Table V.1

^{19}F N.m.r. Chemical Shifts for Aliphatic Perfluorocarbons[193]

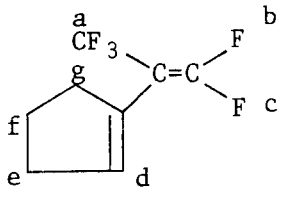
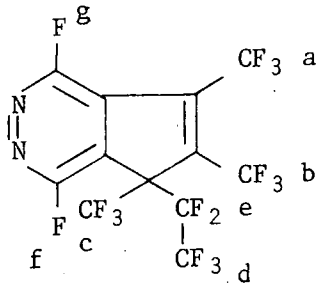
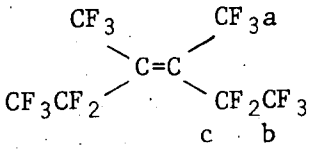
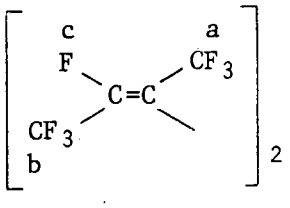
Structural Type†	Approximate Shift Range (p.p.m.)*
$CF_3-C\langle$	60 - 70
$CF_3-C(-)=C\langle$	60 - 70
$\underline{CF_3}-CF\langle$	70 - 80
$\underline{CF_3}-CF_2-$	80 - 90
$\rangle C=CF_2$	60 - 80
$\rangle C=CF-$	90 -120
$-CF_2-$	100 -140
$-CF\langle$	> 160

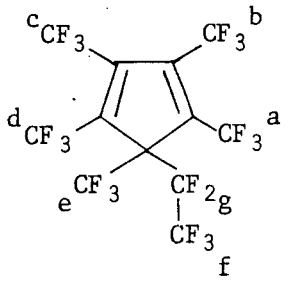
† all unmarked substituents are carbon

* w.r.t. $CFCl_3$

Table V.2

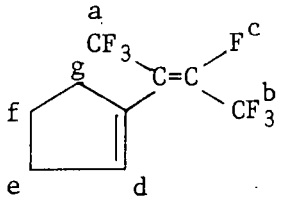
^{19}F N.m.r. Data for Co-oligomers and Related Model Compounds

Model Compounds	δ	Assignment	Ref.
	58.5	a	154
	65.6	b	
	67.4	c	
	111.5	g	
	119.5	d	
	121.4	e	
	133.7	f	
	54.9	a	96
	58.7	b	
	60.8	c	
	78.2	f and g	
	80.0	d	
	106.8	e	
	58.0	a	185
	74.5	b	
	99.8	c	
	62.8	a	185
	70.9	b	
	104.4	c	

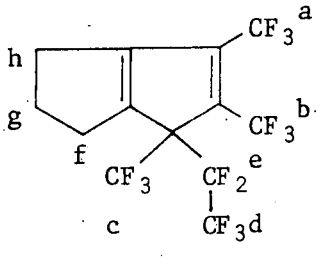


δ	Relative Intensity	Assignment	
57.6	a,d	185	
60.1	e		
61.8	b,c		
82.7	f		
106.3	g		

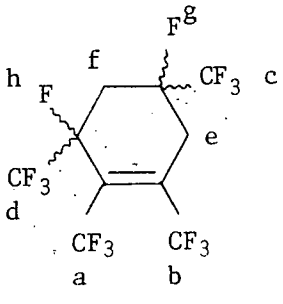
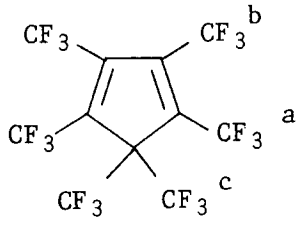
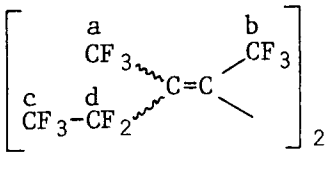
Co-oligomers



δ	Relative Intensity	Assignment
63.2	3	a
72.5	3	b
103.0	1	c
112.5	2	g
122.5	1	d
124.2	2	e
134.2	2	f



δ	Relative Intensity	Assignment
58.2	3	b
62.4	3	a
63.1	3	c
83.5	3	d
111.5, 115.3, 129.6	8	e,f,g,h

	δ	Relative Intensity	Assignment
$C_{10}F_{18}$	61.2	3	
	62.6	7	
	66.8	2	
	76.5	2	
	59.4, 60.4	3	a
	62.3	3	b
	74.1	6	c,d
	96-120	4	e,f
	159.3, 163.0	2	g,h
	58.5	3	a
	62.6	6	b,c
	58.5	6	a,b
	80.3	3	c
	105.9, 108.2	2	d

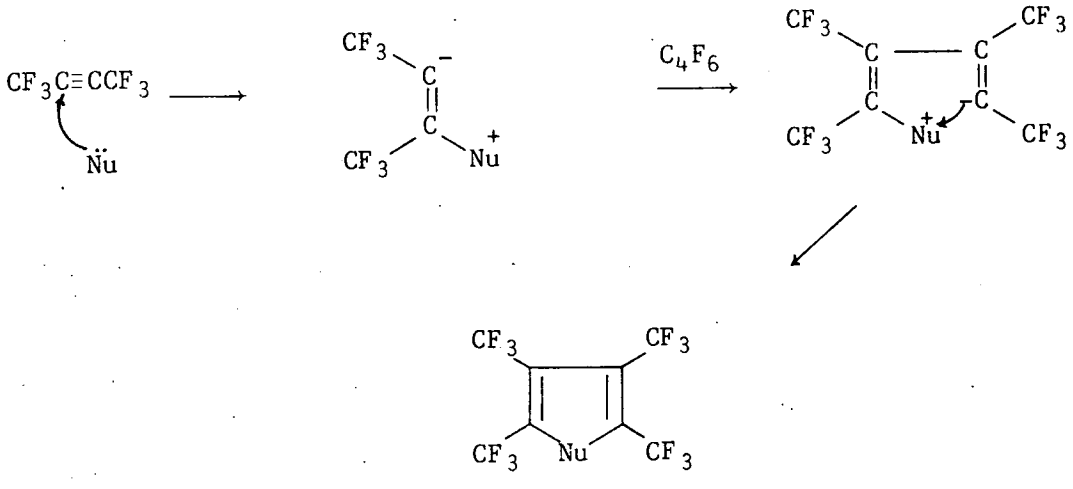
CHAPTER VI

NUCLEOPHILIC ADDITIONS TO HEXAFLUOROBUT-2-YNE

VI.A Introduction

A number of reactions of simple nucleophiles with hexafluorobut-2-yne were discussed in Chapter II. Although information about the stereochemistry of the products has been reported in comparatively few cases, the available data show a clear tendency for alcohols and amines to give predominantly *trans* adducts.

This chapter deals with attempts to prepare cyclic products by reaction of hexafluorobut-2-yne with nucleophiles. Most of these experiments attempted to react two acetylene molecules with one of the nucleophile to give 5 membered ring compounds.

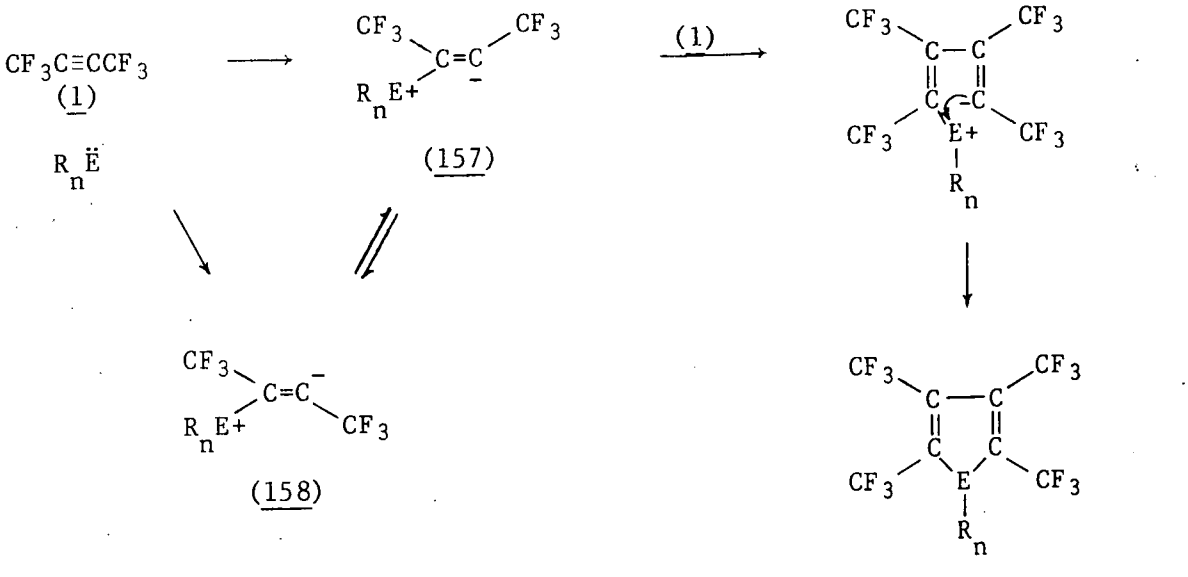


Also, a series of reactions was carried out to investigate some of the factors which were believed to have an influence on the stereochemistry of nucleophilic addition to hexafluorobut-2-yne.

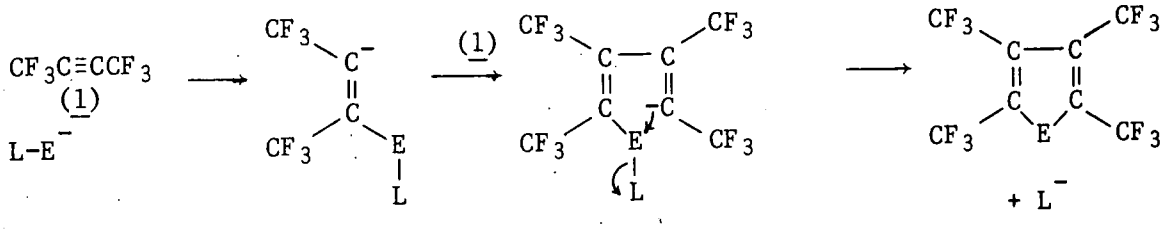
VI.B Cyclisation Reactions of Hexafluorobut-2-yne

VI.B.1 Introduction

In order to obtain cyclic products from hexafluorobut-2-yne, the initial addition to the triple bond must give a *cis* carbanion (157) and this can occur either by *syn* addition, or by *anti* addition followed by isomerisation. Addition of (157) to a further molecule of the acetylene gives an anion which could then cyclise.



This mechanism would only be applicable when E is able to increase its coordination number by 2. For C,N and O nucleophiles, where this is not possible, a suitable leaving group could be employed.



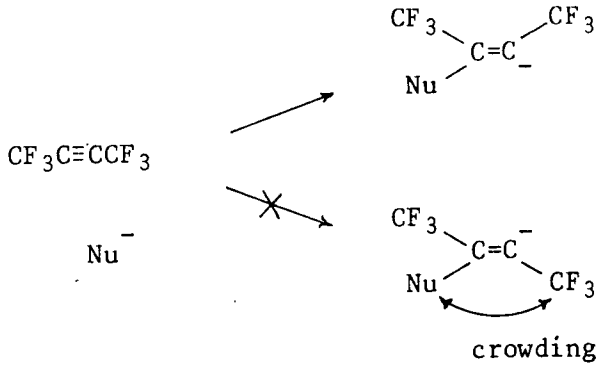
Obviously compounds with mobile hydrogen atoms will give mainly simple adducts rather than cyclic products. Also the use of protic solvents is likely to result in protonation rather than cyclisation.

It was thought that the following factors may encourage the initial addition step to proceed in a *syn* fashion, thus favouring the formation of cyclic products.

1) Use of large nucleophiles

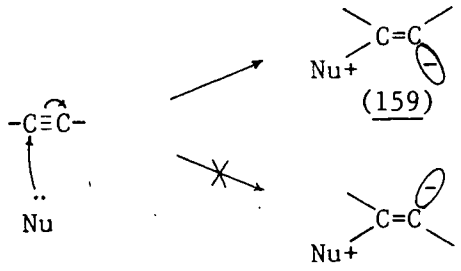
Nucleophiles with large steric requirements, i.e. larger than the CF_3 group, may possibly favour the formation of the less crowded anions

Nu^- larger than CF_3:



2) Use of Neutral Nucleophiles

Uncatalysed reactions of neutral nucleophiles to hydrocarbon acetylenes have been reported to give mainly *syn* addition products.[194] It is possible that under these circumstances the carbanion develops on the same side as the attacking nucleophile because of coulombic attraction between the opposite charges on the zwitterion (159).

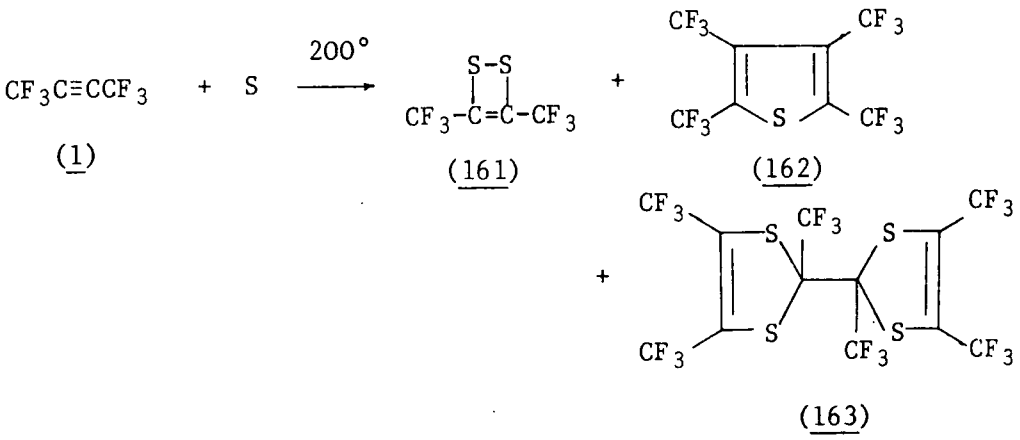


(159)

(160)

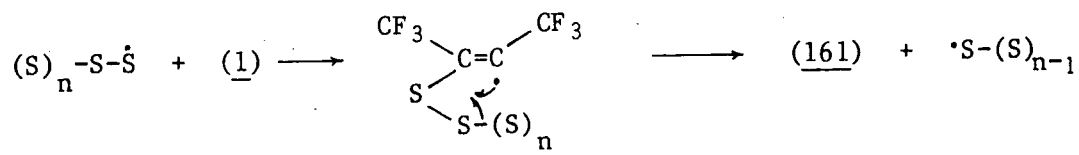
VI.B.2 Reaction with Sulphur

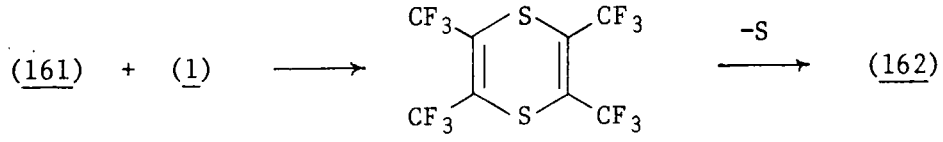
Sulphur satisfies both of the above qualifications, as it is both large and neutral. Hexafluorobut-2-yne has been reacted with sulphur in the presence of iodine at high temperature and pressure to give a mixture of products (161) - (163).[58,83]



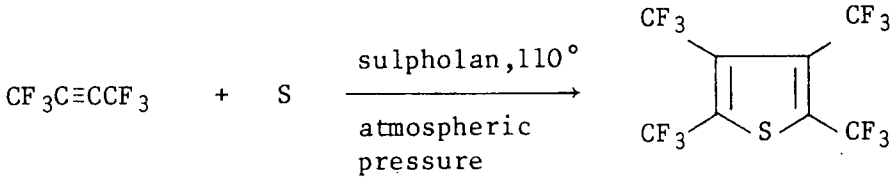
(1) (161) (162) (163)

Further experiments indicated that the dithietene (161) was the primary product from which the other compounds were formed. The mechanism proposed for the reaction involved the addition of the radical end of a sulphur chain to the triple bond to form a vinyl radical which then cyclises to give (161).



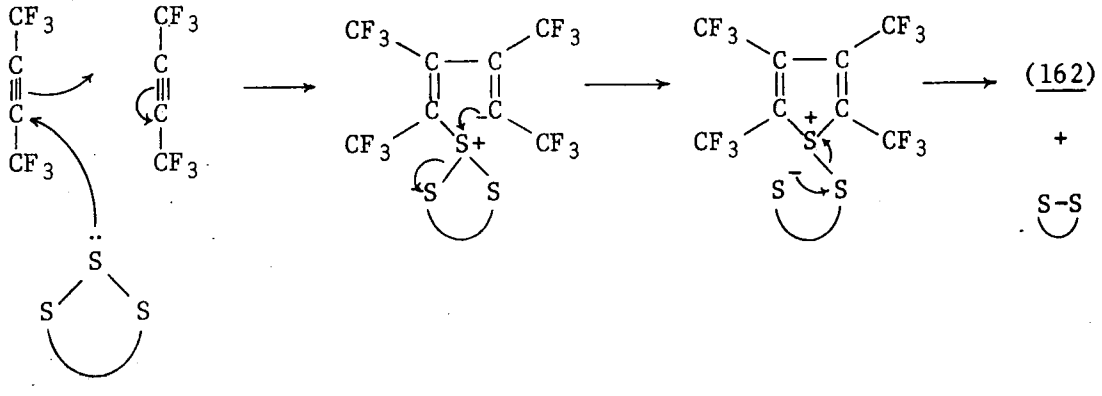


However, previous work in this laboratory has indicated that reaction of sulphur with hexafluorobut-2-yne occurs quite readily at atmospheric pressure and at temperatures as low as 80° to give the thiophene (162) as the only product.[195] These results were confirmed in the course of the present investigation; a 61% yield of (162) was obtained as the only detectable product.



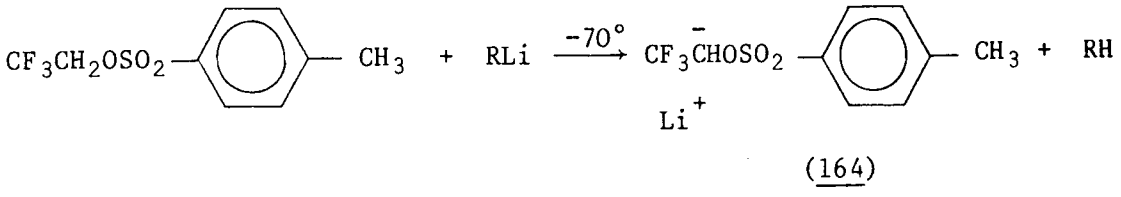
(162) 61%

The absence of any other products such as (161) and (163) indicates that the radical mechanism shown above does not operate at low temperatures. Instead, the reaction could be thought of as proceeding by a nucleophilic mechanism involving *syn* addition to the triple bond.

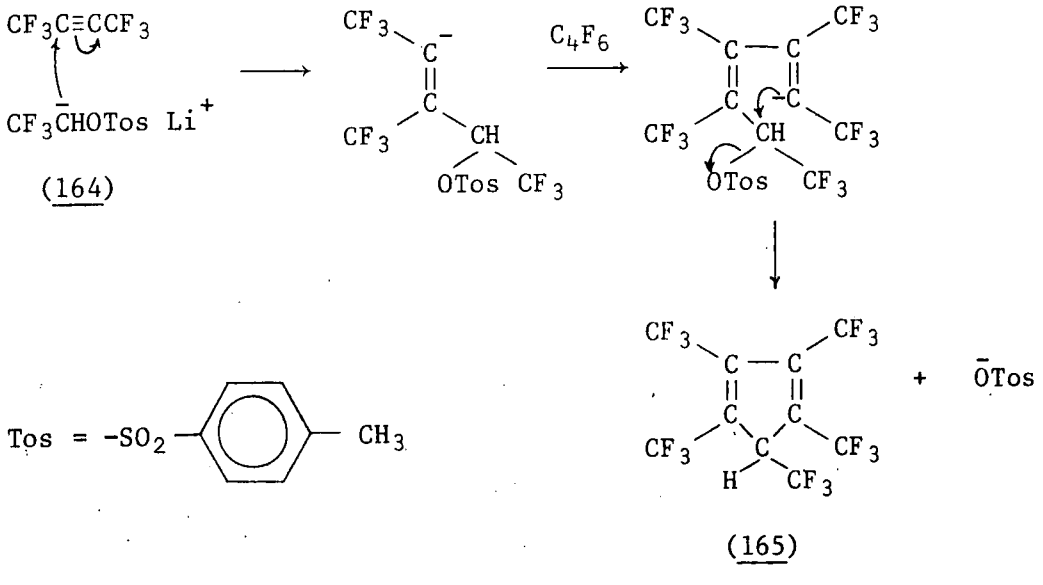


VI.B.3 Reaction with 2,2,2,-Trifluoroethyl-p-toluenesulphonate anion

The anion (164), which is generated on treating 2,2,2-trifluoroethyl-p-toluenesulphonate with an alkyllithium at -70°, seemed to be an ideal system for giving cyclic products from hexafluorobut-2-yne. Not only is it a very bulky anion but it also has a good leaving group attached to the nucleophilic centre. It was therefore anticipated that the following reaction sequence could give the cyclopentadiene (165).



(164)



(165)

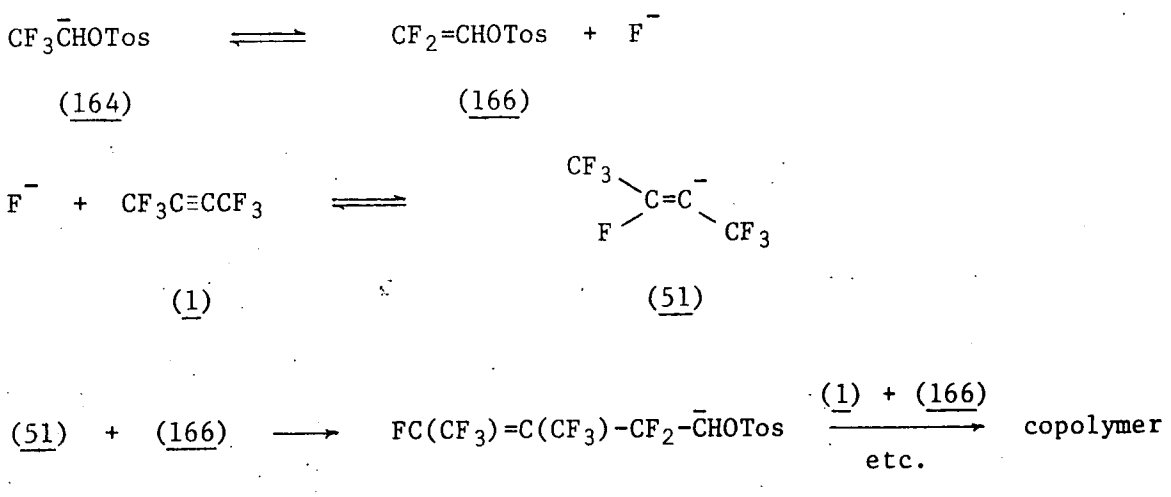
However, on slowly introducing hexafluorobut-2-yne into the reaction mixture containing the anion (164) at -78°, only polymeric materials were obtained. The reaction was repeated under a variety of conditions, using both butyl- and methyllithium to generate the anion. In all cases polymeric solids and tarry residues were the only products. A deficiency

of the alkyllithium was used to ensure that this was not responsible for the polymerisation of the acetylene.

The polymers were soxhlet extracted to remove unreacted starting material and tarry residues, but even then the mass of the polymer was still greater than the mass of hexafluorobut-2-yne used. This showed that the polymer was not simply polyhexafluorobut-2-yne but must contain some material derived from the tosylate and indeed elemental analysis showed the presence of substantial amounts of sulphur. However, the analytical data did not correspond to polyhexafluorobut-2-yne contaminated with starting material.

A possible explanation for these results is that the anion (164) eliminates fluoride ion on warming up to room temperature (Scheme VI.1). The resulting fluoroalkene could then copolymerise with hexafluorobut-2-yne in a fluoride ion induced process.

Scheme VI.1



However, the analysis figures did not fit closely to any of the possible formulations of such a copolymer. Therefore in order to cast more light on this reaction a control experiment was run. The tosylate

anion (164) was generated at -78° as before and then allowed to warm up in the absence of hexafluorobut-2-yne. A brown polymeric material and a tarry residue were obtained as in the previous experiments. Elemental analysis showed that the polymeric material was not a simple polymer of (166), since the sulphur content was too low and the fluorine too high (see Table VI.1).

Table VI.1

Elemental Analyses for Various Possible Polymers Derived from CF_3CH_2OTos

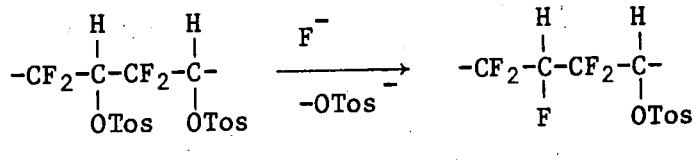
	A	B	C
C	35.32	46.15	41.77
H	2.28	3.42	2.85
F	27.7	16.24	30.06
S	10.02	13.68	10.13

A Values found for polymer obtained from $CF_3CH_2OTos + CH_3Li$

B Values calculated for $\leftarrow CF_2\text{-}CHOTos\rightarrow_n$

C Values calculated for $\leftarrow CF_2\text{-}CHF\text{-}CF_2\text{-}CHOTos\rightarrow_n$

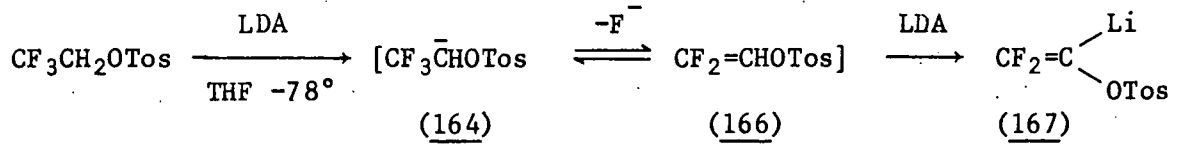
A better fit is obtained by assuming that 50% of the tosyl groups have been replaced by fluorine (column C in Table VI.1). This does not seem unreasonable considering that tosylate is an excellent leaving group.



It therefore seems likely that the polymer obtained from the reaction of (164) with hexafluorobut-2-yne is in fact a copolymer containing some

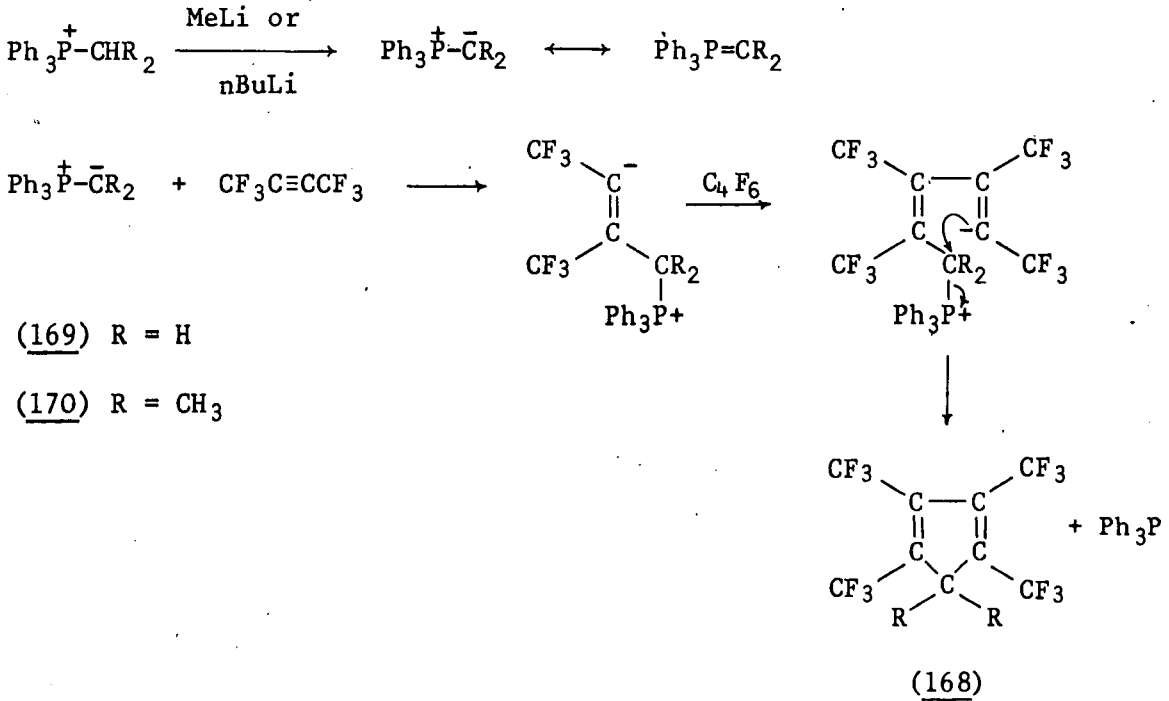
combination of $-C(CF_3)=C(CF_3)-$, $-CF_2-CHOTos-$ and $-CF_2-CHF-$ units.

Recently, Japanese workers have proposed the formation of a lithium salt (167) by reaction of trifluoroethyltosylate with 2 equivalents of lithium diisopropylamide (LDA).[196] The salt (167) was not isolated but was reacted in situ with a variety of carbonyl compounds to give α-keto acids. These findings give support to the copolymerisation mechanism discussed above.



VI.B.4 Reactions with Phosphonium Ylids

Phosphonium ylids were considered to be the most likely type of nucleophile to give cyclic products with hexafluorobut-2-yne. They are bulky, electrically neutral, and the phosphine part of the molecule forms a good leaving group. Reactions were therefore attempted with methylene- and isopropylidenetriphenylphosphorane to see whether cyclopentadienes (168) could be produced.



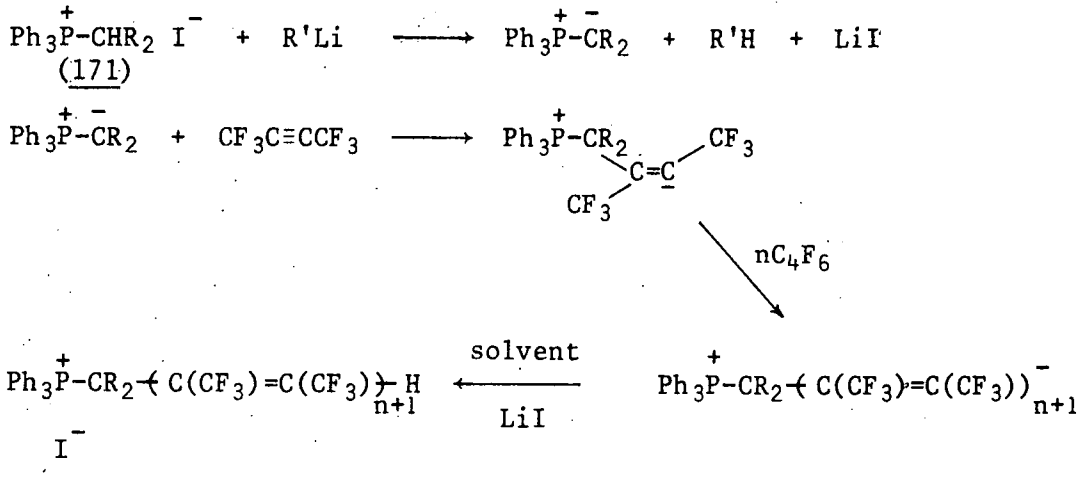
(169) R = H

(170) R = CH_3

The reaction with methylenetriphenylphosphorane (169) gave only polymeric material and it was thought that perhaps the steric requirements of this ylid were not sufficiently large to cause *syn* addition. Instead the ylid was possibly merely initiating the polymerisation of the acetylene. Therefore reactions were attempted using the more crowded isopropylidene ylid (170). However, once again no volatile products were recovered and only polymeric material was obtained.

The infrared spectrum of this polymer was similar to that of polyhexafluorobut-2-yne except for the presence of a few extra weak peaks, These may be due to the end groups in the polymer, although the possibility that they arise from some contaminant cannot be ruled out. Elemental analysis showed the presence of phosphorus and iodine and indicated that the polymer contained approximately 16 hexafluorobut-2-yne units for every phosphonium group. In addition ^{31}P n.m.r. showed that the phosphorus atom was 5 coordinate. The following reaction scheme is therefore proposed to account for the results.

Scheme VI.2

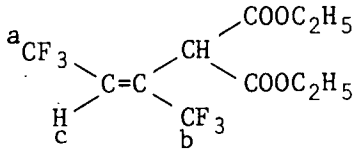


However, the results of a subsequent experiment suggested an alternative explanation for the formation of polymers. When the phosphonium salt (171, R = CH_3) was treated with a deficiency of butyllithium at 25°, butane was slowly evolved over a period of one hour. A sample of the reaction mixture was treated with bromine and the resulting liquid was found to contain butyl bromide, indicating that some butyllithium was still present. Even on repeating this test after heating the mixture at 55° overnight some butyl bromide was still detectable. Furthermore, ^{31}P n.m.r.[197] on the reaction mixture showed the presence of six different phosphorus containing species but no starting material (171) was left. It is somewhat mystifying how all the phosphonium salt can react and still leave butyllithium in the reaction mixture; no explanation for these apparently conflicting observations has been found but it is obvious that the formation of the required ylids does not proceed readily under the conditions employed. Therefore, although polymeric materials were obtained in the reaction with hexafluorobut-2-yne, it is not clear whether the polymerisation was in fact initiated by the ylid or by residual butyllithium. If the latter is the case it is quite possible that further experiments, using a more stable ylid which can be isolated, will give the anticipated cyclisation reaction.

VI.B.5 Reaction with the Sodium Salt of Diethyl Malonate

Hexafluorobut-2-yne reacted smoothly with a solution of the sodium salt of diethyl malonate in tetraglyme to give a small recovery of a multicomponent oil. A better recovery of material was obtained when the reaction was performed in dimethylformamide but it was impossible to separate the products by either g.l.c. or distillation because of their involatility. However, ^{19}F n.m.r. indicated the possible presence

of the *trans* adduct (172) as well as other components with resonances in the CF_3 region (Table VI.2)



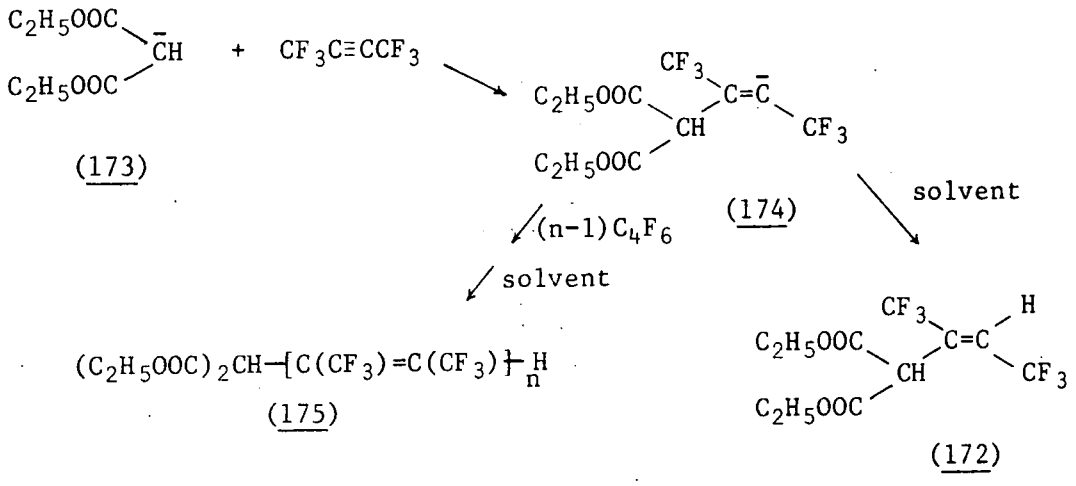
(172)

Table VI.2

^{19}F N.m.r. Data for Product Mixture Obtained from Reaction of Diethyl Malonate with Hexafluorobut-2-yne

Shift p.p.m.	Fine Structure Coupling constants in Hz	Relative Intensity	Assignment
61.42	Doublet $J_{ac} = 7$	1	a
64.29 64.72 65.04	Complex signals	5.3	
66.70	Singlet	1	b

The formation of the *trans* adduct (172) would imply that the malonate anion (173) does not add to hexafluorobut-2-yne in a *syn* manner as had been hoped. Instead *anti* addition occurs giving the anion (174) which can then presumably either extract a proton from the solvent or react with more hexafluorobut-2-yne. It seems likely that the other products of this reaction are higher oligomers of the type (175).

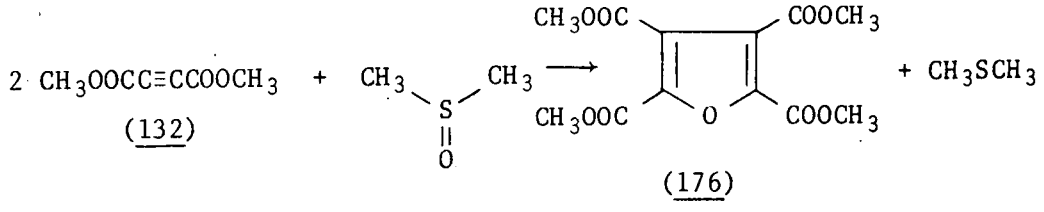


(173) (174) (175) (172)

VI.B.6 Reaction with Dimethyl Sulphoxide

VI.B.6.a Introduction

Winterfeldt has reported an interesting two stage reaction of dimethyl acetylene dicarboxylate with dimethyl sulphoxide to give the tetrasubstituted furan (176).[198] The overall process can be represented by the following equation.

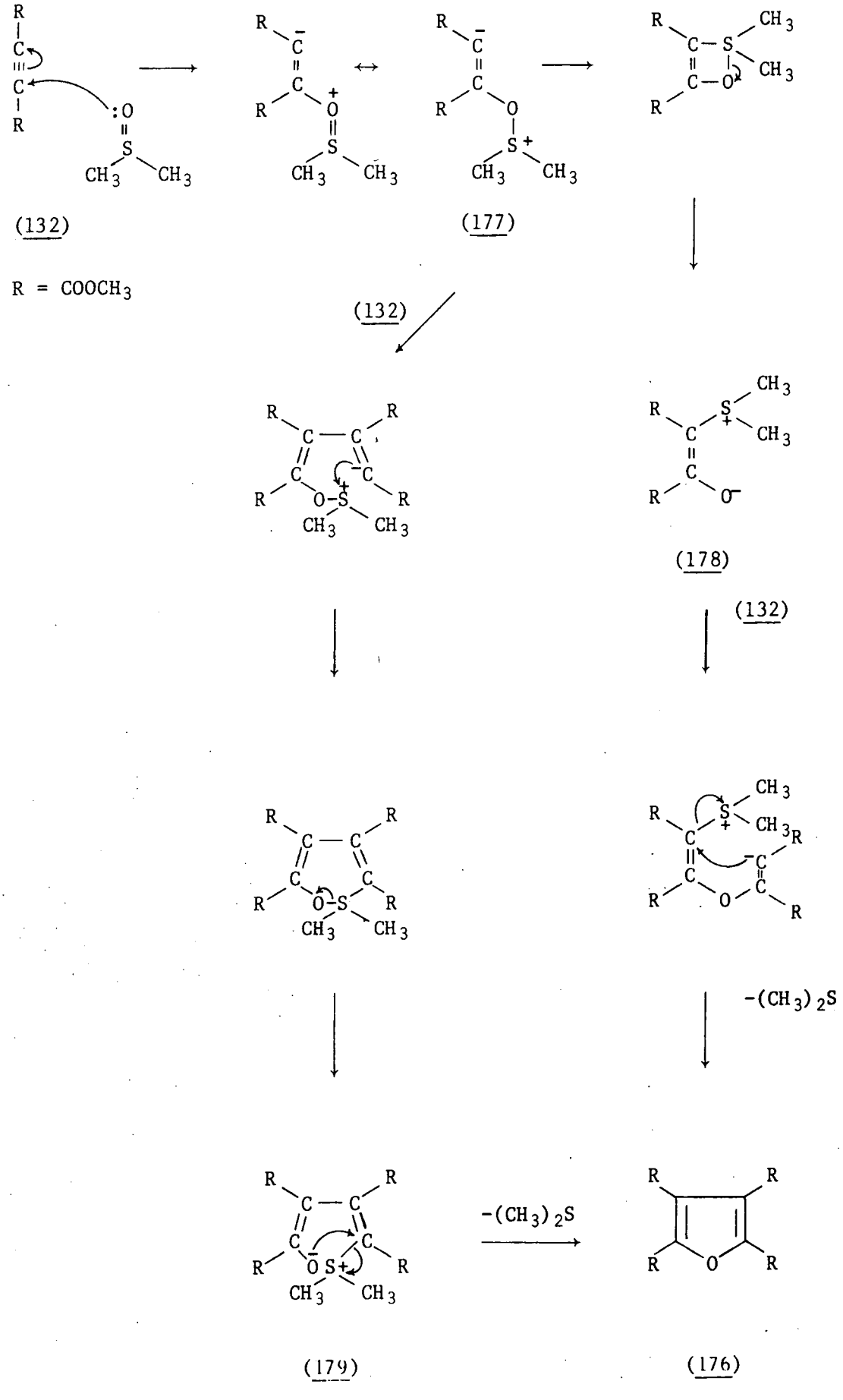


(132) (176)

Two products were isolated on heating (132) with excess dimethyl sulphoxide. The first, a 1:1 adduct, was found to be not the primary addition product (177) but the rearranged adduct (178). A 2:1 adduct (179) resulting from reaction of (177) with a further molecule of acetylene, was also isolated. Addition of more (132) to the 1:1 adduct gave the furan (176) and the same compound was also obtained on heating (179) under vacuum. The complete mechanism is given in Scheme VI.3.

Although the furan expected from an analogous reaction of hexafluorobut-2-yne with dimethyl sulphoxide is a known compound,[199] this would

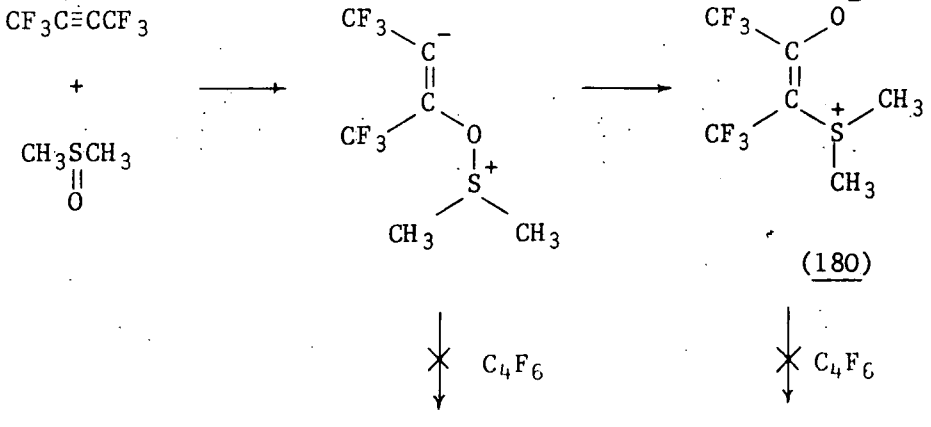
Scheme VI.3



be a far more convenitent route than the existing ones.

VI.B.6.b Results

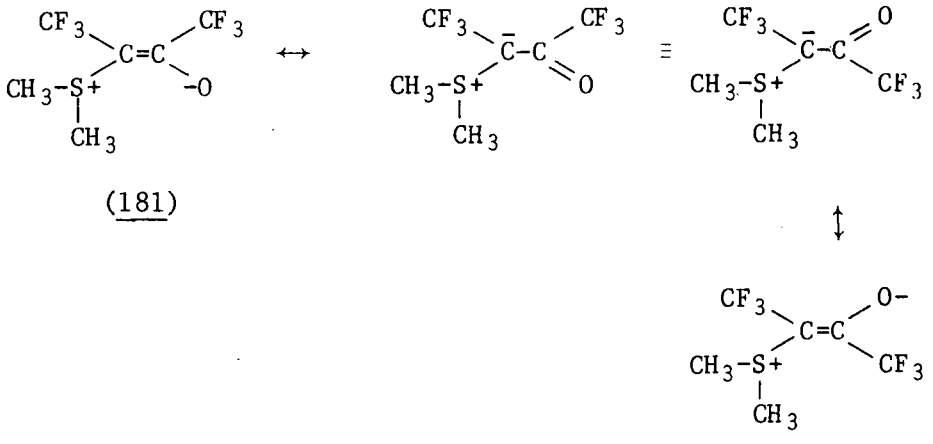
On heating hexafluorobut-2-yne with dimethyl sulphoxide the 1:1 adduct (180) was formed as the only product. No trace of a 2:1 adduct analogous to (179) was detected. Furthermore, heating the 1:1 adduct (180) with further hexafluorobut-2-yne failed to give any reaction under any of the conditions employed. Reactions were attempted a) without a solvent at 120°; b) in sulpholan at 130°, atmospheric pressure; c) in sulpholan at 130°, autogenous pressure; in each case a quantitative recovery of both (180) and the butyne was obtained. The reason for the difference in reactivity between dimethyl acetylene-dicarboxylate and hexafluorobut-2-yne is not clear, although it may well be that Winterfeldt's mechanism is an oversimplification and the ester groups play an essential role in the reaction.



(180)

In contrast to the ester adduct (178) where the ^{1}H n.m.r. spectrum indicated the presence of only one isomer, the ^{19}F n.m.r. spectrum of the hexafluorobut-2-yne adduct (180) showed it to be a mixture of *cis* and *trans* isomers in the ratio of 3.5:1. The formation of two isomers

is not inconsistent with the proposed mechanism since isomerisation via an ylid type intermediate would seem perfectly feasible under the reaction conditions. The *cis* isomer is presumably the more stable form because of coulombic interactions between the opposite charges and this could account for it being the major product.



(181)

Variable temperature n.m.r. studies of the adduct showed that at elevated temperatures free rotation about the central C-C bond occurs.

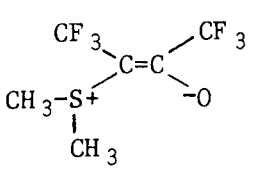
VI.B.6.c Structural Assignment

Spectroscopic data for the *cis* and *trans* 1:1 adducts are given in Table VI.3. For comparison the data for the diester adduct (178) are also shown.

Assignment of *cis* and *trans* isomers followed from the respective n.m.r. coupling constants as described in Chapter IV. Spectra were taken at various temperatures between 40° and 135°. As the temperature was raised the CF_3-CF_3 coupling quickly disappeared; next the four signals broadened and moved closer together. Finally at 135°, only two

Table VI.3

Spectroscopic Data for Dimethyl Sulphoxide Adducts



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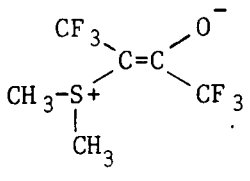

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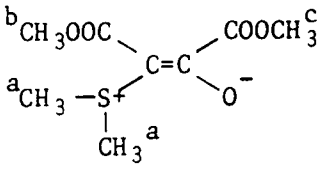


^{1}H n.m.r.

3.02 Singlet	2.86 Singlet	3.0 Singlet a CH_3
		3.65, 3.80 Singlets b,c CH_3

^{19}F n.m.r.

49.1, 73.4 Quartets J = 11 Hz	51.9, 70.2 Singlets

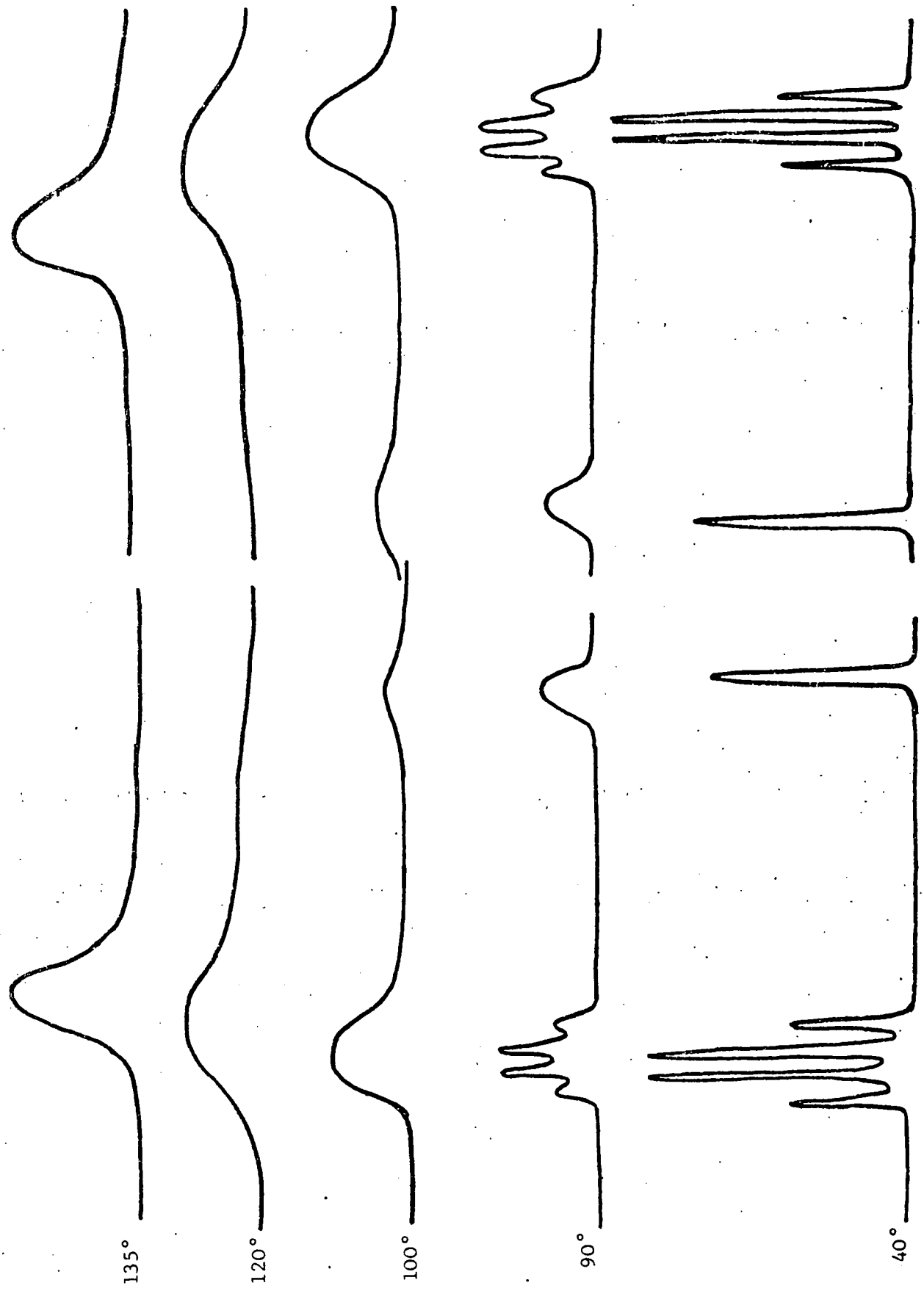
Infrared

$\nu_{C=C}$	1608 cm^{-1} (broad)	1580 cm^{-1}

* n.m.r. data measured at 40°C

Figure 2 ^{19}F N.m.r. Spectra of (180) at Various Temperatures

Solvent: DMSO

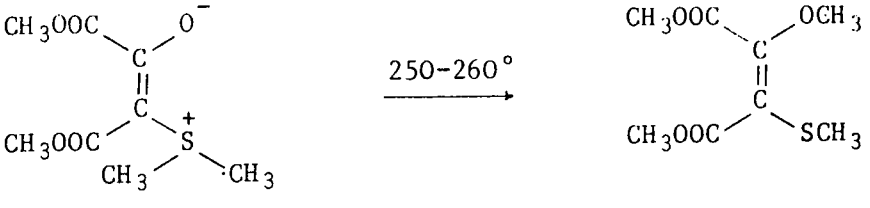


signals can be seen and this is interpreted as being due to free rotation about the central C-C bond. On cooling, the sequence was reversed until the original spectrum was seen again at 40°. The relevant parts of the spectra are reproduced in Figure 2.

VI.B.6.d Reactions of the Dimethyl Sulphoxide Adduct (180)

i) Pyrolysis

On heating to 250-260°, the dimethyl sulphoxide adduct of dimethyl acetylenedicarboxylate has been reported to rearrange to (181).[198]

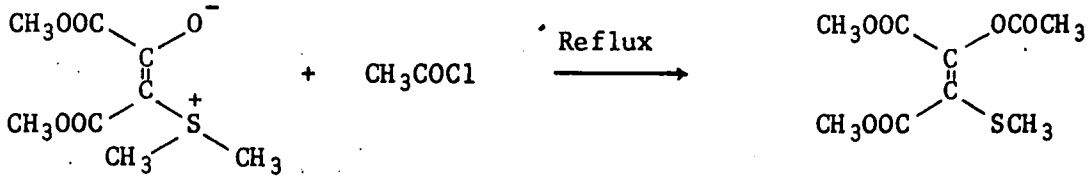


(178) (181) 62%

The hexafluorobut-2-yne adduct (180) was heated in vacuo a) at 110° for 2 hours, b) at 170° for 24 hours and c) at 250° for 15 hours. No reaction was observed in the first two experiments but at 250° the adduct decomposed to give a black solid, a complex mixture of liquid products and a trace of gas. These products could not be identified.

ii) With Acetyl Chloride

No reaction occurred on refluxing (180) with acetyl chloride and this result again illustrates the difference in reactivity between the hexafluorobut-2-yne adduct and the ester adduct (178) which has been shown to give an acetate (182) under these conditions.[198]



(178) (182)

iii) With Water

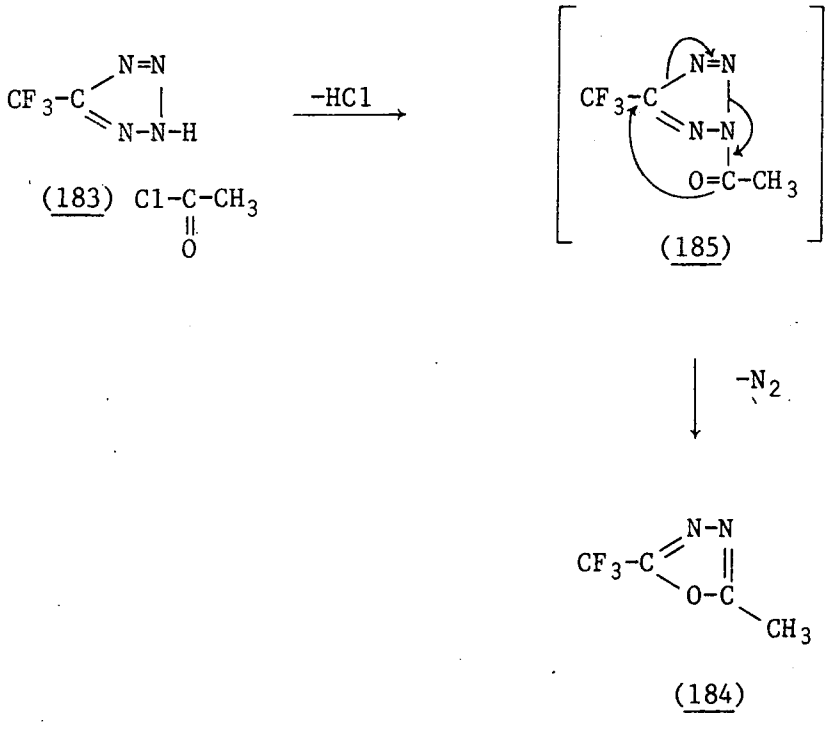
The adduct (180) was recovered unchanged after stirring with water at room temperature for several days.

VI.B.7 Reaction with Triphenylphosphine Oxide

Unlike dimethyl sulphoxide, triphenylphosphine oxide failed to react with hexafluorobut-2-yne under moderate conditions. Quantitative recoveries of starting materials were obtained when the phosphine oxide was heated at 100° with the acetylene, whether a solvent was employed or not. At 170° some reaction was observed and ^{31}P n.m.r.[197] showed that the recovered phosphine oxide was contaminated with two other phosphorus containing species. Of these, the major component showed a triplet which may be due to a compound such as Ph_3PF_2 and this would indicate that decomposition of the butyne occurs under these circumstances.

VI.B.8 Reaction with 5-Trifluoromethyltetrazole Derivatives

A remarkable reaction between 5-trifluoromethyltetrazole (183) and acyl chlorides has been reported to give 1,3,4-oxadiazoles (184). Nucleophilic attack by nitrogen on the carbonyl group gives an unisolable acetyl intermediate (185) which cyclises with elimination of nitrogen to give (184).[200]

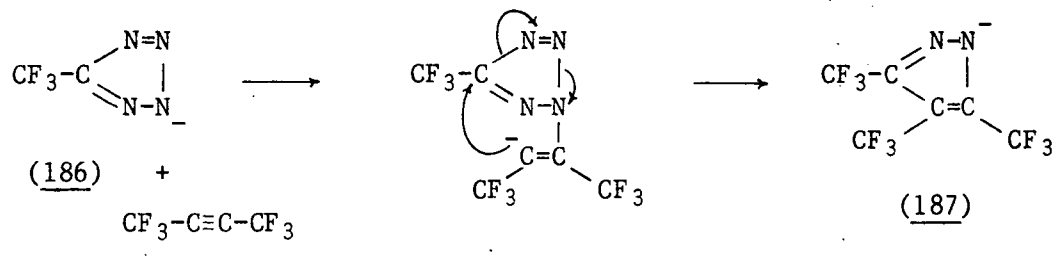


(183)

(185)

(184)

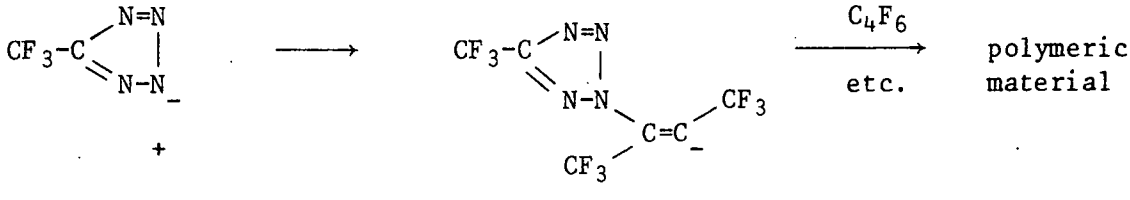
It was of considerable interest to determine whether a similar type of reaction would occur with hexafluorobut-2-yne. The tetrazole itself would probably just add across the triple bond but using the sodium salt it was anticipated that a diazole derivative (187) would be produced.



(186) + $CF_3-C\equiv C-CF_3$

(187)

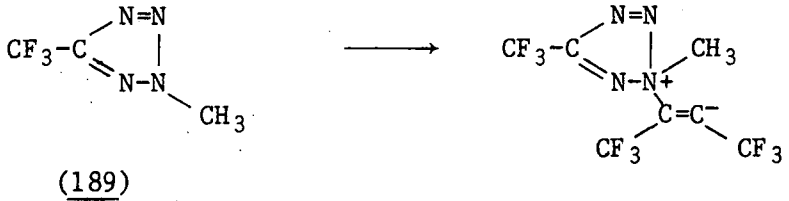
However, although hexafluorobut-2-yne reacted very readily with a solution of the sodium salt in acetonitrile, the product was an intractable tarry material. Also no nitrogen was evolved, indicating that the anion (186) adds to hexafluorobut-2-yne to give the *trans* carbanion (188) rather than the *cis* intermediate necessary for cyclisation to occur.



+ $CF_3C\equiv CCF_3$

(188)

The N-methyl derivative (189) was then prepared as it was thought that a neutral nucleophile would favour *syn* addition.



(189) + $CF_3C\equiv CCF_3$

Unfortunately (189) failed to react with hexafluorobut-2-yne even under forcing conditions and this is attributed to the low nucleophilicity

of the system.

VI.B.9 Summary

Cyclic products were obtained only in the reaction with sulphur; most of the other nucleophiles either gave polymers or *trans* adducts. Only dimethyl sulphoxide gave a *cis* addition product but this does not necessarily indicate that it was formed by *syn* addition.

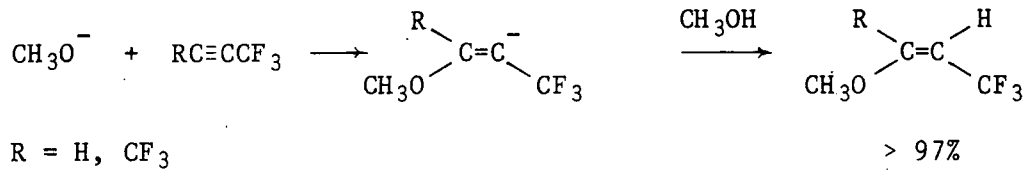
From these results it would seem that the stereochemistry of the initial addition depends on the size of the attacking atom and not on the size of the nucleophile as a whole.

VI.C Investigation of the Stereochemistry of Nucleophilic Additions to Hexafluorobut-2-yne

VI.C.1 Introduction

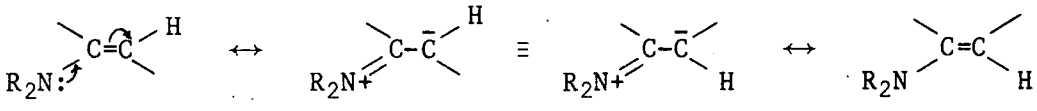
Although the stereochemistry of addition of nucleophiles to activated hydrocarbon acetylenes has been extensively studied[201] and reviewed,[194] little attention has been paid to the stereochemical course of additions to trifluoromethyl activated acetylenes. The stereochemistry of these reactions is of particular interest since in contrast to carbonyl, nitrile and sulphone activated triple bonds, the activation here should be largely inductive in nature.

The base catalysed addition of methanol to trifluoropropyne and hexafluorobut-2-yne gave predominantly *trans* products.[71] Since the *cis* adduct was not isomerised under the reaction conditions, the *trans* adducts obtained in these reactions must be kinetic products.

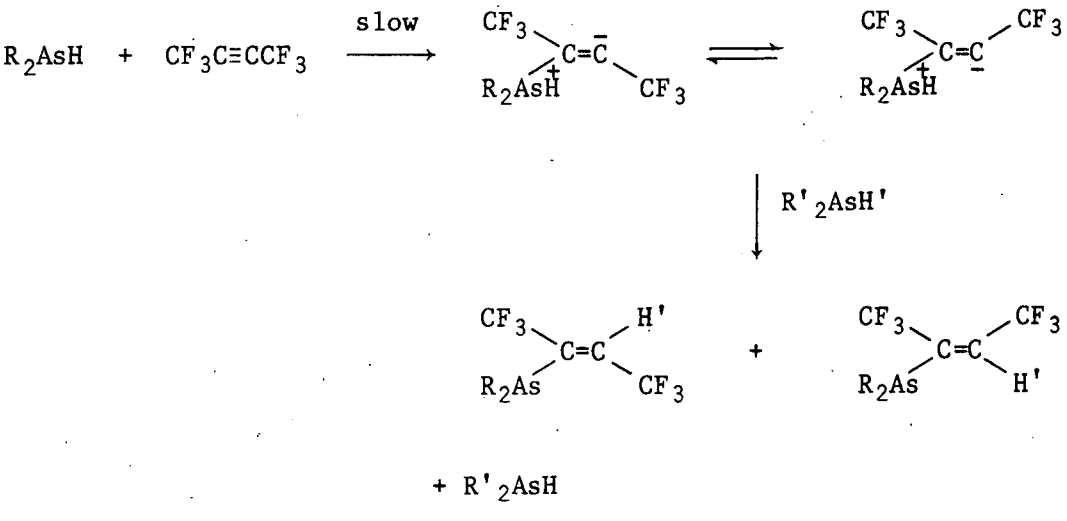


R = H, CF_3 > 97%

Dimethylamine reacts with hexafluorobut-2-yne to give a mixture of *cis* and *trans* adducts in the ratio of 1:6.[75] However, isomerisation of the products occurs over a period of several days to give an increase in the *cis* isomer content. Isomerisation has also been observed for other amine adducts and a mechanism involving the formation of an immonium type intermediate has been proposed.[202]



The only other detailed study of nucleophilic addition to hexafluorobut-2-yne which has been published concerns the addition of dimethylarsine.[203] A 96:4 ratio of *trans*:*cis* products was obtained and competition reactions indicated that the mechanism does not involve an intramolecular proton transfer. Several mechanisms were considered but the following fitted the experimental observations most closely.



In view of the dearth of information about additions of simple nucleophiles to hexafluorobut-2-yne, the reactions with a range of alcohols were investigated.

VI.C.2 Addition of Alcohols

The aim of these experiments was to investigate some of the factors which influence the stereochemistry of nucleophilic addition of alcohols to hexafluorobut-2-yne. In particular, the effects of catalyst, solvent, temperature and the nature of the alcohol were studied.

VI.C.2.a Catalysed Reactions

Sodium alkoxide catalysed additions to hexafluorobut-2-yne were carried out under a variety of conditions. Isomer ratios were measured by the simple ^{19}F n.m.r. technique described in Chapter IV. Predominantly *anti* addition was observed regardless of the nature of the alcohol and neither temperature nor the use of a solvent caused the isomer ratio to change significantly (Table VI.4).

Table VI.4

Base Catalysed Additions to Hexaflurorbut-2-yne

ROH	Solvent	Temp. °C	% *trans*	% *cis*
CH_3OH	-	20	96	4
n-C_3H_7OH	-	20	92	8
n-C_4H_9OH	-	20	89	11
n-C_4H_9OH	-	117	86	14
n-C_4H_9OH	sulpholan	117	92	8
2-C_4H_9OH	-	20	91	9
t-C_4H_9OH	-	20	86	14

VI.C.2.b Uncatalysed Reactions

Uncatalysed additions required elevated temperatures for the reaction to proceed to an appreciable extent. Reactions between the neat alcohol and hexafluorobut-2-yne gave products with similar isomer ratios to those obtained in the catalysed additions. However, when aprotic dipolar solvents are used *syn* addition predominates. (Table VI.5).

Table VI.5

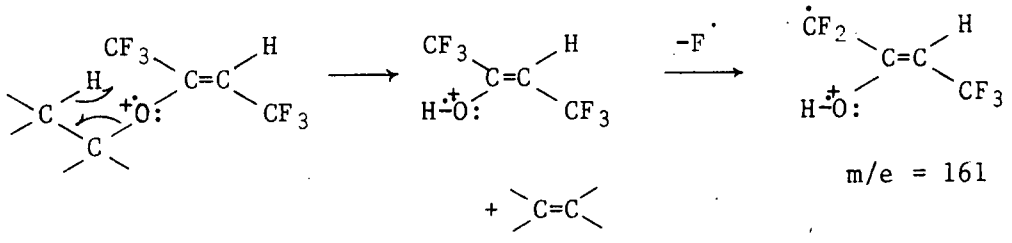
Uncatalysed Additions to Hexafluorobut-2 yne

ROH	Solvent	Temp. °C	% *trans*	% *cis*
CH_3OH	-	95	92	8
n-C_4H_9OH	-	95	90	10
n-C_4H_9OH	ether	95	†	†
n-C_4H_9OH	ether	150	27	63
n-C_4H_9OH	sulpholan	100	†	†
n-C_4H_9OH	sulpholan	150	30	70
t-C_4H_9OH	-	95	†	†
t-C_4H_9OH	-	150	90	10

† no detectable reaction

VI.C.2.c Structure of the Products

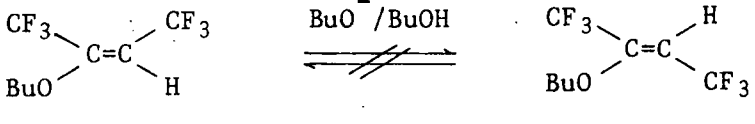
Isomer ratios were obtained for the crude reaction products using the ^{19}F n.m.r. technique described in Chapter IV and product mixtures were also studied by m.s./g.l.c. Molecular ion peaks were not observed, the high mass peaks arising from loss of either fluorine or alkyl groups. All the adducts show a peak at m/e = 161, which may be due to the fragmentation process shown below. A similar type of break-down has been reported for other ethers.[172]



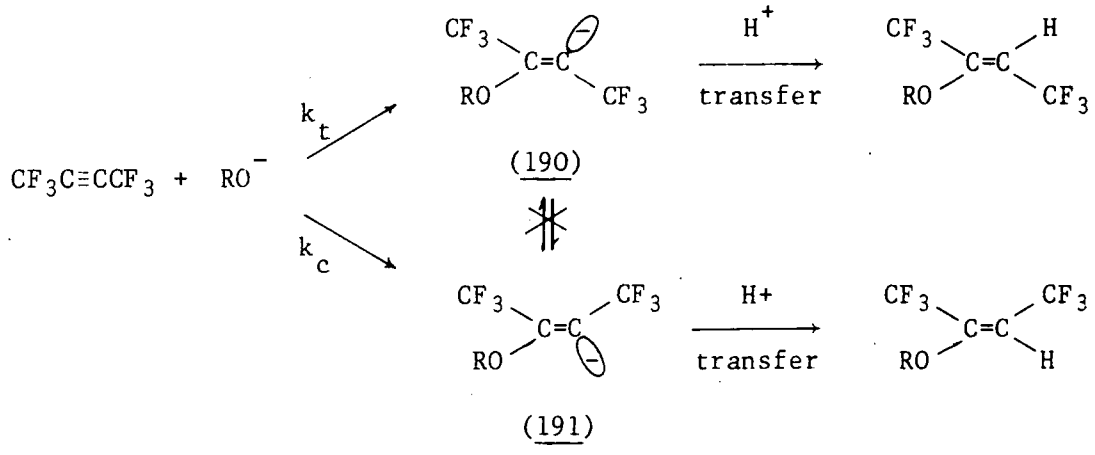
VI.C.2.d Discussion

Predominantly *anti* addition was observed for all the catalysed reactions and also for all the uncatalysed reactions which did not employ a solvent. Steric effects do not appear to be of prime importance although the amount of *cis* addition product did increase slightly as the steric demand of the alcohol increased.

Also it was established, for the *n*-butanol adduct, that isomerisation does not take place at temperatures up to 150° even in the presence of base. This rules out the possibility that the observed isomer compositions are a result of an equilibrium which is set up between the *cis* and *trans* adducts.



Furthermore, it is difficult to imagine a mechanism for the isomerisation of vinyl anions (190) and (191); indeed calculations for the vinyl anion itself indicate that the barrier to inversion is very high.[204] It therefore seems unlikely that (190) and (191) are in equilibrium and therefore the *cis*/*trans* isomer ratio is a reflection of the ratio of the rate constants (k_c and k_t) for the addition step.

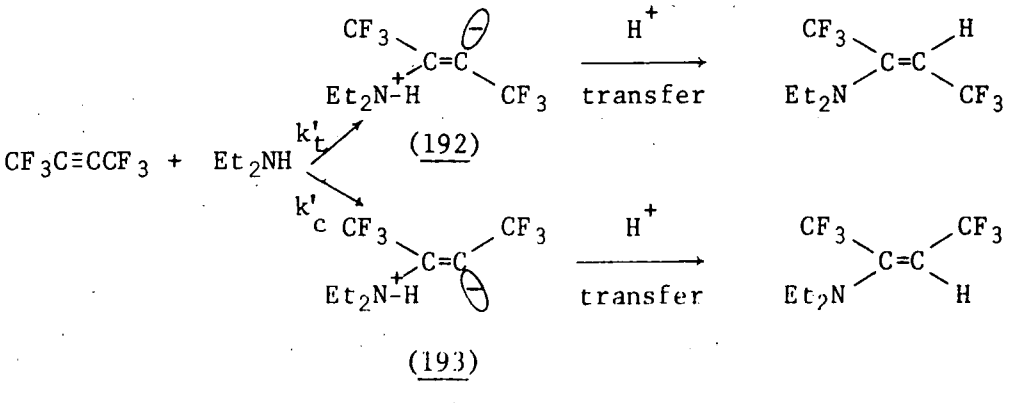


(190)

(191)

It is interesting to compare the results of the alcohol addition reactions with the addition of diethylamine reported by another worker in this laboratory.[205] A reaction in sulpholan proceeded rapidly at room temperature to give predominantly the *trans* adduct. This is in contrast to the uncatalysed addition of *n*-butanol in sulpholan, which gave 70% *cis* addition product.

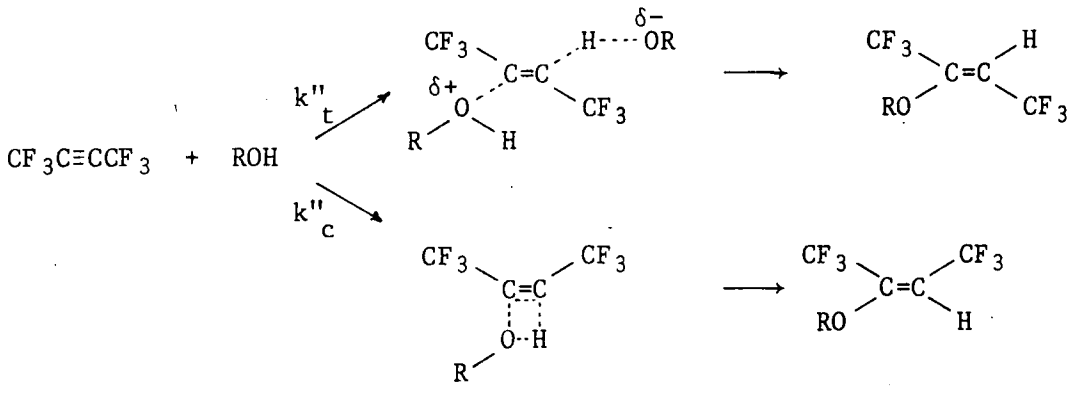
The mechanism proposed to account for the amine addition involves the formation of zwitterionic intermediates (192) and (193) which are protonated to give *trans* and *cis* adducts. Protonation of (192) probably occurs via an intermolecular process, whereas (193) can be protonated either inter- or intramolecularly. The fact that *trans* addition predominates indicates that $k'_t \gg k'_c$.



(192)

(193)

However, it would appear that a different mechanism operates for the uncatalysed alcohol addition reactions. Here, the use of a solvent has a major effect on the *cis/trans* isomer ratio and this suggests a concerted mechanism such as that shown below.

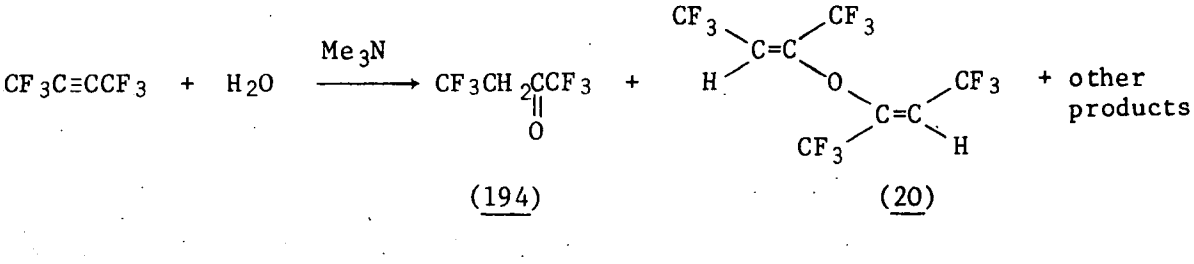


In the reactions with the neat alcohol *trans* products predominate, i.e. $k''_t \gg k''_c$.

However, employing an inert aprotic solvent, which acts as a diluent, the rate of intermolecular protonation is reduced and the intramolecular proton transfer, leading to *cis* products, becomes the major process.

VI.D Reaction of Hexafluorobut-2-yne with Water

As already discussed in Chapter II, hexafluorobut-2-yne reacts with water in the presence of an amine catalyst[54] to give a complex mixture of compounds including the expected product, hexafluorobutanone (194). The major product, however, was the ether (20), which may be formed by attack of the enol form of (194) on a further molecule of acetylene.



(194) (20)

However, since alcohols have been shown to add to hexafluorobut-2-yne in the absence of a catalyst it was anticipated that water would behave similarly. As with the alcohols, no reaction occurred between hexafluorobut-2-yne and water in an aprotic solvent at room temperature. However, at 85° a slow, low conversion reaction occurred to give a liquid consisting of two components. The major component (> 90%) was identified by n.m.r. and mass spectroscopy as the butanone (194), whereas the minor component showed a high mass peak in the mass spectrum which could be derived from the ether (20) by loss of a CF_3 group. At 110° the reaction gave a good conversion with the butanone (194) as the only detectable product.

$$CF_3C{\equiv}CCF_3 + H_2O \xrightarrow[110°]{\text{tetraglyme}} CF_3CH_2\overset{\overset{O}{\|}}{C}CF_3$$

(194) 91%

This reaction is therefore much cleaner than the catalysed process and provides a convenient high yield route to the butanone.

EXPERIMENTAL

INSTRUMENTATION

Infrared spectra were recorded on a Perkin-Elmer 457 Grating Infrared Spectrophotometer using KBr discs or plates.

Proton and fluorine n.m.r. spectra were recorded on a Varian A56/60D spectrometer operating at 60 and 56.4 MHz respectively. Chemical shifts are quoted relative to external TMS and $CFCl_3$. Variable temperature facilities were available for recording spectra at temperatures other than the standard probe temperature of 40°. The phosphorus n.m.r. spectra were recorded on a Fourier transform spectrometer operating at 24.29 MHz. Chemical shifts are quoted relative to external H_3PO_4.[197]

Mass spectra were recorded on an A.E.I. M.S. 9 Spectrometer or on a V.G. Micromass 12B Spectrometer fitted with a Pye 104 gas chromatograph.

Gas liquid chromatographic analyses were carried out on a Varian Aerograph Model 920 or Pye 104 Gas Chromatograph using columns packed with 30% silicone gum rubber SE-30 on chromosorb P (column O), 20% diisodecylphthalate on chromosorb P (column A) or 17% 2-cyanomethyl-silicone on chromosorb P (column Z). Preparative scale gas liquid chromatography was performed on a Varian Aerograph Model 920 using columns O,A or Z.

Fractional distillations of product mixtures were carried out using Fischer-Spaltrohr MS 200 and HMS 500 systems.

Carbon, hydrogen and nitrogen analyses were obtained using a Perkin-Elmer 240 Elemental Analyser. Analyses for halogens were performed by the literature method.[209]

Boiling points were determined by Siwoloboff's method and are uncorrected.

Solvents

Tetraglyme was purified by stirring with sodium metal at 95° for 24 hours, followed by fractional distillation under vacuum, the middle fraction being collected over molecular sieve (type 4A) and stored under nitrogen.

Sulpholan was purified by fractional vacuum distillation. The middle fraction was collected over dry molecular sieve (type 4A) and stored under nitrogen.

CHAPTER VII

EXPERIMENTAL TO CHAPTER III

VII.A General Procedure for Flow Reactions

The starting material was placed in a two necked flask maintained at different temperatures depending on the reagent used: -35° for hexafluorobut-2-yne (b.p. -26°), -10° for hexafluorocyclobutene (b.p. 0°) and 20° for 2,3-dichlorohexafluorobut-2-ene (b.p. 65°). Dry nitrogen was bubbled into the liquid at a known rate and the resulting gas passed through a silica tube packed with the appropriate material. The contact time was estimated from the nitrogen flow rate.

Five different packings were used for these reactions: coarse iron filings, zinc dust, platinum foil, caesium fluoride and potassium fluoride. In all cases except for platinum, the packing was renewed after approximately 30 - 40 g of material had been passed.

A thermostatically controlled furnace was used to maintain the tube at the required temperature. The products were trapped out by passing the effluent gases through two liquid air cooled vessels packed loosely with glass wool to provide a large surface area for condensation. When all the material had passed through the tube the contents of the cold traps were transferred under vacuum to a flask fitted with a flexible gas reservoir. Gaseous products were studied by g.l.c. and infra-red spectroscopy before being transferred to a cylinder for storage.

VII.B Dechlorination of 2,3-Dichlorohexafluorobut-2-ene

VII.B.1 Flow Reactions

VII.B.1.a Over Iron Filings

In a typical experiment, 2,3-dichlorohexafluorobut-2-ene (2.02g, 8.67 mmol) was passed over iron filings at 300° (contact time 30 secs) and a liquid (1.05g, 52% recovery) was collected. This was shown to be unchanged starting material by g.l.c. (Col. O, 70°).

Results of similar experiments employing a variety of conditions were summarised in Table III.1 (Chapter III). Small amounts of gaseous products were obtained from the reactions at 456°, 565° and 610°. Data on these products are summarised in Table VII.1.

Table VII.1

Reaction temperature	g.l.c.[a]	i.r. data	Mass spectrum (major peaks)
456°	1 peak	spectrum of (1) + extra absorptions at 1108 and 1114 cm^{-1}	
565°	1 peak	spectrum of (1) + extra absorptions at 1030 and 735 cm^{-1}	
610°	1 peak	absorptions at 1030 and 735 cm^{-1} only	28, 43, 59, 106

a Columns A and O, room temperature

In a control run to test the trapping efficiency of the system, 2,3-dichlorohexafluorobut-2-ene (3.06g) was passed through the tube at 20°. A recovery of 84% was obtained. Similarly, when hexafluorobut-2-yne (2.54g) was used, 80% was recovered. Hexafluorobut-2-yne (2.20g) was passed through the tube at 450° to give recovered starting material

(1.21g, 54%) and the iron filings had gained in weight by 0.8g. Passing hexafluorobut-2-yne (1.11g) through the tube at 500° gave recovered starting material (0.14g, 13%) and the iron filings had gained in weight by 0.7g.

VII.B.1.b Over Zinc Dust

2,3-Dichlorohexafluorobut-2-ene (4.95g) was passed over zinc dust at 410° (contact time 60 secs). Starting material (4.20g, 85%) and a gas (0.05g) were recovered. The gas was identified as hexafluorobut-2-yne by comparison of its i.r. spectrum with that of an authentic sample.

Passing hexafluorobut-2-yne (2.01g) over zinc under the same conditions gave a gas (1.40g, 70%), shown by i.r. to be unchanged starting material. The tube gained in weight by 0.2g.

VII.B.1.c Over Platinum Foil

Passing 2,3-dichlorohexafluorobut-2-ene (2.00g) over platinum foil at 450° (contact time 30 secs) gave recovered starting material (1.46g, 75%) as a mixture of 63% *trans* and 37% *cis* isomers.

At 656° (contact time 30 secs), 2,3-dichlorohexafluorobut-2-ene (2.98g) gave recovered starting material (1.54g, 52%) as a mixture of 54% *trans* and 46% *cis* isomers. A little gas (0.03g) was also formed. The infrared spectrum showed this to be starting material vapour contaminated with a gas which absorbs at 1290, 1116 and 1108 cm^{-1}.

VII.B.2 Reactions in a Sealed System

VII.B.2.a Reaction of Hexafluorobut-2-yne with Iron Filings

No reaction occurred when hexafluorobut-2-yne (2.05g) and iron filings (4.12g) were heated in a Carius tube at 200° for 24 hours.

At 400° hexafluorobut-2-yne (5.60g) and iron filings (5.64g) gave volatile material (2.65g) and a black solid (8.94g) after 24 hours. The volatile material consisted of a trace of a complex mixture of liquid products, which were not investigated, together with a gas which was shown by m.s. / g.l.c. to be a mixture of four components with high mass peaks at 195, 293, 316 and 395. The black solid dissolved partially in concentrated hydrochloric acid giving a green solution and a black powder which was washed with water and dried. (Found: C, 70.12; F, 9.61; Cl, 3.08%).

VII.B.2.b Reaction of 2,3-Dichlorohexafluorobut-2-ene with Zinc Dust

A stainless steel bomb was loosely packed with alternating layers of glass wool and zinc dust (65.0g, 1 mol) and 2,3-dichlorohexafluorobut-2-ene (47.6g, 0.21 mol) was added. The bomb was sealed and heated at 200° for 18 hours. Starting material (43.2g, 91%) was recovered and no trace of gaseous products was detected.

A similar reaction using zinc dust (99.0g) and 2,3-dichlorohexafluorobut-2-ene (25.0g) heated at 270° for 22 hours gave a gas (24.0g), shown by g.l.c. (Col. A, 40°) to be a mixture of hexafluorobut-2-yne and 7 other major components of longer retention time. The products were not investigated further.

A reaction was attempted using zinc dust which had been activated by washing with acetic acid and dried in vacuo. When activated zinc

dust (100g) and 2,3-dichlorohexafluorobut-2-ene (25.0g) were heated at 270° for 20 hours, a gas (2.9g) was recovered and a black solid had formed in the bomb. (Found: C, 68.14; F, 7.81; Cl, 4.65%). The gas was a very complicated mixture (8 major components) containing some hexafluorobut-2-yne.

A reaction using unactivated zinc dust (29.5g) and 2,3-dichlorohexafluorobut-2-ene (15.9g) heated at 325° for 48 hours gave a gas (1.6g) containing hexafluorobut-2-yne, starting material and 7 other components. A black solid (14.0g) was also produced. (Found: C, 76.61; F, 9.96%).

VII.B.3 Reactions in Solution

VII.B.3.a General Methods for Dechlorinations in Solution

The solvent and zinc dust were refluxed in a large three-necked flask fitted with mechanical stirrer, dropping funnel and reflux condenser. A cold finger maintained at -15°C (CO_2 / ethylene glycol) was fitted at the top of the condenser to prevent starting material and reduction products from distilling over into the liquid air cooled receivers. 2,3-Dichlorohexafluorobut-2-ene was added to the mixture at such a rate as to maintain a steady reflux. This usually took 6 - 8 hours, after which time the mixture was refluxed for a further 24 hours. The contents of the traps were then transferred under vacuum into a cylinder for storage. Products from several such runs were combined and distilled at low temperature through a vacuum jacketed column packed with glass helices. The top of the column was fitted with an efficient cold finger maintained at -15°C. The distillate was shown to be ca. 99% hexafluorobut-2-yne by g.l.c. (Columns A and O) and by infrared spectroscopy.

VII.B.3.b Using Zinc in Dioxan

2,3-Dichlorohexafluorobut-2-ene (46.6g, 0.20 mol) in dioxan (72 ml) was added over a period of 6 hours to a stirred suspension of zinc dust (65.0g, 1 mol) in refluxing dioxan (100 ml). After a further 15 hours starting material contaminated with reduction products and dioxan (11.2g) was recovered from the reaction mixture. The gas which had collected in the traps (9.1g, 36% based on consumption of 36g of butene) was ca. 95% hexafluorobut-2-yne.

VII.B.3.c Using Zinc in Dioxan / Sulpholan (40:60)

2,3-Dichlorohexafluorobut-2-ene (48.3g, 0.21 mol), dioxan (65 ml), sulpholan (100 ml) and zinc dust (64.1g, 1 mol) gave impure hexafluorobut-2-yne (9.6g) after 24 hours. Starting material heavily contaminated with 2-chlorohexafluorobut-2-ene and several other by-products (20.0g) was distilled from the residue.

VII.B.3.d Using Zinc in Acetic Anhydride

2,3-Dichlorohexafluorobut-2-ene (46.6g, 0.20 mol) in acetic anhydride (100 ml) was added to a suspension of zinc dust (96.0g, 1.5 mol) in refluxing acetic anhydride. After 30 hours, starting material contaminated with reduction products (12.5g) was recovered from the reaction mixture. The gaseous product (16.3g, 65% based on consumption of 36g of starting material) was shown to be ca. 92% hexafluorobut-2-yne.

VII.B.3.e Using Magnesium in Tetrahydrofuran

2,3-Dichlorohexafluorobut-2-ene (10.0g, 43 mmol) was added to a stirred mixture of magnesium in refluxing THF. A small crystal of iodine was required to initiate the reaction. After 24 hours a gas (1.0g) had been evolved and no starting material was recovered from the tarry reaction mixture. The gas was ca. 90% hexafluorobut-2-yne.

VII.C Isomerisation of Hexafluorocyclobutene

These reactions were carried out using the flow system described at the beginning of this chapter. Hexafluorocyclobutene (96) was passed over caesium or potassium fluoride at temperatures between 540 and 690°. The results are summarised in Table VII.2.

Table VII.2

Results of Fluoride Ion Induced Isomerisation Reactions of (96)

Temp.	Contact time(s)	Packing material	Mass of (96) used (g)	Mass of liq. collected(g)	Mass of gas collected(g)	Total% recovery	% (1) in gas
540°	20	CsF	19.5	0.0	16.6	85	45
560°	30	CsF	21.6	0.0	17.6	82	50
590°	20	CsF	15.7	0.0	12.7	81	90
560°	20	KF	14.6	0.0	13.9	95	50
580°	80	KF	164.0	47.3	93.6	86	90
580°	30	KF	20.9	0.4	19.4	95	85
600°	30	KF	33.3	0.8	31.6	95	94
630°	30	KF	30.0	2.1	24.4	88	95
645°	20	KF	62.4	7.9	49.1	91	96
690°	20	KF	12.0	2.8	6.8	80	96

The percentage hexafluorobut-2-yne (1) in the product gas was determined by g.l.c. The liquid products were complex mixtures containing components of molecular weight higher than that of hexafluorobut-2-yne. For example, the liquid obtained from the reaction at 690° consisted of 11 major components; m.s. / g.l.c. gave the following high mass figures: 343 (C_8F_{13}), 393 (C_9F_{15}), 374 (C_9F_{14}) (3 isomers), 405 ($C_{10}F_{15}$), 367 ($C_{10}F_{13}$), 336 (C_9F_{12}), 448 ($C_{12}F_{16}$), 398 ($C_{11}F_{14}$) and 784 ($C_{21}F_{28}$).

Similar liquid products were obtained when hexafluorobut-2-yne was passed over KF at 695°.

CHAPTER VIII

EXPERIMENTAL TO CHAPTER IV

VIII.A Reagents

Acetaldehyde was fractionally distilled through a 20 cm Vigreux column and stored over type 4A molecular sieve under nitrogen in the fridge. Other aldehydes were distilled under nitrogen after checking for peroxides.

Dimethyl ether was used straight from the cylinder and other reagents were either used as supplied or, where necessary, purified by standard methods.

VIII.B General Procedure

All addition reactions were carried out in glass Carius tubes of approximately 100 cm^3 volume. Reagents were thoroughly degassed before sealing the tubes under vacuum. Standard vacuum line techniques were used to manipulate gaseous reagents and products.

Gamma ray initiated reactions were performed by exposing the tubes to a known dose of radiation from a ^{60}Co source. Unless otherwise stated, catalytic amounts of peroxides (ca. 1% by weight) were used in the chemically initiated reactions. Where reactions were performed more than once a typical set of reaction conditions is given. Yields are based on the quantity of hexafluorobut-2-yne consumed.

VIII.C Preparation and Reactions of Polyhexafluorobut-2-yne

VIII.C.1 Preparation

Irradiation of hexafluorobut-2-yne (18.0g, 111 mmol) to a dose of 6×10^6 rads gave a white solid identified as polyhexafluorobut-2-yne (14.4g, 80%), (Found: C, 29.36; F, 70.76%. Calc. for $(C_4F_6)_n$: C, 29.63; F, 70.37%), I.r. spectrum no. 2.

VIII.C.2 Reactions

VIII.C.2.a Pyrolysis

Polyhexafluorobut-2-yne (1.25g) was placed in a silica tube which was connected to a vacuum line via a liquid air cooled trap. The polymer was heated to ca. 600° at 0.01 mm Hg for 4 hours. A little brown solid sublimed onto the cooler parts of the apparatus. No liquid or gas was collected in the trap and a brown powder (1.09g) was recovered. (Found: C, 29.82; F, 70.70%).

VIII.C.2.b Reaction with Fluorine

The polymer was spread thinly along the length of a glass tube which was heated to the required temperature using a heating tape. A stream of fluorine diluted with nitrogen was slowly passed through the tube and the nitrogen flow rate gradually decreased until the polymer was finally exposed to an atmosphere of neat fluorine. The results are summarised in Table VIII.1.

Table VIII.1

Fluorination of Polyhexafluorobut-2-yne

Mass of polymer (g)	Mass of F_2 passed (g)	Length of exposure (hrs)	Temp.	Elemental analysis C %	F %
0.20	9.0	24	20°	29.08	71.14
0.33	9.0	21	55°	28.72	71.20
0.20	6.0	24	90°	29.67	71.22
0.53	2.0	∿	120°	*	

* Polymer spontaneously ignited

VIII.C.2.c Reaction with Bromine

Polyhexafluorobut-2-yne (0.10g) was sealed in a pyrex tube with bromine (1 cm^3) and left to stand in sunlight for 1 week. A white solid was recovered (0.10g). (Found: C, 29.88%. Calc. for $(C_4F_6)_n$: C, 29.63%). The experiment was repeated using the same quantities of starting materials but this time the tube was exposed for 20 hours to u.v. radiation from a high pressure mercury lamp. A white solid was recovered. (Found: C, 29.76%).

VIII.C.2.d Reaction with Potassium Hydroxide Solution

Polyhexafluorobut-2-yne (1.05g) was stirred in a glass vessel with aqueous potassium hydroxide solution (20 ml, 5M) at reflux temperature. The apparatus was connected to a vacuum line to monitor any gas formation. The solution slowly turned brown and no gas was evolved. After 9 days, unreacted polymer (0.55g) was recovered by filtration. Acidification of the brown solution gave a brown solid (7.3g) whose i.r. spectrum closely

resembled that of silica.

Repeating the experiment using polyhexafluorobut-2-yne (0.52g) and potassium hydroxide solution (20 ml, 5M) in a teflon beaker, unchanged polymer (0.39g) was recovered after 1 week. Acidification, concentration and solvent extraction of the residual brown solution did not give any organic products.

VIII.D Attempted Copolymerisation Reactions

VIII.D.a With Dimethylacetylene Dicarboxylate

Dimethylacetylene dicarboxylate (1.68g, 18 mmol) and hexafluorobut-2-yne (3.9g, 24 mmol) were irradiated to a dose of 7×10^6 rads. A quantitative recovery of both reagents was obtained.

VIII.D.b With Styrene

Styrene (6.1g, 59 mmol) which had been treated with alumina to remove the stabiliser and hexafluorobut-2-yne (9.2g, 57 mmol) were irradiated to 7×10^6 rads. A quantitative recovery of both reagents was obtained.

VIII.D.c With Methyl Methacrylate

Irradiation of methyl methacrylate (5.5g, 55 mmol) and hexafluorobut-2-yne (7.9g, 49 mmol) to a dose of 1×10^6 rads gave polymethyl methacrylate as the only product. Hexafluorobut-2-yne (7.8g) was recovered.

VIII.D.d Attempted Homopolymerisation of Dimethylacetylene Dicarboxylate

The acetylenic diester (1.51g) was irradiated to 7×10^6 rads and a quantitative recovery of unchanged starting material was obtained.

VIII.E Additions of Aldehydes

VIII.E.1 Acetaldehyde

VIII.E.1.a By Gamma Ray Initiation

A mixture of acetaldehyde (5.01g, 114 mmol) and hexafluorobut-2-yne (19.7g, 122 mmol) was irradiated to a dose of 1.1×10^7 rad. Hexafluorobut-2-yne (11.0g) was recovered and the residual mixture was washed with water, the fluorocarbon layer separated, dried (P_2O_5) and the product was transferred under vacuum to give (E)-3-trifluoromethyl-1,1,1-trifluoropent-2-en-4-one (105), (3.3g, 30%), identified by comparison with an authentic sample.[165]

VIII.E.1.b By Benzoyl Peroxide Initiation

(i) With Excess Hexafluorobut-2-yne

Acetaldehyde (4.4g, 100 mmol), hexafluorobut-2-yne (19.0g, 120 mmol) and benzoyl peroxide (0.20g, 0.8 mmol) were heated at 70° for 16 hours. Hexafluorobut-2-yne (8.2g) was recovered and the residual mixture filtered to remove a solid which was sublimed and recrystallised from chloroform to give 3,4-bistrifluoromethylhexa-2,5-dione (106), (2.3g, 17%); m.p. 122 - 3°; (Found: C, 38.4; H, 3.2; F, 45.6%. $C_8H_8F_6O_2$ requires C, 38.68; H, 3.01; F, 45.20%). N.m.r. spectrum no. 1, i.r. spectrum no. 4, mass spectrum no. 1. The filtrate was washed with water, the fluorocarbon lower layer separated, dried (P_2O_5) and transferred under vacuum. The

resulting liquid (8.1g) was shown by g.l.c. (Col. A, 70°) to consist of 1 major and 4 minor components. The major component was isolated by preparative scale g.l.c. and identified as (105), (4.2g, 31%).

(ii) With Excess Acetaldehyde

Acetaldehyde (5.8g, 130 mmol), hexafluorobut-2-yne (8.4g, 52 mmol) and benzoyl peroxide (0.20g, 0.8 mmol) were heated at 75° for 16 hours. The liquid part of the product was separated from the solid and after a work up similar to that described in the previous experiment (105), (1.9g, 18%) and (106), (6.0g, 46%) were isolated.

(iii) Photolysis of (E)-3-trifluoromethyl-1,1,1-trifluoropent-2-en-4-one (105)

Three experiments were carried out using 300 nm radiation and details are given in Table VIII.2. The 1:1 acetaldehyde adduct was sealed under vacuum in a 300 ml silica tube. Only the vapour was irradiated, the liquid being shielded from direct exposure. In each case three major products were observed in different proportions. A small amount of a fourth component was also detectable. The three major components were identified by m.s./g.l.c. and ^{19}F n.m.r. as (105); (Z)-3-trifluoromethyl-1,1,1-trifluoropent-2-en-4-one, (110); n.m.r. spectrum no. 3, i.r. spectrum no. 5, mass spectrum no. 2; and 1,2-bis-trifluoromethyl-3-methyl-4-oxacyclobutene, (111), n.m.r. spectrum no. 4.

Table VIII.2

Photolysis of (105)

Mass of (105) (g)	Irradiation time (hrs)	Products % (105)	(111)	(106)	Minor component
1.80	90	30	29	39	1
0.48	94	10	73	11	5
1.75	352	12	72	12	4

Compounds (105) and (106) were isolated by preparative scale g.l.c. (Col. A, 78°) but the fraction which should have contained (111) was found to consist of a mixture of (105) and (106) in the ratio of 44:56.

VIII.E.2 Propanal

Propanal (2.2g, 38 mmol), hexafluorobut-2-yne (7.4g, 46 mmol) and benzoyl peroxide (0.20g, 0.8 mmol) were heated at 75° for 16 hours. Hexafluorobut-2-yne (3.1g) was recovered along with a liquid (2.9g) and a white solid (3.4g). The liquid was distilled to give (E)-3-trifluoromethyl-1,1,1-trifluorohex-2-en-4-one (112), (2.3g, 40%); b.p. 93 - 94°; (Found: C, 38.3; H, 2.8; F, 51.6%. $C_7H_6F_6O$ requires C, 38.18; H, 2.73; F, 51.82%). N.m.r. spectrum no. 5, i.r. spectrum no. 6, mass spectrum no. 3. The solid was sublimed to give a product identified as a mixture of 4,5-bistrifluoromethyl-octa-3,6-dione (114), and 4-trifluoromethyl-4-(2,2,2-trifluoroethyl)-hepta-3,5-dione (113), (3.4g, 47%) (Found: C, 42.9; H, 4.2; F, 40.6%. $C_{10}H_{12}F_6O_2$ requires C, 43.16; H, 4.32; F, 41.01%). N.m.r. spectra nos. 6 and 7, i.r. spectrum no. 7, mass spectrum no. 4. Ratio of (114) : (113) = 88 : 12.

VIII.E.3 Butanal

VIII.E.3.a By Benzoyl Peroxide Initiation

Heating butanal (3.2g, 44 mmol), hexafluorobut-2-yne (10g, 62 mmol) and benzoyl peroxide (0.28g, 1.2 mmol) at 80° for 17 hours gave a liquid (9.0g) and recovered acetylene (4.1g). The liquid showed 3 major and 4 minor components by m.s./g.l.c.; the high mass peaks are given below. (Calc. for 1:1 adduct: M = 234; for 2:1 adduct: M = 306.)

Component	High Mass Peak	Assignment
1 (minor)	233	1:1 adduct M-H
2 (major)	234	1:1 adduct M
3 (major)	234	1:1 adduct M
4 (major)	234	1:1 adduct M
5 (minor)	278	2:1 adduct M-C_2H_4
6 (minor)	263	2:1 adduct M-C_3H_7
7 (minor)	235	2:1 adduct M-C_3H_7CO

A liquid (4.0g) distilled from the mixture at 80-90°/0.5 mm Hg. This contained three 1:1 adducts which were separated by preparative scale g.l.c. (Col. O, 130°). One of these was identified as (E)-3-trifluoromethyl-1,1,1-trifluorohept-2-en-4-one (118). (Found: C, 41.12; H, 3.30; F, 49.01%. $C_8H_8F_6O$ requires C, 41.03; H, 3.42; F, 48.72%). N.m.r. spectrum no. 8, i.r. spectrum no. 8, mass spectrum no. 5. The other components were not identified, and due to its complexity the distillation residue (5.0g) was not investigated further.

VIII.E.3.b By Gamma Ray Initiation

A mixture containing butanal (2.9g, 40 mmol) and hexafluorobut-2-yne (7.8g, 68 mmol) was irradiated to a dose of 4.3×10^6 rads. Hexafluorobut-2-yne (4.9g) was recovered leaving a clear liquid (5.2g) shown by m.s./g.l.c. to contain unreacted aldehyde and the same components as were observed in the reaction above. The mixture was not investigated further.

VIII.E.4 Pentanal

Pentanal (3.5g, 41 mmol), hexafluorobut-2-yne (9.6g, 59 mmol) and benzoyl peroxide (0.28g, 1.2 mmol) were heated at 80° for 18 hours. After collecting the unreacted butyne (1.5g) the residue was a pale yellow liquid (10.1g) containing 2 major and 4 minor components. The 2 major components were isolated by preparative scale g.l.c. (Col. O, 160°). The component with the shorter retention time was identified as (E)-3-trifluoromethyl-1,1,1-trifluorooct-2-en-4-one (121). (Found: C, 53.01; H, 3.38; F, 38.90%. $C_9H_{10}F_6O$ requires C, 52.70; H, 3.38; F, 38.51%), n.m.r. spectrum no. 9, i.r. spectrum no. 9, mass spectrum no. 6.

VIII.E.5 (E)-But-2-enal

(E)-But-2-enal (crotonaldehyde) (3.1g, 44 mmol), hexafluorobut-2-yne (9.8g, 60 mmol) and benzoyl peroxide (0.2g, 0.8 mmol) were heated at 82° for 18 hours. An almost quantitative recovery of hexafluorobut-2-yne was obtained and no products were detectable by g.l.c. (Col. O, 160°).

VIII.F Reaction with 2,2,2-Trifluoroethanol

2,2,2-Trifluoroethanol (9.6g, 96 mmol) and hexafluorobut-2-yne (5.4g, 33 mmol) were irradiated to a dose of 1.6×10^7 rads. Hexafluorobut-2-yne (4.0g) was recovered and excess trifluoroethanol was partially removed by distillation to leave a liquid (2.1g) containing the alcohol and three other components. Two fractions were collected by preparative scale g.l.c. (Col. Z, 145°) and these were identified as: (E)-3-trifluoromethyl-1,1,1,5,5,5-hexafluoropent-2-en-4-ol (122), (0.5g, 22%), (Found: C, 27.18; H, 1.10; F, 65.36%. $C_6H_3F_9O$ requires C, 27.48; H, 1.15; F, 65.27%), n.m.r. spectrum no. 10, i.r. spectrum no. 10, mass spectrum no. 7; and (Z)-3-trifluoromethyl-1,1,1,5,5,5-hexafluoropent-2-en-4-ol (123), (0.5g, 22%), (Found: C, 27.25; H, 1.09; F, 65.32%. $C_6H_3F_9O$ requires C, 27.48; H, 1.15; F,65.27%), n.m.r. spectrum no. 11, i.r. spectrum no. 11, mass spectrum no. 8.

VIII.G Reactions Attempted with Other Compounds Containing C-H Bonds

A series of free radical additions to hexafluorobut-2-yne were attempted using a variety of compounds containing C-H bonds. Both gamma ray and peroxide initiation were used. The quantities of reactants and the reaction conditions are summarised in Table VIII.3, which also gives details of any products obtained.

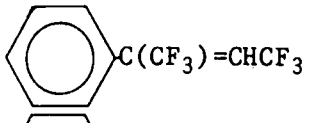
Table VIII.3

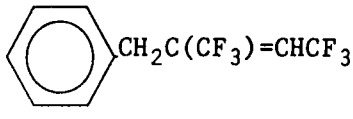
Experimental Conditions for Attempted Free Radical Additions

Reagent		Hexafluoro-but-2-yne		Initiator	Dose/Reaction time	Products
g	mmoles	g	mmoles			
$HCON(CH_3)_2$						
2.7	38	5.2	32	γ	4.3×10^6 rad	None
2.3	31	2.6	16	A	16 hours	None
CH_3OCH_3						
8.1	176	11.6	72	γ	1.2×10^7 rad	None
1.9	41	6.5	40	γ, 80°	2.7×10^6 rad	None
4.8	100	5.5	34	A	21½ hours	None
$CH_3CH_2OCH_2CH_3$						
7.4	100	5.2	32	γ	1.1×10^7 rad	None
CF_3COCF_2H						
3.0	20	4.3	27	γ	1.2×10^7 rad	Polyhexafluorobut-2-yne (0.8g)
Toluene						
3.5	38	6.2	38	γ	8.0×10^6 rad	Polyhexafluorobut-2-yne (0.3g) + 2 products (ca. 2% combined yield)
1.5	16	2.9	18	A	17 hours	3 products (ca. 4% combined yield)
2.0	22	3.5	22	B	18 hours	Yellow liquid (2.1g) 12 components
o-Xylene						
2.1	20	7.4	46	γ	2.7×10^6 rad	Polyhexafluorobut-2-yne (0.5g)
p-Methylanisole						
4.1	33	7.0	43	γ	1.5×10^7 rad	Polyhexafluorobut-2-yne (0.5g)
1.2	10	2.5	15	B	18 hours	Yellow liquid (1.9g) 7 components

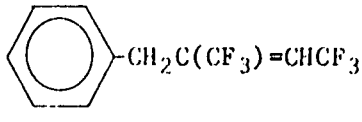
A Benzoyl peroxide B Di-*tert*-butyl peroxide

The products obtained from the reactions with toluene and p-methylanisole were analysed by m.s./g.l.c. The high mass peaks for the major components were as follows. Formulae are assigned where possible.

Toluene (A) Component 1 $M^+ = 240$ 

Components 2 and 3 $M^+ = 254$ 

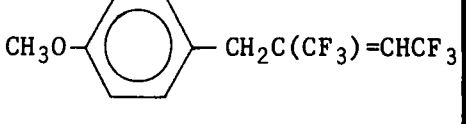
(B) Component 1 $M^+ = 178$ $CH_3-C(CF_3)=CHCF_3$

Components 2 and 3 $M^+ = 254$ 

A large quantity of toluene was also present in these mixtures.

p-Methylanisole (B) Component 1 $M^+ = 178$ $CH_3-C(CF_3)=CHCF_3$

Component 2 $M^+ = 218$

Component 3 $M^+ = 284$ 

p-Methylanisole was also detected in the product mixture.

VIII.H Attempted Reaction of Hexafluorobut-2-yne with Benzoyl Peroxide

Hexafluorobut-2-yne (2.5g, 15 mmol) and benzoyl peroxide (0.11g, 0.45 mmol) were heated at 70° for 21.5 hours. A quantitative recovery of both compounds was obtained. Neither showed any change in infrared spectrum. The same result was obtained when the reaction was repeated with the same quantities of starting materials heated at 75° for 24 hours. To check that the peroxide had not decomposed, a sample was used to initiate the reaction between acetaldehyde and hexafluorobut-2-yne. Results similar to those given in VIII.E.1.b were obtained.

VIII.I Reaction with Di-*tert*-butyl Peroxide

Hexafluorobut-2-yne (1.7g, 10 mmol) and di-*tert*-butyl peroxide (0.1g, 0.7 mmol) were heated at 132° for 18 hours. The yellow liquid (0.4g) which was obtained showed 9 components on g.l.c. (Col. A, 76°). The high mass peaks of the major components are given below.

Component 1	$M^+ = 178$	$CH_3-C(CF_3)=CHCF_3$
Component 2	$M^+ = 340$	$CH_3-[C(CF_3)=C(CF_3)]_2-H$
Component 3	$M^+ = 58$	Acetone
Component 4	$M^+ = 340$	Isomer of component 2
Component 5	$M^+ = 502$	$CH_3-[C(CF_3)=C(CF_3)]_3-H$
Component 6	$M^+ = 664$	$CH_3-[C(CF_3)=C(CF_3)]_4-H$

VIII.J Reactions Attempted with Compounds Containing C-X Bonds

The experimental conditions and results of these gamma ray induced reactions are summarised in Table VIII.4. No adducts were observed in any of these reactions.

Table VIII.4

Experimental Conditions for Attempted Additions of C-X Compounds

Reagent g	Reagent mmoles	Hexafluorobut-2-yne g	Hexafluorobut-2-yne mmoles	Dose rad	Products
$CHCl_3$					
4.8	40	6.9	43	9×10^6	None
CCl_4					
5.7	36	6.0	37	3×10^6	Polyhexafluorobut-2-yne (0.4g)
$CFCl_3$					
4.7	34	5.0	31	3×10^6	Polyhexafluorobut-2-yne (1.0g)

Reagent		Hexafluoro-but-2-yne		Dose rad	Products
g	mmoles	g	mmoles		
CF_2Br_2					
6.8	32	5.2	32	9×10^6	Polyhexafluorobut-2-yne (0.1g)
CH_3COCl					
1.5	19	3.1	19	9×10^6	Polyhexafluorobut-2-yne (0.1g)

CHAPTER IX

EXPERIMENTAL TO CHAPTER V

IX.A Reagents

Dimethyl- and diethyl-acetylene dicarboxylates were available commercially and used as supplied.

Perfluorocyclohexene was available within this laboratory and perfluorocyclo-pentene and -butene were prepared by technical staff using literature methods. Other perfluoroalkenes were obtained from commercial sources.

The caesium fluoride was reagent grade and was dried using strong heating (ca. 180°) under high vacuum with frequent agitation and periodic grinding under an atmosphere of dry nitrogen.

IX.B Polymerisation and Copolymerisation Reactions

IX.B.1 Polymerisation of Hexafluorobut-2-yne

A flask containing anhydrous caesium fluoride (3.1g, 20 mmol) and sulpholan (50 ml) and fitted with a magnetic stirrer was evacuated until degassing of the solvent had ceased. A trap fitted with a flexible reservoir (a football bladder) was charged with hexafluorobut-2-yne (22.7g, 140 mmol) and attached to the reaction vessel. A slow reaction occurred which could be followed by the collapse of the reservoir. After 4 days the uptake of gas had virtually ceased and the residual hexafluorobut-2-yne (6.2g) was transferred to a cold trap. The reaction mixture was poured into water and a pale brown solid was removed by filtration. This was dried by heating under high vacuum to give an off-white solid

(14.2g) (Found: C, 29.36; F, 70.26%. Calc. for $(C_4F_6)_n$: C, 29.63; F, 70.37%), i.r. spectrum no. 3.

IX.B.2 Copolymerisation of Hexafluorobut-2-yne with Acetylenic Esters

IX.B.2.a With Dimethyl Acetylenedicarboxylate

A mixture of dimethyl acetylenedicarboxylate (7.6g, 53 mmol), caesium fluoride (1.0g, 6.6 mmol) and tetraglyme (50 ml) was stirred at room temperature and hexafluorobut-2-yne (10.0g, 62 mmol) allowed into the reaction vessel at a pressure of one atmosphere. After 30 hours the residual hexafluorobut-2-yne (0.9g) was removed and the bright red reaction mixture was poured into water. The solid was separated by filtration, washed with methanol and dried in vacuo to give a pale brown solid (10.6g) (Found: C, 31.91; H, 1.11; F, 65.04% Copolymer of formula $(C_6H_6O_4)_n(C_4F_6)_{9\cdot5n}$ requires C, 31.41; H, 0.36; F, 64.43%), i.r. spectrum no. 12.

In a second experiment dimethyl acetylenedicarboxylate (12.2g, 86 mmol) was added dropwise over a period of 24 hours to a stirred suspension of caesium fluoride (7.2g, 47 mmol) in tetraglyme (80 ml) while under an atmosphere of hexafluorobut-2-yne (11.0g, 68 mmol). After 48 hours all the gas had been consumed and after the same work-up procedure as described above a light brown coloured solid (14.0g) was recovered. (Found: C, 35.89; H, 0.80; F, 49.85%. Copolymer of formula $(C_6H_6O_4)_n(C_4F_6)_{2.1n}$ requires C, 35.84; H, 1.24; F, 49.64%). The mass spectrum showed strong peaks at m/e = 55, 57, 69, 71, 73, 83 and 119.

IX.B.2.b With Diethyl Acetylenedicarboxylate

A mixture of caesium fluoride (3.0g, 20 mmol), diethyl acetylenedicarboxylate (9.4g, 66 mmol) and sulpholan (70 ml) was stirred at 50°

under an atmosphere of hexafluorobut-2-yne (5.0g, 31 mmol). After 72 hours the residual gas (1.3g) was recovered and after an aqueous work-up a deep brown solid (6.1g) was obtained (Found: C, 52.21; H, 5.16; F, 6.96%. Copolymer of formula $(C_4F_6)_n(C_8H_{10}O_4)_{6n}$ requires C, 52.79; H, 5.08; F, 9.64%). The polymer was completely soluble in ether.

IX.B.2.c Reaction of Dimethyl Acetylenedicarboxylate with Caesium Fluoride

A mixture of dimethyl acetylenedicarboxylate (4.6g, 32 mmol), caesium fluoride (3.0g, 20 mmol) and tetraglyme (50 ml) was stirred for 72 hours. No starting material could be detected in the resulting solution by t.l.c. (eluent ether) and no volatiles transferred on heating to 100° at 0.1 mm Hg.

IX.B.2.d Attempts to Hydrolyse the Copolymer of (132) and (1)

Several attempts were made to hydrolyse the copolymer of (132) and (1) but in all cases the recovered material was shown by i.r. spectroscopy to be identical with starting material. The following experiments are typical.

i) The copolymer (0.50g), water (2g) and concentrated hydrochloric acid (2 ml) were sealed under vacuum in a Carius tube and heated at 140° for 28 hours. A brown solid was separated by filtration, washed with water and dried in vacuo. The resulting solid (0.45g) was identified as starting material.

ii) A mixture of copolymer (0.5g), acetone (10 ml), water (2.5 ml) and concentrated hydrochloric acid (2.5 ml) was refluxed for 24 hours. Water (100 ml) was then added and a brown solid was filtered off. After further washing and drying the resulting solid (0.42g) was shown to be unchanged starting material.

A series of experiments using several anionic and non-ionic surfactants also failed to bring about hydrolysis. For example, a mixture of copolymer (0.50g), acetone (10 ml), water (2.5 ml), concentrated hydrochloric acid (2.5 ml) and Monflor 31 (an anionic surfactant) was refluxed for 24 hours. The recovered solid (0.36g) was shown to be unchanged starting material.

IX.C Co-oligomerisation with Fluoroalkenes

IX.C.1 Hexafluorocyclobutene

Caesium fluoride (7.6g, 50 mmol) and tetraglyme (50 ml) were placed in a dry flask fitted with magnetic stirrer and the mixture was thoroughly degassed. Two traps containing hexafluorobut-2-yne (12.5g, 77 mmol) and hexafluorocyclobutene (11.0g, 68 mmol) were attached to the reaction vessel. Equal pressures of the two gases were allowed into the reaction vessel to a total pressure of one atmosphere and the mixture was stirred for 24 hours. The residual gases (1.8g) were then transferred to a cold trap and the reaction mixture flash distilled to give a liquid (3.1g) shown by g.l.c. (Col. 0,60°) to consist of 6 components. Three isomers of C_8F_{12} (M^+ = 324) were detectable by m.s./g.l.c. The flash distillation residue was poured into water to give a pale yellow liquid (6.0g) (4 components) and a deep brown intractable material (11.6g) (6 components including some tetraglyme). The components of these

mixtures could not be separated by preparative scale g.l.c. (Cols. O and A).

The experiment was repeated using caesium fluoride (7.1g, 47 mmol), tetraglyme (50 ml), hexafluorobut-2-yne (9.7g, 60 mmol) and hexafluorocyclobutene (10.1g, 62 mmol). After removing the residual gases (1.0g) the reaction mixture was steam distilled to give a pale yellow oil (4.7g) shown by g.l.c. (Col. O, 100°) to contain 10 major components which were not investigated further.

IX.C.2 Perfluorocyclopentene

A mixture of perfluorocyclopentene (15.5g, 73 mmol), caesium fluoride (11.8g, 78 mmol) and tetraglyme (50 ml) was stirred at room temperature and a trap containing hexafluorobut-2-yne (26.8g, 165 mmol) was attached. After 24 hours the residual gas (0.6g) was condensed into a cold trap and the reaction mixture flash distilled. The resulting liquid (12.2g) was shown by g.l.c. (Col. O, 80°) to contain 10 components. Part of this liquid (9.3g) was separated by preparative scale g.l.c. and the two major components were identified as perfluoro-(E)-2-(cyclopent-1'-enyl)but-2-ene (141) (0.5g), b.p. 108°, (Found: C, 28.71; F, 70.79%. C_9F_{14} requires C, 28.88; F, 71.12%), n.m.r. spectrum no. 12, i.r. spectrum no. 13, mass spectrum no. 9; and perfluoro-2,3,4-trimethyl-4-ethylbicyclo[3.3.0]octa-(1,5)(2,3)-diene (142) (2.9g), b.p. 141°, (Found: C, 28.80; F, 71.36%. $C_{13}F_{22}$ requires C,29.10; F, 70.90%), n.m.r. spectrum no. 13, i.r. spectrum no. 14, mass spectrum no. 10. The overall yields (based on perfluorocyclopentene) of compounds (141) and (142) are 2% and 10% respectively. One of the minor components of the mixture was identified by m.s./g.l.c. as perfluoro—bicyclopentylidene (143), (M^+ 424, Calc. for $C_{10}F_{16}$: M 424). The mass spectrum of this compound was

identical with that of an authentic sample of (143).

The experiment was repeated using hexafluorobut-2-yne (10.1g, 62 mmol), cyclopentene (11.0g, 52 mmol), caesium fluoride (4.0g, 26 mmol) and tetraglyme (40 ml) and after 24 hours the reaction mixture was steam distilled to give a liquid (12.6g, 60% recovery of material) shown by g.l.c. (Col. O, 80°) to contain 10 components as in the previous experiment. The mixture was not investigated further.

IX.C.3 Perfluorocyclohexene

IX.C.3.a At 20°

A mixture of caesium fluoride (8.0g, 53 mmol), tetraglyme (25 ml) and perfluorocyclohexene (10.4g, 40 mmol) was stirred at 20° while hexafluorobut-2-yne (15.0g, 93 mmol) was allowed to enter the reaction vessel. After 18 hours a large amount of solid had formed in the flask and the reaction was terminated. Hexafluorobut-2-yne (5.3g) was recovered and volatiles were transferred under vacuum to a cold trap. The recovered liquid (7.9g) was shown by g.l.c. (Col. A, 50°) to be unreacted perfluorocyclohexene contaminated with a little hexafluorobut-2-yne. The reaction mixture was filtered, the solid thoroughly washed with water and dried in vacuum to give an off-white powder (8.1g) identified from its i.r. spectrum as polyhexafluorobut-2-yne.

IX.C.3.b At 60°

A similar reaction was carried out at 60° using caesium fluoride (9.3g, 61 mmol), tetraglyme (30 ml) and perfluorocyclohexene (10.8g, 41 mmol). Hexafluorobut-2-yne (10.3g, 64 mmol) was allowed to enter the reaction vessel and after 4 days the residual gas (0.7g) was recovered.

Again only perfluorocyclohexene (9.0g) and polyhexafluorobut-2-yne (7.9g) were obtained.

IX.C.4 Hexafluoropropene

IX.C.4.a Using a Small Excess of Hexafluoropropene

A suspension of caesium fluoride (9.9g, 65 mmol) in tetraglyme (20 ml) was stirred in a flask attached to two traps containing hexafluorobut-2-yne (9.0g, 56 mmol) and hexafluoropropene (10.1g, 67 mmol). Equal pressures of each gas were allowed into the flask and thereafter the gases were left to diffuse into the reaction mixture at a pressure of one atmosphere. After 16 hours the residual gas (1.6g) was recovered and the reaction mixture was flash distilled to give a colourless liquid (9.9g). Three major components were detectable using m.s./g.l.c. with high peaks at 462, 474 and 624 corresponding to compounds $C_{10}F_{18}$, $C_{11}F_{18}$ and $C_{14}F_{24}$. Three fractions were isolated by preparative scale g.l.c. (Col. O, 70°) and two of these were identified as perfluorohexamethylcyclopentadiene (145) (0.8g, 6.0%), b.p. 119°, (Found: C,27.62; F, 72.29%. $C_{11}F_{18}$ requires C, 27.85; F, 72.15%), n.m.r. spectrum no. 14, i.r. spectrum no. 15, mass spectrum no. 11; and perfluoro-1,2,4,5-tetramethylcyclohexene (146) (0.4g, 2.6%), (Found: C, 26.15; F, 74.13%. $C_{10}F_{18}$ requires C, 25.97; F, 74.03%), n.m.r. spectrum no. 15; i.r. spectrum no. 16, mass spectrum no. 12. The third fraction (0.5g) showed signals at 61.2 (3), 62.6 (7), 66.8 (2) and 76.5 (2) in the ^{19}F n.m.r. spectrum, the mass spectrum showed a high mass peak at m/e = 462, which corresponds to $C_{10}F_{18}$, and a weak C=C stretch at 1650 cm^{-1} was visible in the i.r. spectrum. This fraction was not identified and probably consists of a mixture of compounds. A similar reaction was carried out using caesium fluoride (6.0g, 39 mmol), tetraglyme (35 ml), hexafluoropropene (14.6, 97 mmol) and hexafluoro-

but-2-yne (14.4g, 89 mmol). After 40 hours the residual gases (1.8g) were removed and the reaction mixture steam distilled to give a 10 component liquid (10.5g, 36% recovery) which was not investigated further. A white solid (8.1g) identified as polyhexafluorobut-2-yne, was recovered from the steam distillation residue.

IX.C.4.b Using an Excess of Hexafluorobut-2-yne

A similar experiment was carried out using caesium fluoride (16.4g, 108 mmol), tetraglyme (25 ml), hexafluorobut-2-yne (21.2g, 131 mmol) and hexafluoropropene (14.8g, 99 mmol). The gases were added in such a way as to ensure that the partial pressure of the butyne was approximately twice that of the propene. After 24 hours the residual gases (8.0g) were recovered and volatile material (6.7g) was transferred under vacuum to a cold trap. A portion of the resulting liquid (5.6g) was separated by preparative scale g.l.c. (Col. A, 60°) to give two fractions. The first fraction (2.2g) was shown by m.s./g.l.c. to consist of a mixture of at least 3 $C_{10}F_{18}$ isomers and the second fraction (0.8g) was identified as (145). The reaction mixture was filtered to give a solid, which, after a thorough washing with water and drying under vacuum, was identified as polyhexafluorobut-2-yne (15.0g).

IX.C.5 Perfluorobut-2-ene

A mixture of caesium fluoride (10.1g, 66 mmol), tetraglyme (60 ml) and octafluorobut-2-ene (20.0g, 105 mmol) was stirred at room temperature and hexafluorobut-2-yne (6.9g, 43 mmol) was allowed to diffuse into the reaction vessel. After 6 days octafluorobut-2-ene (1.6g) was recovered by transference under vacuum to a cold trap. The reaction

mixture was then flash distilled to give a liquid (16.6g) consisting of 4 major components. Fractional distillation gave a liquid (8.3g) which boiled at 80 - 90° and was identified as impure perfluoro-3,4-dimethylhex-3-ene (134). The major component of the distillation residue was separated by preparative scale g.l.c. and identified as perfluoro-3,4,5,6-tetramethylocta-3,5-diene (135) (4.4g, 18%), n.m.r. spectrum no. 16, i.r. spectrum no. 17, mass spectrum no. 13. One of the unseparable components was identified by m.s./g.l.c. as (136). The mass spectrum of this component was identical with that of an authentic sample.[185]

CHAPTER X

EXPERIMENTAL TO CHAPTER VI

X.A Starting Materials

2,2,2-Trifluoroethyl-p-toluenesulphonate was prepared from 2,2,2-trifluoroethanol and p-toluenesulphonyl chloride by the method of E. Schätzle and coworkers.[206] The crude product was purified by sublimation at 95°/0.1 mm Hg.

Methyltriphenylphosphonium bromide was available commercially and was used after drying at 60° in vacuo for several days. Isopropyltriphenylphosphonium iodide was prepared by heating triphenylphosphine with excess 2-iodopropane in acetone in a large carius tube at 90° for 40 hours. The crystalline solid which separated on cooling was dissolved in dichloromethane and the resulting solution washed with sodium thiosulphate solution to remove the iodine which was present as a contaminant. After drying and removing the solvent the remaining solid was shown by ^{31}P n.m.r.[197] to be the required phosphonium iodide.

The sodium salt of 5-trifluoromethyl-tetrazole was prepared from trifluoroacetonitrile and sodium azide by the method of Norris.[207] After drying in vacuo at 100° the product was used without further purification (n.m.r. spectrum no. 17). Treating the sodium salt of the tetrazole with methyl iodide in refluxing THF gave the 2-methyl derivative in 50% yield (n.m.r. spectrum no. 18).

Trifluoroacetonitrile was prepared using a modified version of the method reported by Gilman and Jones.[208] An intimate mixture of phosphorus pentoxide (202g, 1.42mol) and trifluoroacetamide (86g, 0.76 mol) was placed in a dry flask fitted with an efficient condenser connected to a

trap cooled in liquid air. The mixture was heated over a period of 2 hours up to a temperature of 180° and then the residue was heated strongly with a bunsen burner for 1 hour. The contents of the trap were transferred at -70° and the resulting gas (58.3g, 81%) was shown by g.l.c. and infrared spectroscopy to be pure trifluoroacetonitrile.

X.B Nucleophilic Additions to Hexafluorobut-2-yne

X.B.1 Sulphur

A suspension of sulphur (3g) in sulpholan (40 ml) was stirred at 110° under an atmosphere of hexafluorobut-2-yne (6.0g). After 5 days, hexafluorobut-2-yne (2.5g) was recovered and volatile material was transferred at 80° under vacuum to a cold trap. The resultant liquid (2.4g) was shown by g.l.c. (Col. O, 170°) to consist of one component, identified as tetrakistrifluoromethylthiophene (162) (2.4g, 61%): b.p. 134°, (lit. 134-5°[58]). (Found: C, 26.89; F, 64.26; S, 9.29%. Calc. for $C_8F_{12}S$: C, 26.97; F, 64.04; S, 8.99%); n.m.r. spectrum no. 18, i.r. spectrum no. 18, mass spectrum no. 14.

X.B.2 2,2,2-Trifluoroethyl-p-toluenesulphonate Anion

Several experiments were attempted using both butyllithium and methyllithium to generate the anion and varying the conditions under which the hexafluorobut-2-yne was added. The following set of results is typical.

A flask was charged with 2,2,2-trifluoroethyl-p-toluenesulphonate (8.2g, 32 mmol) dissolved in dry ether (60 ml) and then cooled to -78° whilst purging with dry nitrogen. An ethereal solution of methyllithium (15.0 ml, 2M, 30 mmol) was added over a period of 30 mins. Then a

flexible reservoir containing hexafluorobut-2-yne (11.0g, 68 mmol) was attached to the reaction vessel and the gas allowed to react over a period of 4 hours. The flask was then allowed to warm slowly up to room temperature and at approximately -40° a thick mass of solid precipitated out. No hexafluorobut-2-yne was recovered. The reaction mixture was then filtered and the solid washed with ether and water. The resulting material was dried in vacuo to give a brown solid (16.0g) (Found: C, 32.36; H, 1.00; F, 53.58; S, 9.84%). A tarry brown residue (3.0g) was obtained from the ether layer and washings.

A control experiment was run in exactly the same manner except that no hexafluorobut-2-yne was added. The tosylate (6.5g, 26 mmol) was dissolved in ether (50 ml) and methyllithium (12 ml, 2M solution, 24 mmol) was added at -78°. On warming up to room temperature a brown solid formed. This was thoroughly washed with ether and water to give a polymeric material (1.0g) (Found: C, 35.32; H, 2.28; F, 27.2; S, 10.02%). A brown tar (5.1g) was recovered from the ether layer.

X.B.3 Phosphonium Ylids

X.B.3.a Methylenetriphenylphosphorane

Butyllithium (32 ml, 1.5M solution in hexane, 48 mmol) was added under an atmosphere of dry nitrogen to a solution of methyltriphenylphosphonium bromide (17.9g, 50 mmol) in dry ether (75 ml) at such a rate as to maintain a steady temperature of 25°C. The mixture was stirred for 1 hour after addition was complete and then the orange solution was filtered under nitrogen to remove the precipitated lithium bromide. A flexible reservoir containing hexafluorobut-2-yne (6.7g, 41 mmol) was then attached to the reaction vessel, which was cooled to -25°. The gas was allowed into the flask in small portions and when addition was

complete the mixture was allowed to warm up to room temperature. No gas was recovered. Volatiles were transferred under vacuum into a cold trap but no fluorocarbon was detectable in the resulting liquid. The solid residue was washed with water and dichloromethane to leave a brown solid (4.4g), identified by i.r. as polyhexafluorobut-2-yne. A brown tarry material (18.9g) was recovered from the organic washings and ^{31}P n.m.r.[197] revealed the presence of 3 phosphorus containing species with resonsnces at -22.7, -12.9 and +6.5 p.p.m. (relative to H_3PO_4).

X.B.3.b Isopropylidenetriphenylphosphorane

Butyllithium (4.8 ml, 1.5M solution, 7.2 mmol) was slowly added under an atmosphere of dry nitrogen to a suspension of isopropyltriphenylphosphonium iodide (3.2g, 7.5 mmol) in dry pentane (10 ml). The reaction was monitored by observing the evolution of butane gas. After 2 hours no more gas was evolved and a flexible reservoir containing hexafluorobut-2-yne (4.0g) was attached to the reaction vessel. After a further 2 hours the reaction appeared to have stopped and hexafluorobut-2-yne (1.9g) was recovered. Volatiles were transferred under vacuum to a cold trap but the resulting liquid contained no detectable quantity of fluorocarbon. The solid residue was washed with dichloromethane to leave a brown solid (1.6g) whose i.r. spectrum resembled that of polyhexafluorobut-2-yne except for a few extra weak peaks at 2950, 1710, 1625, 1520 and 1445 cm^{-1}. (Found: C, 28.42; H, 0.42; F, 60.69; P, 1.12; I, 9.5%). A brown tar (3.0g) was recovered from the organic washings.

Control Experiment

The previous experiment was repeated but this time the reaction

mixture was investigated by ^{31}P n.m.r. prior to adding the hexafluorobut-2-yne. Butyllithium (4 ml, 1.5M solution, 6 mmol) was added to a suspension of isopropyltriphenylphosphonium iodide (3.6g, 8.4 mmol) in dry hexane (10 ml). The mixture was stirred at 55° for 2½ hours, by which time the evolution of butane had ceased. An aliquot of the resulting solution was quenched with bromine and the presence of butyl bromide was shown by g.l.c. (Col. O). The reaction mixture showed 6 phosphorus containing species on ^{31}P n.m.r. with resonances at -109.6, -64.5, -51.6, -22.7, -9.8 and +6.5 p.p.m. (rel. to H_3PO_4). Hexafluorobut-2-yne (3.1g, 19 mmol) was allowed to diffuse into the reaction vessel and after 24 hours the volatiles were transferred under vacuum to a cold trap. No fluorocarbon was detectable in the resulting liquid. A polymer (1.6g) was obtained from the solid residue and shown to be of similar composition to that described in the previous experiment.

X.B.4 Diethyl Malonate Anion

Experiments were carried out using both tetraglyme and D.M.F. as solvents. Similar results were obtained in both cases and therefore only one experiment will be described.

Diethylmalonate (16.1g, 0.10 mol) was slowly added to a stirred suspension of sodium hydride (2.4g, 0.10 mol) in tetraglyme (50 ml). The mixture was stirred for 1 hour after addition was complete and then the flask was evacuated. A flexible reservoir containing hexafluorobut-2-yne (18.1g, 0.11 mol) was attached to the flask and the gas allowed to enter at such a rate as to maintain a pressure of approximately 50 cm Hg. After 3½ hours the uptake of gas had ceased and hexafluorobut-2-yne (3.6g) was recovered. An evacuated cold trap was connected to the flask but no volatiles transferred at 100°/0.1 mm Hg. The reaction mixture was then

poured into water and a brown oil (7.9g) separated out. Three major components were detectable by g.l.c. (Col. O, 170°), one of which had the same retention time as diethyl malonate. The components could not be separated by preparative scale g.l.c., distillation or column chromatography. However, ^{19}F n.m.r. on the crude mixture showed several signals in the CF_3 region including a singlet at 66.70 p.p.m. and a doublet at 61.42 p.p.m. which is possibly due to the *trans* 1:1 adduct (172).

X.B.5 Dimethyl Sulphoxide

X.B.5.a Preparation of Adduct (180)

Dimethyl sulphoxide (25.6g, 328 mmol) and hexafluorobut-2-yne (7.3g, 45 mmol) were sealed in a Carius tube and heated at 70° for 7 hours. Hexafluorobut-2-yne (0.3g) was recovered and the excess dimethyl sulphoxide was removed under vacuum to leave a pale yellow solid (10.0g). This was sublimed (70°/0.1 mm Hg) to give a white solid identified as 3-dimethylsulphuranylhexafluorobutan-2-one (180), (7.8g, 75%): m.p. 95-6°; (Found: C, 30.17; H, 2.50; F, 47.27; S, 13.3%. $C_6H_6F_6OS$ requires C, 30.00; H, 2.50; F, 47.50; S, 13.33%); n.m.r. spectrum no. 20; i.r. spectrum no. 19; mass spectrum no. 15.

X.B.5.b Attempted Reaction of (180) with Hexafluorobut-2-yne

i) The adduct (180) (1.0g, 4.2 mmol) and hexafluorobut-2-yne (1.6g, 10 mmol) were sealed in a Carius tube and heated at 120° for 20 hours. A quantitative recovery of starting materials was obtained.

ii) A solution of the adduct (180) (1.0g, 4.2 mmol) in sulpholan (5 ml) was stirred at 130° under an atmosphere of hexafluorobut-2-yne for 48 hours. No uptake of gas was observed and ^{19}F n.m.r. showed that the sulpholan solution contained only unreacted (180).

iii) The adduct (180) (1.0g, 4.2 mmol), sulpholan (5 ml) and hexafluorobut-2-yne (1.6g, 10 mmol) were sealed in a Carius tube and heated at 130° for 20 hours. Hexafluorobut-2-yne (1.6g) was recovered and ^{19}F n.m.r. showed that the sulpholan contained only unreacted (180).

X.B.5.c Pyrolysis of (180)

i) The adduct (180) (1.0g) was sealed under vacuum in a Carius tube and heated at 110° for 2 hours. The recovered solid was identified as unreacted starting material and was then heated at 170° for 24 hours. Again only (180) was recovered.

ii) The adduct (0.43g) was sealed under vacuum in a Carius tube and heated at 250° for 15 hours. A black solid (0.15g), a colourless liquid (0.22g) and a little acidic gas were recovered from the tube. The liquid was shown by g.l.c. (Col. A, 125°) to consist of 6 major components and was not investigated further.

X.B.5.d Attempted Reaction of (180) with Acetyl Chloride

The adduct (180) (0.31g, 1.3 mmol) and acetyl chloride (4.5 ml) were refluxed for 3 hours and then the acid chloride was distilled off to leave a pale yellow solid. This was sublimed to give a white solid (0.28g) which was identified as (180).

X.B.5.e Attempted Reaction of (180) with Water

A suspension of the adduct (180) (1.83g, 7.8 mmol) in water (1.8 ml) was stirred at room temperature for 48 hours. The solid was filtered off and dried in vacuo to give a quantitative recovery of (180).

X.B.6 Triphenylphosphine Oxide

Triphenylphosphine oxide (4.7g, 17 mmol) and hexafluorobut-2-yne (2.8g, 17 mmol) were sealed in a Carius tube and heated at 100° for 12 hours. No visible reaction had occurred and the tube was therefore heated at 170° for 12 hours. Hexafluorobut-2-yne was recovered together with a black shiny solid (6.2g). This solid was washed with ethanol to remove unreacted phosphine oxide leaving a black solid which was dried in vacuo (0.8g). The ^{31}P n.m.r. spectrum showed it to be mainly triphenylphosphine oxide (δ =-30.7 p.p.m.) but there were smaller peaks at 27.5, 54.9, 82.2 (components of a triplet, J = 660 Hz) and -16.2 p.p.m.

The experiment was repeated using a solvent, but no reaction occurred on heating a mixture of triphenylphosphine oxide (5.9g, 21 mmol), hexafluorobut-2-yne (4.3g, 26 mmol) and dichloromethane (20 ml) at 100° for 15 hours.

X.B.7 5-Trifluoromethyltetrazole Anion

A solution of the sodium salt of 5-trifluoromethyltetrazole (4.4g, 27 mmol) in acetonitrile (60 ml) was degassed and a flexible reservoir containing hexafluorobut-2-yne (5.5g) was attached to the reaction vessel. The pressure of hexafluorobut-2-yne was maintained at approximately

10 cm Hg. After 48 hours the reservoir was deflated and the residual gas (0.5g) was condensed into a cold trap. The solvent was removed under vacuum to leave a brown tar (9.1g). Molecular distillation gave a little brown oil (1.1g) which was shown to contain 6 major components by g.l.c. (Col. O, 162°).

X.B.8 2-Methyl-5-trifluoromethyltetrazole

i) A solution of 2-methyl-5-trifluoromethyltetrazole (2.1g, 14 mmol) in acetonitrile (20 ml) was stirred under an atmosphere of hexafluorobut-2-yne for 48 hours. No uptake of gas was observed and a quantitative recovery of unreacted tetrazole was obtained on removing the solvent.

ii) Hexafluorobut-2-yne (7.0g, 43 mmol) was sealed in a Carius tube with 2-methyl-5-trifluoromethyltetrazole (2.0g, 13 mmol) and acetonitrile (20 ml). The tube was heated at 80° for 16 hours. Hexafluorobut-2-yne (6.9g) was recovered and a quantitative recovery of unreacted tetrazole was obtained on removing the acetonitrile.

iii) Hexafluorobut-2-yne (4.0g, 24 mmol) was sealed in a nickel tube with 2-methyl-5-trifluoromethyltetrazole (1.0g, 6.6 mmol) and acetonitrile (10 ml). The tube was heated at 140° for 20 hours. Hexafluorobut-2-yne (4.0g) was recovered and n.m.r. showed that only unreacted tetrazole was present in the acetonitrile solution.

X.C Addition of Alcohols to Hexafluorobut-2-yne

X.C.1 Reaction Conditions and Products

Most of the addition reactions were performed in glass Carius tubes

of approximately 100 ml volume but nickel tubes were used for reactions at temperatures above 100°. Hexafluorobut-2-yne was sealed in the tube with an excess of the alcohol and the tube was either heated or left to stand at room temperature for approximately 20 hours. The catalysed reactions were carried out by dissolving the appropriate amount of sodium in the alcohol in order to give a solution containing 4-5% of the alkoxide. Catalysed reactions at elevated temperatures were carried out at atmospheric pressure, the hexafluorobut-2-yne being introduced into the reaction vessel from a flexible reservoir. Experimental conditions and results are summarised in Table X.1.

Table X.1

Base Catalysed Reactions

Alcohol	Solvent (g)	Hexafluoro-but-2-yne (g, mmol)	Temp.	Recovered hexafluoro-but-2-yne(g)	% *trans*
CH_3OH					
5.1, 160	-	6.0, 37	20°	0.0	96
n-C_3H_7OH					
8.1, 135	-	4.0, 25	20°	0.0	92
n-C_4H_9OH					
9.0, 120	-	5.3, 33	20°	0.0	89
15.8, 214	-	6.8, 42	117°	0.0	86
5.2, 70	sulpholan, 25.0	3.8, 23	117°	0.0	92
2-C_4H_9OH					
4.6, 62	-	2.4, 15	20°	0.0	91
t-C_4H_9OH					
9.9, 130	-	4.0, 25	20°	2.2	86

Uncatalysed Reactions

Alcohol (g, mmol)	Solvent (g)	Hexafluoro-but-2-yne (g, mmol)	Temp.	Recovered hexafluoro-but-2-yne(g)	% *trans*
CH_3OH					
4.5, 140	-	4.5, 28	95°	0.0	92
n-C_4H_9OH					
8.0, 110	-	6.1, 38	95°	3.7	90
1.8, 24	Ether, 6.5	5.5, 34	95°	5.5	-
3.5, 47	Ether, 14.2	10.0, 62	150°	7.5	27
1.8, 24	Sulpholan, 12.7	5.8, 36	100°	5.8	-
1.2, 16	Sulpholan, 9.0	4.8, 28	150°	3.4	30
t-C_4H_9OH					
18.6, 251	-	4.2, 26	95°	4.2	-
9.8, 130	-	3.0, 19	150°	2.5	90

The products were not isolated but were studied by ^{19}F n.m.r. and m.s./g.l.c. on the crude reaction mixture. Isomer ratios were determined using the method described in Chapter IV. The following data were obtained: (Z)-2-methoxy-1,1,1,4,4,4-hexafluorobut-2-ene (195): n.m.r. spectrum no. 21; (E)-2-methoxy-1,1,1 , 4,4,4-hexafluorobut-2-ene (196): n.m.r. spectrum no. 22; (Z)-2-*n*-propoxy-1,1,1,4,4,4-hexafluorobut-2-ene (197): n.m.r. spectrum no. 23, mass spectrum no. 16; (E)-2-*n*-propoxy-1,1,1,4,4,4-hexafluorobut-2-ene (198): n.m.r. spectrum no. 24; (Z)-2-*n*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (199): n.m.r. spectrum no. 25, mass spectrum no. 17; (E)-2-*n*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (200): n.m.r. spectrum no. 26; (Z)-2-*sec*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (201): n.m.r. spectrum no. 27, mass spectrum no. 18; (E)-2-*sec*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (202): n.m.r. spectrum

no. 28, mass spectrum no. 19; (Z)-2-*tert*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (203): n.m.r. spectrum no. 29, mass spectrum no. 20; (E)-2-*tert*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (204): n.m.r. spectrum no. 30.

X.C.2 Attempted Equilibrium Reactions

(i) At 20°

A portion of the mixture obtained from the uncatalysed reaction of *n*-butanol with hexafluorobut-2-yne in sulpholan at 150° (i.e. a mixture of 30% (199) and 70% (200)) was stirred at 20° with an equal volume of a 5% solution of sodium *n*-butoxide in *n*-butanol. The ratio of isomers (199) and (200) was found to remain unaltered over a period of 48 hours.

(ii) At 150°

The above experiment was repeated in a Carius tube which was heated for 48 hours at 150°. On cooling to 20° and opening the tube the recovered liquid was found to contain isomers (199) and (200) in the ratio of 30:70 i.e. no isomerisation had occurred.

X.D Reaction of Hexafluorobut-2-yne with Water

Water (2.0g, 110 mmol), hexafluorobut-2-yne (6.3g, 39 mmol) and tetraglyme (8.4g) were sealed in a Carius tube which was shaken in an oil bath at 85° for 64 hours. On opening the tube hexafluorobut-2-yne (4.2g) was recovered and volatile material was transferred under vacuum to a cold trap. The resulting liquid was dried over P_2O_5 and transferred

under vacuum to give a colourless liquid (2.0g), shown by g.l.c. (Col. A, 80°) to consist of 2 components. The major component (> 90%) identified by m.s./g.l.c. and n.m.r. as 1,1,1,4,4,4-hexafluorobutan-2-one (194): n.m.r. spectrum no. 31; M^+ not observed, peak at m/e = 161 i.e. $M^+ - 19(F)$. The minor component was probably bis(hexafluorobut-2-enyl) ether (20): M^+ not observed, peak at m/e = 273 i.e. $M^+ - 69(CF_3)$.

The reaction was repeated using water (2.2g, 120 mmol), hexafluorobut-2-yne (10.9g, 67 mmol) and sulpholan (10g). After 114 hours at 110° hexafluorobut-2-yne (5.0g) was recovered and volatiles were transferred under vacuum to a cold trap. The resulting liquid was dried (P_2O_5) and transferred under vacuum to give a colourless liquid, shown by g.l.c. (Col. A 70°) to be one component and identified as the butanone (194) (5.9g, 91%); b.p. 56°, (lit. 54.2° at 747 mm Hg[74]),(Found: C, 26.55; H, 1.08; F, 63.49%. Calc. for $C_4H_2F_6O$: C, 26.67; H, 1.11; F, 63.33%), n.m.r. spectrum no. 31, i.r. spectrum no. 20.

APPENDICES

APPENDIX I

N.M.R. SPECTRA

1) 3,4-bistrifluoromethyl-hexa-2,5-dione (106)

2) (E)-3-trifluoromethyl-1,1,1-trifluoropent-2-en-4-one (105)

3) (Z)-3-trifluoromethyl-1,1,1-trifluoropent-2-en-4-one (110)

4) 1-methyl-2,3-bistrifluoromethyl-4-oxacyclobutene (111)

5) (E)-3-trifluoromethyl-1,1,1-trifluorohex-2-en-4-one (112)

6) 4,5-bistrifluoromethyl-octa-3,6-dione (114)

7) 4-trifluoromethyl-4-(2,2,2-trifluoroethyl)-hepta-3,5-dione (113)

8) (E)-3-trifluoromethyl-1,1,1-trifluorohept-2-en-4-one (118)

9) (E)-3-trifluoromethyl-1,1,1-trifluorooct-2-en-4-one (121)

10) (E)-3-trifluoromethyl-1,1,1,5,5,5-hexafluoropent-2-en-4-ol (122)

11) (Z)-3-trifluoromethyl-1,1,1,5,5,5-hexafluoropent-2-en-4-ol (123)

12) Perfluoro-(E)-2-(cyclopent-1'-enyl)-but-2-ene (141)

13) Perfluoro-2,3,4-trimethyl-4-ethylbicyclo[3.3.0]octa-(1,5),(2,3)-diene (142)

14) Perfluorohexamethylcyclopentadiene (145)

15) Perfluoro-1,2,4,6-tetramethylcyclohexene (146) isomer mixture

16) Perfluoro-3,4,5,6-tetramethylocta-3,5-diene (135)

17) 5-trifluoromethyltetrazole sodium salt (186)

18) 2-methyl-5-trifluoromethyltetrazole (189)

19) Tetrakistrifluoromethylthiophene (162)

20) 3-dimethylsulphuranylhexafluorobutan-2-one (180)

21) (Z)-2-methoxy-1,1,1,4,4,4-hexafluorobut-2-ene (195)

22) (E)-2-methoxy-1,1,1,4,4,4-hexafluorobut-2-ene (196)

23) (Z)-2-*n*-propoxy-1,1,1,4,4,4-hexafluorobut-2-ene (197)

24) (E)-2-*n*-propoxy-1,1,1,4,4,4-hexafluorobut-2-ene (198)

25) (Z)-2-*n*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (199)

26) (E)-2-*n*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (200)

27) (Z)-2-*sec*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (201)

28) (E)-2-*sec*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (202)

29) (Z)-2-*tert*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (203)

30) (E)-2-*tert*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (204)

31) 1,1,1,4,4,4-hexafluorobutan-2-one (194)

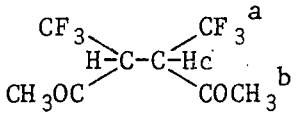
The following abbreviations are used in this appendix:
S, singlet; D, doublet; T, triplet; Q, quartet; P, pentet; Sx, sextet; M, multiplet.

Unless otherwise stated spectra were recorded at 40° as neat liquids.

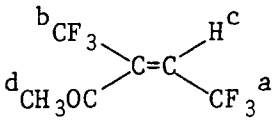
External $CFCl_3$ and TMS were used as references for ^{19}F and ^{1}H spectra respectively.

For ^{1}H spectra downfield shifts are quoted as positive (delta scale), whilst for ^{19}F spectra, upfield shifts are quoted as positive.

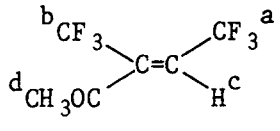
Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
1. 3,4-bistrifluoromethyl-hexa-2,5-dione (106)			
^{19}F			
63.9	S	-	a
^{1}H			
2.4	S	3	b
4.1	S	1	c
Recorded as a solution in $CDCl_3$			



(106)



(105)

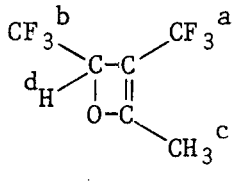


(110)

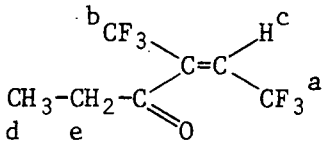
2. (E)-3-trifluoromethyl-1,1,1-trifluoropent-2-en-4-one (105)			
^{19}F			
63.1	D, J_{ac} = 7.5	3	a
67.5	S	3	b
^{1}H			
2.50	S	3	d
6.45	Q, J_{ca} = 7.5	1	c
3. (Z)-3-trifluoromethyl-1,1,1-trifluoropent-2-en-4-one (110)			
^{19}F			
60.9	Complex M	3	a
62.1	Q, J_{ba} = 10	3	b
^{1}H			
2.50	S	3	d
6.93	Q, J_{ca} = 8	1	c

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
4. 1-methyl-2,3-bistrifluoromethyl-4-oxacyclobutene (111)			
^{19}F			
62.4	S	3	a
81.2	S	3	b
^{1}H			
2.18	S	3	c
5.58	Broad S	1	d

Spectrum recorded as a mixture with compounds (105) and (110)



(111)



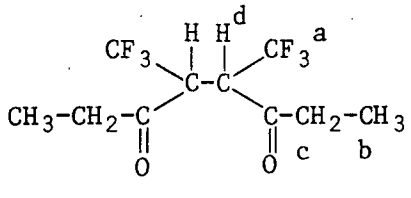
(112)

5. (E)-3-trifluoromethyl-1,1,1-trifluorohex-2-en-4-one (112)

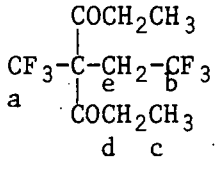
^{19}F			
63.0	D, J_{ac}=7 of Q, J_{ab}= 1.6	3	a
67.3	Broad S	3	b
^{1}H			
1.08	T, J_{de}= 7	3	d
2.69	Q, J_{ed}= 7	2	e
6.40	Q, J_{ca}= 7 of Q, J_{cb}= 1.3	1	c

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
6. 4,5-bistrifluoromethyl-octa-3,6-dione (114)			
^{19}F			
64.2	Broad M	-	a
^{1}H			
1.13	Broad M	-	b
2.68	Broad Q	-	c
4.08	Broad S	-	d

Spectrum recorded as a 88:12 mixture of (114) and (113) using $CDCl_3$ as solvent



(114)

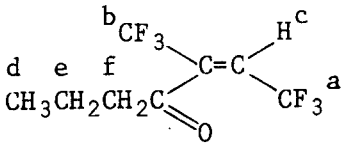


(113)

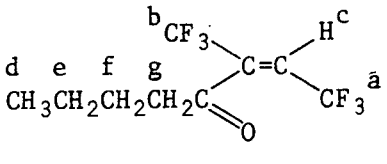
7. 4-trifluoromethyl-4-(2,2,2-trifluoroethyl)-hepta-3,5-dione (113)			
^{19}F			
60.2	Broad S	3	a
69.6	Broad S	3	b
^{1}H			
1.13	Broad M	-	c
2.68	Broad Q	-	d,e

Spectrum recorded as a 12:88 mixture of (113) and (114) using $CDCl_3$ as solvent

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
8. (E)-3-trifluoromethyl-1,1,1-trifluorohept-2-en-4-one (118)			
^{19}F			
62.7	D, J_{ac}=7.5 of Q, J_{ab}= 1.5	3	a
67.0	S	3	b
^{1}H			
0.95	T, J_{de}= 7	3	d
1.71	Sx, J= 7	2	e
2.72	T, J_{fe}= 7	2	f
6.42	Q, J_{ca}=7.5 of Q, J_{cb}= 1.3	1	c



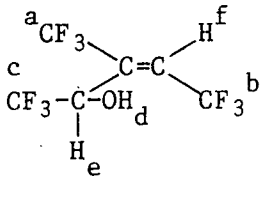
(118)



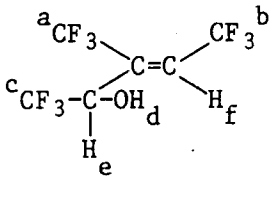
(121)

9. (E)-3-trifluoromethyl-1,1,1-trifluorooct-2-en-4-one (121)			
^{19}F			
57.5	D, J_{ac}= 7	3	a
61.5	S	3	b
^{1}H			
0.86	T, J_{de}= 7	3	d
1.40	Broad M	4	e,f
2.60	T, J_{gf}= 7	2	g
6.23	Q, J_{ca}= 7	1	c

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
10. (E)-3-trifluoromethyl-1,1,1,5,5,5-hexafluoropent-2-en-4-ol (122)			
^{19}F			
61.5	Broad	3	a
64.9	D, J_{bc} = 7.8	3	b
77.6	Broad	3	c
^{1}H			
3.80	S	1	d
5.15	Q, J_{ec} = 6.4	1	e
6.30	Q, J_{fb} = 7.8	1	f



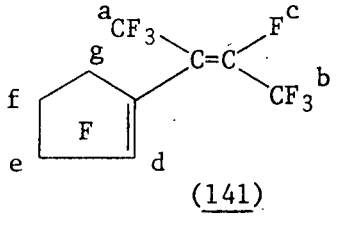
(122)



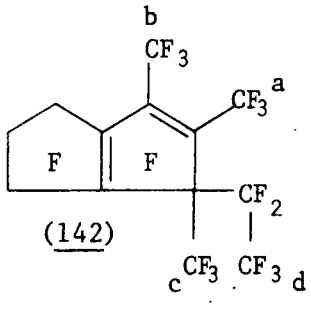
(123)

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
11. (Z)-3-trifluoromethyl-1,1,1,5,5,5-hexafluoropent-2-en-4-ol (123)			
^{19}F			
61.5	Q, J_{ab} = 10	3	a
62.7	Complex M	3	b
80.0	Broad	3	c
^{1}H			
3.10	D, J_{de} = 5.2	1	d
4.63	Broad	1	e
6.42	Q, J_{fb} = 8.0	1	f

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
12. Perfluoro-[(E)-2-(cyclopent-1'-enyl)-but-2-ene] (141)			
63.2	D, J_{ac} = 20	3	a
72.5	Broad S	3	b
103.0	Broad M	1	c
112.5	Broad D	2	g
122.5	Broad S	1	d
124.2	M	2	e
134.2	M	2	f



(141)



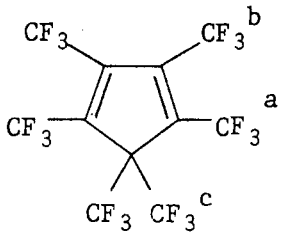
(142)

13. Perfluoro-(2,3,4-trimethyl-4-ethylbicyclo[3.3.0]octa-(1,5),(2,3)-diene) (142)

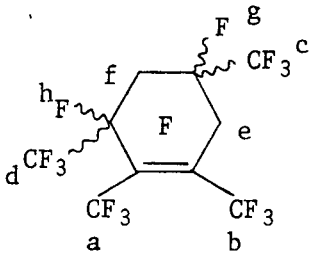
58.2	Broad S	3	a
62.4	Q, J_{ba} = 10.5	3	b
63.1	M	3	c
83.5	S	3	d

Signals at 111.5, 115.3 and 129.6 equivalent to 8F (4 CF_2 groups)

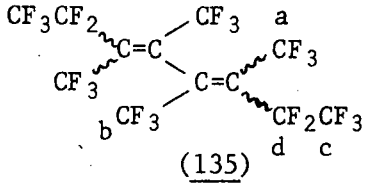
Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
14. Hexakistrifluoromethyl cyclopentadiene (145)			
58.5	Broad S	3	a
62.6	Broad M	6	b,c



(145)



(146)



(135)

15. Perfluoro-(1,2,4,6-tetramethylcyclohexene) isomer mixture (146)			
59.9 60.4	Broad S	3	a
62.3	Broad M	3	b
74.1	Broad S	6	c,d
159.3	Broad S	1	g,h
163.0	Broad S	1	

Weak signals between 96.0 and 120.0 p.p.m. due to AB splitting of CF_2 groups e and f were unassigned

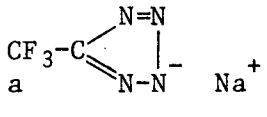
16. Perfluoro-3,4,5,6-tetramethylocta-3,5-diene isomer mixture (135)			
58.5	Broad M	6	a,b
80.3	S	3	c
105.9 108.2	Broad M	2	d

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
17. 5-trifluoromethyltetrazole sodium salt (186)			
62.2	S	-	a

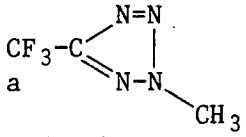
Recorded as a solution in CH_3CN

18. 2-methyl-5-trifluoromethyltetrazole (189)			
^{19}F			
64.6	S	-	a
^{1}H			
4.49	S	-	b

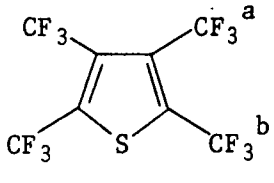
Recorded as a solution in $CDCl_3$



(186)



(189)



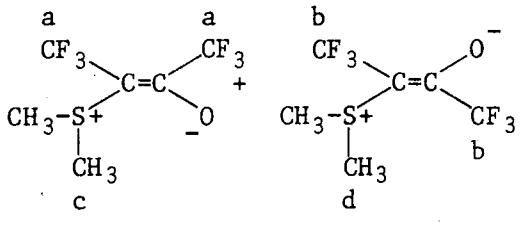
(162)

19. Tetrakistrifluoromethylthiophene (162)

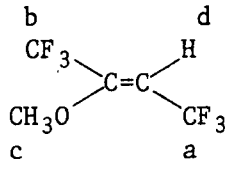
56.5	S	3	a
58.2	S	3	b

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
20. 3-dimethylsulphuranylhexafluorobutan-2-one (180)			
^{19}F			
49.1	Q, J = 11	3.5	a
51.9	S	1	b
70.2	S	1	b
73.4	Q, J = 11	3.5	a
^{1}H			
2.86	S	1	d
3.02	S	3.5	c

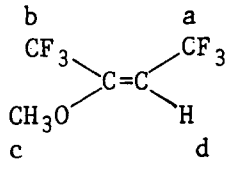
Recorded as a solution in d_6-acetone



(180)



(195)



(196)

21. (Z)-2-methoxy-1,1,1,4,4,4-hexafluorobut-2-ene (195)*

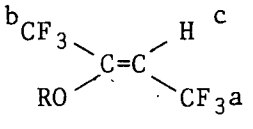
^{19}F			
57.8	D, J_{ad} = 7.5	3	a
70.9	Broad S	3	b
^{1}H			
3.80	S	3	c
5.57	Q, J_{da} = 7.5	1	d

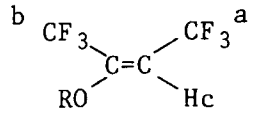
Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
22. (E)-2-methoxy-1,1,1,4,4,4-hexafluorobut-2-ene (196)*			
^{19}F			
54.4	M	3	a
68.8	Q, J_{ba} = 11	3	b
^{1}H			
3.50	S	3	c
4.86	Q, J_{da} = 7.5	1	d

* Spectrum run as a mixture of 96% (Z) and 4% (E) isomers

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
23. (Z)-2-*n*-propoxy-1,1,1,4,4,4-hexafluorobut-2-ene (197)*			
^{19}F			
59.0	D, J_{ac} = 7.5	3	a
71.5	S	3	b
24. (E)-2-*n*-propoxy-1,1,1,4,4,4-hexafluorobut-2-ene (198)*			
^{19}F			
55.1	M	3	a
69.8	Q, J_{ab} = 10	3	b

* Spectrum run as a mixture of 92% (Z) and 8% (E) isomers in propan-1-ol





(197) R = *n*-C_3H_7 (198) R = *n*-C_3H_7

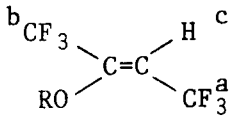
(199) R = *n*-C_4H_9 (200) R = *n*-C_4H_9

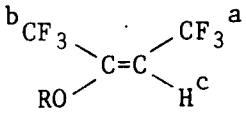
25. (Z)-2-*n*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (199)†			
^{19}F			
58.9	D, J_{ac} = 7.5	3	a
71.5	S	3	b
26. (E)-2-*n*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (200)†			
^{19}F			
55.0	M	3	a
69.7	Q, J_{ab} = 10	3	b

† Spectrum run as a mixture of 89% (Z) and 11% (E) isomers in butan-1-ol

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
27. (Z)-2-*sec*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (201)*			
^{19}F			
59.5	D, J_{ac} = 7.5	3	a
70.0	S	3	b
28. (E)-2-*sec*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (202)*			
^{19}F			
54.6	M	3	a
69.9	Q, J_{ab} = 10.5	3	b

* Spectrum run as a mixture of 91% (Z) and 9% (E) isomers in butan-2-ol





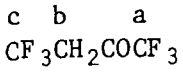
(201) R = $C_2H_5CH(CH_3)$- (202) R = $C_2H_5CH(CH_3)$-

(203) R = $(CH_3)_2C$- (204) R = $(CH_3)_2C$-

29. (Z)-2-*tert*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (203)†			
^{19}F			
59.5	D, J_{ac} = 7.5	3	a
70.1	S	3	b
30. (E)-2-*tert*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (204)†			
^{19}F			
61.5	M	3	a
68.2	M	3	b

† Spectrum run as a mixture of 86% (Z) and 14% (E) isomers in 2-methylpropan-2-ol

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
31. 1,1,1,4,4,4-hexafluorobutan-2-one (194)			
^{19}F			
60.6	S	3	a
86.7	S	3	c
^{1}H			
5.2	S	-	b

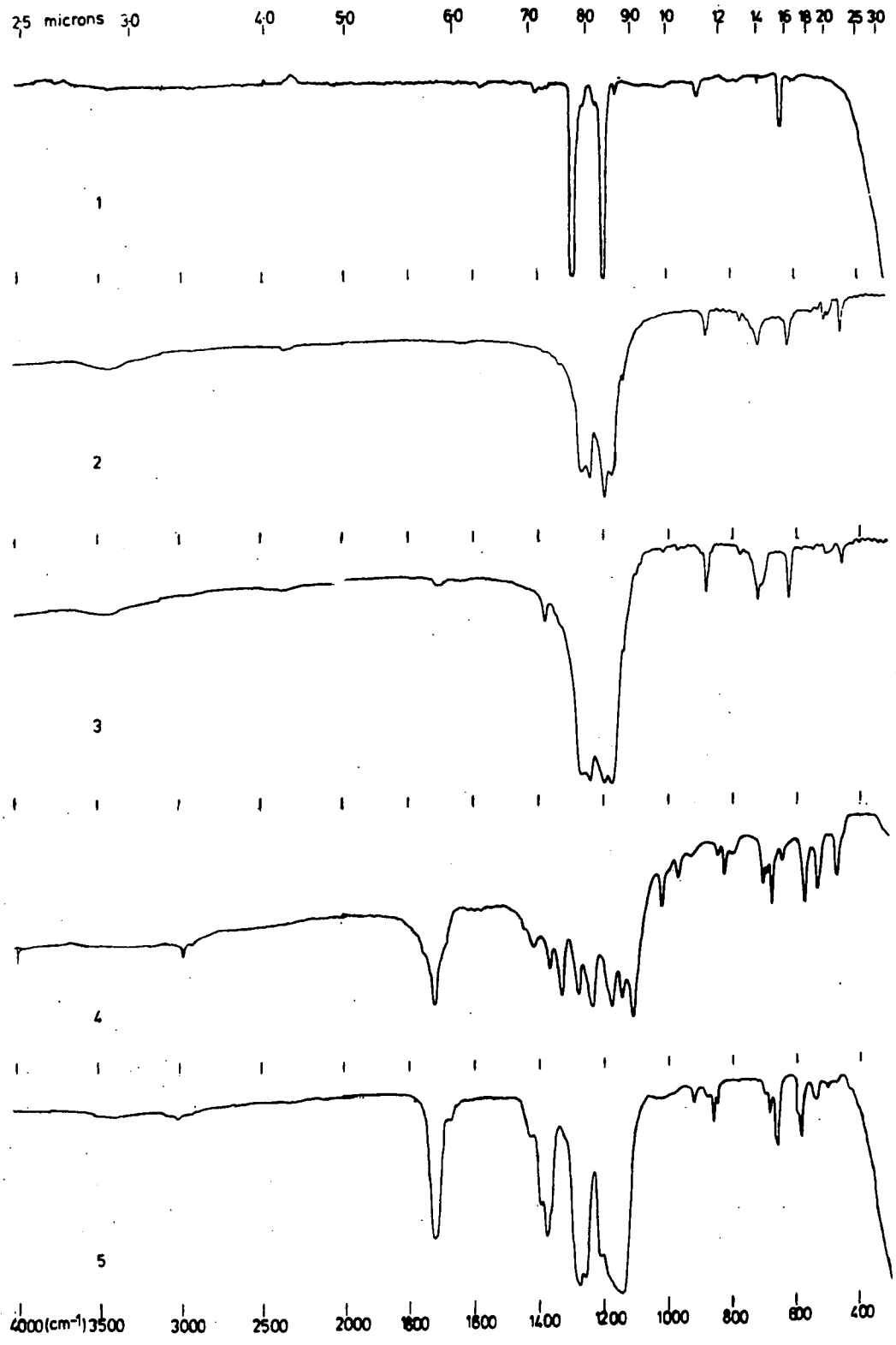


(194)

APPENDIX II

INFRARED SPECTRA

1) Hexafluorobut-2-yne (1)
2) Polyhexafluorobut-2-yne (prepared by gamma irradiation)
3) Polyhexafluorobut-2-yne (prepared using CsF in sulpholan)
4) 3,4-bistrifluoromethyl-hexa-2,5-dione (106)
5) (Z)-3-trifluoromethyl-1,1,1-trifluoropent-2-en-4-one (110)
6) (E)-3-trifluoromethyl-1,1,1-trifluorohex-2-en-4-one (112)
7) 4,5-bistrifluoromethyl-octa-3,6-dione (114) and 4-trifluoromethyl-4-(2,2,2-trifluoroethyl)-hepta-3,5-dione (113) mixture
8) (E)-3-trifluoromethyl-1,1,1-trifluorohept-2-en-4-one (118)
9) (E)-3-trifluoromethyl-1,1,1-trifluorooct-2-en-4-one (121)
10) (E)-3-trifluoromethyl-1,1,1,5,5,5-hexafluoropent-2-en-4-ol (122)
11) (Z)-3-trifluoromethyl-1,1,1,5,5,5-hexafluoropent-2-en-4-ol (123)
12) Copolymer of hexafluorobut-2-yne and dimethylacetylene dicarboxylate (2.1:1)
13) Perfluoro-(E)-2-(cyclopent-1'-enyl)-but-2-ene (141)
14) Perfluoro-2,3,4-trimethyl-4-ethylbicyclo[3.3.0]octa-(1,5),(2,3)-diene (142)
15) Hexakistrifluoromethyl cyclopentadiene (145)
16) Perfluoro-1,2,4,6-tetramethylcyclohexene (146) isomer mixture
17) Perfluoro-3,4,5,6-tetramethylocta-3,5-diene (135)
18) Tetrakistrifluoromethylthiophene (162)
19) 3-dimethylsulphuranylhexafluorobutan-2-one (180)
20) 1,1,1,4,4,4-hexafluorobutan-2-one (194)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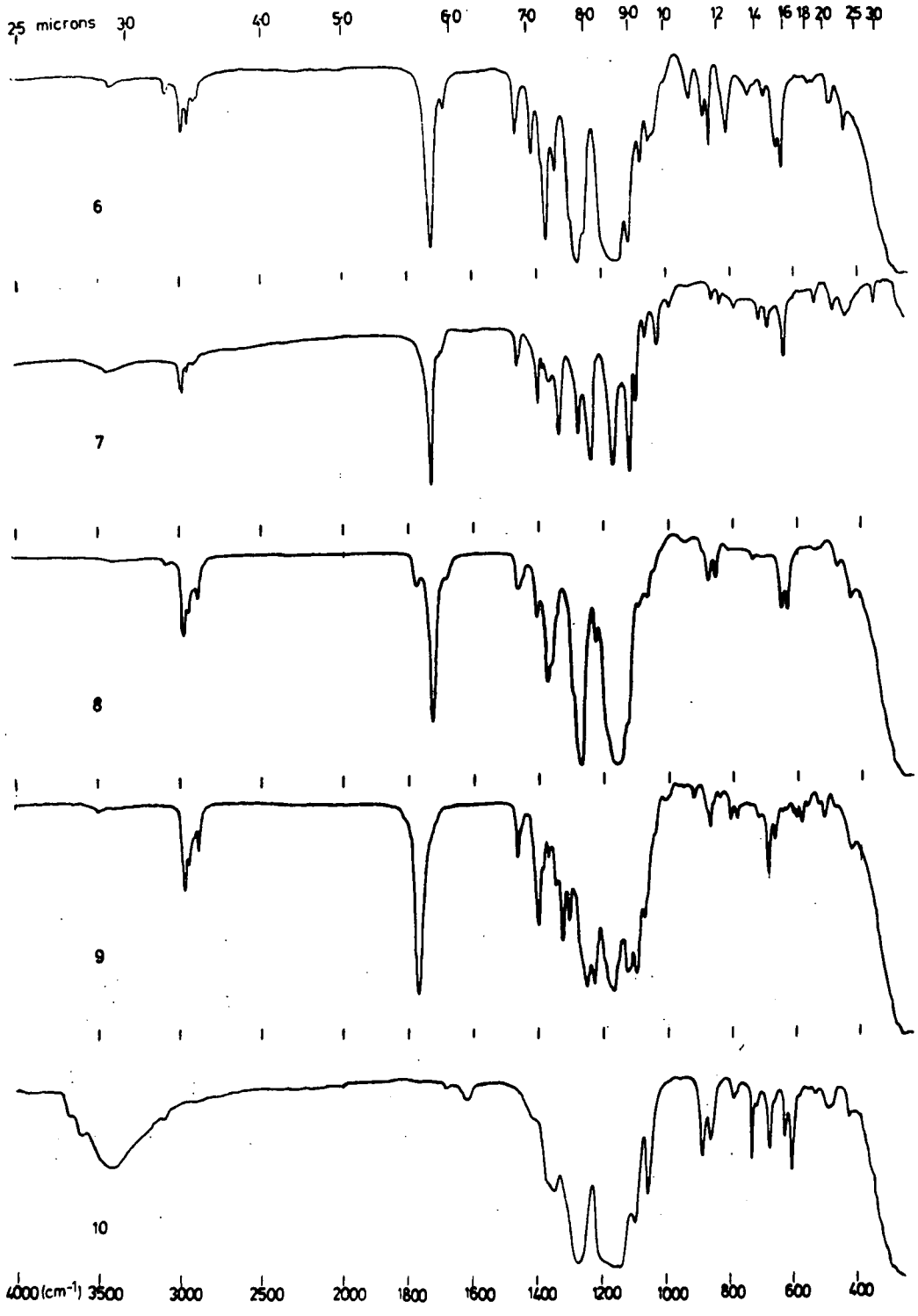
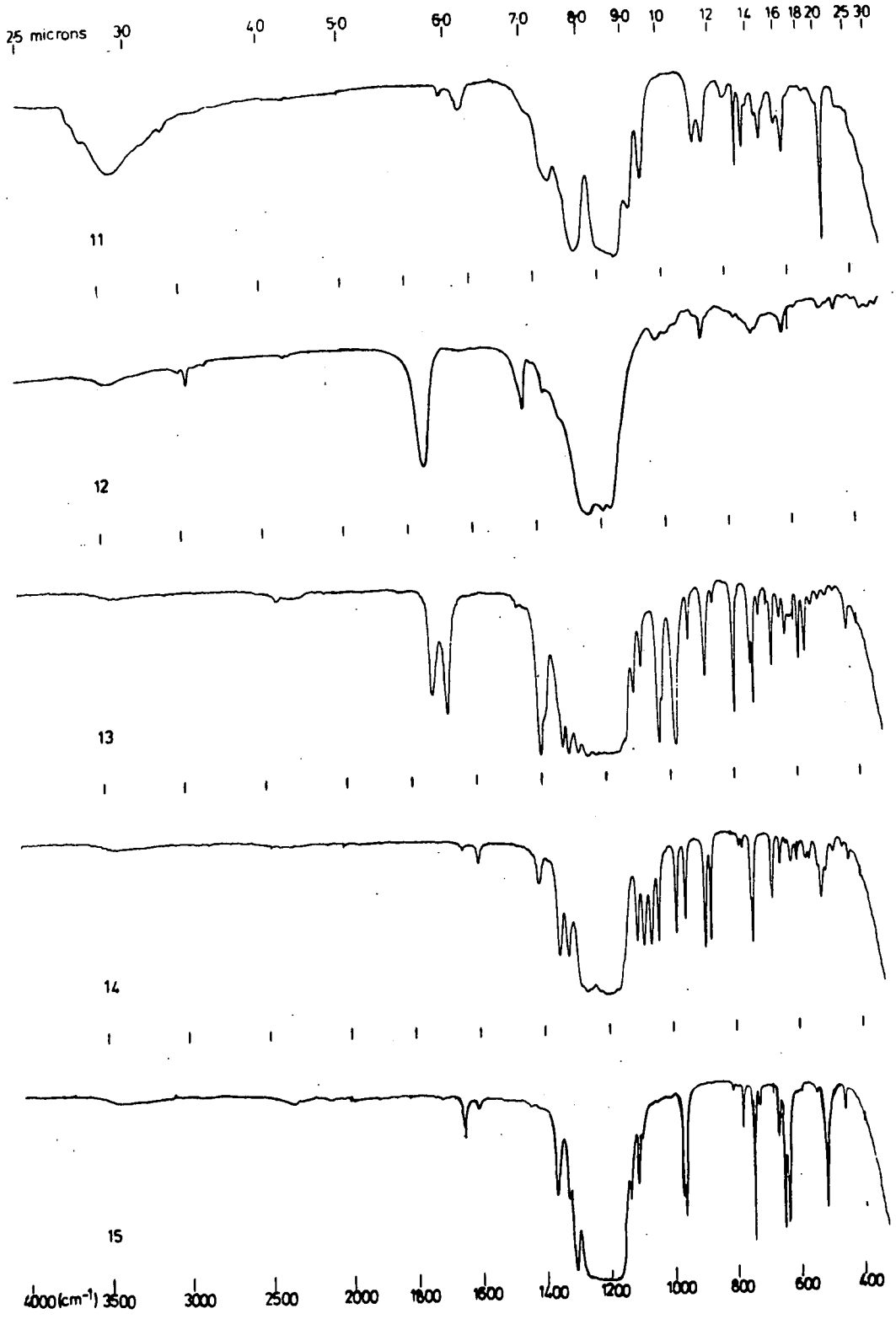
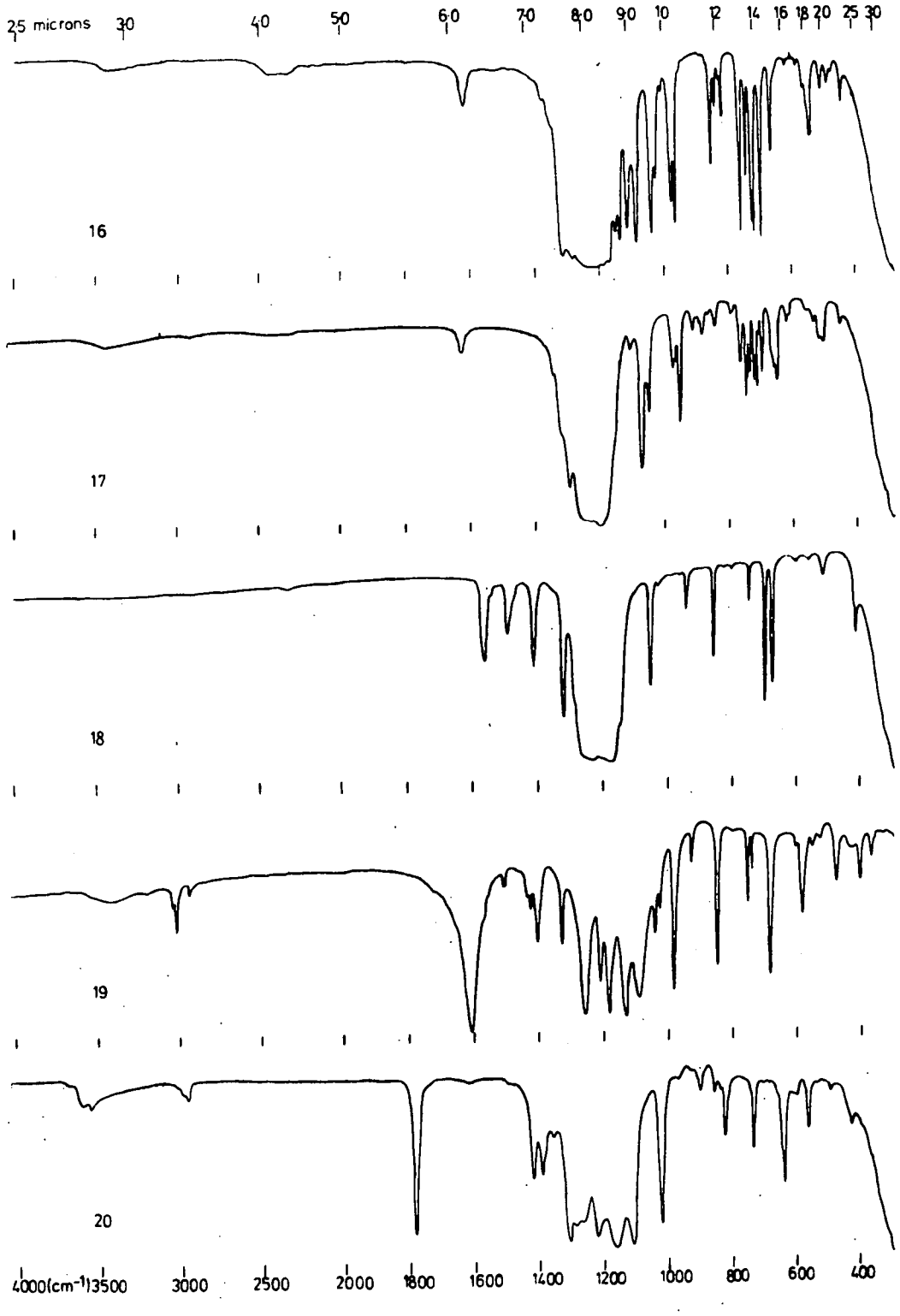
1
2
3
4
5
4000(cm⁻¹) 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400


25 microns 30 40 50 60 70 80 90 10 12 14 16 18 20 25 30
6
7
8
9
10
4000 (cm⁻¹) 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

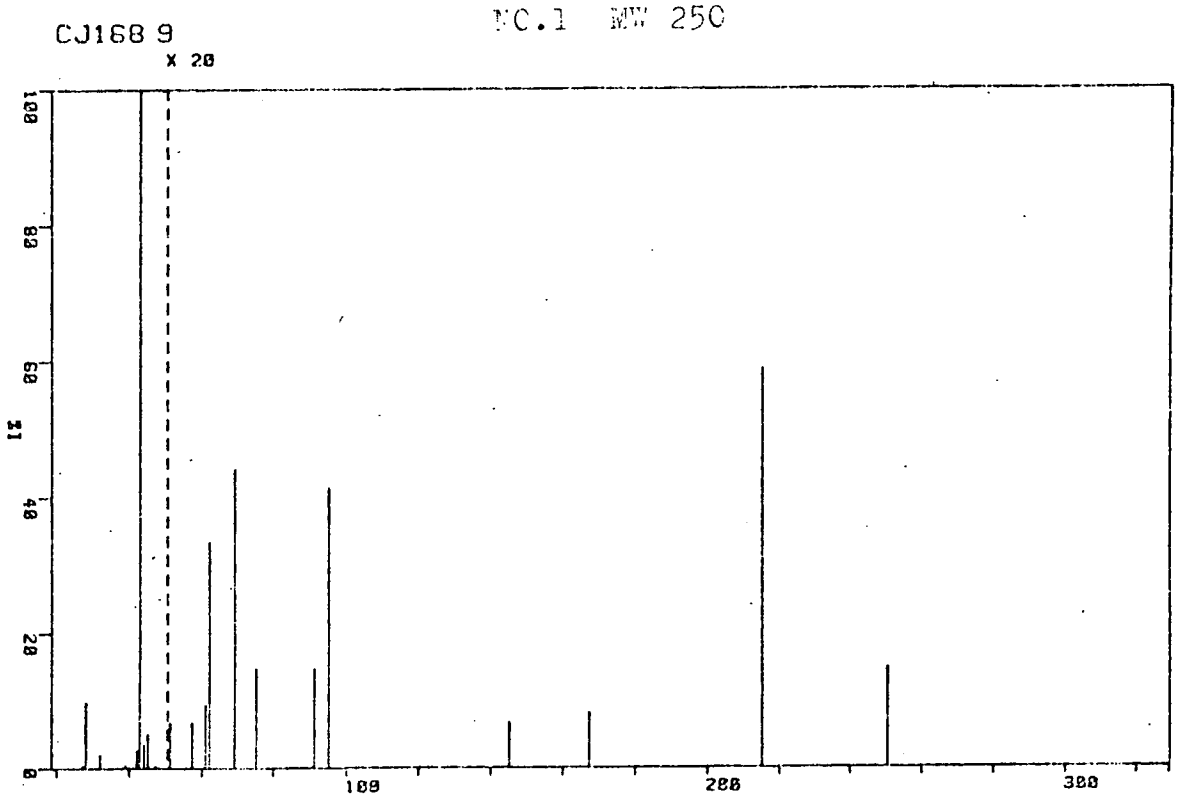

25 microns 30 40 50 60 70 80 90 10 12 14 16 18 20 25 30
11
12
13
14
15
4000 (cm⁻¹) 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400


25 microns 30 40 50 60 70 80 90 10 12 14 16 18 20 25 30
16
17
18
19
20
4000(cm⁻¹)3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

APPENDIX III

MASS SPECTRA

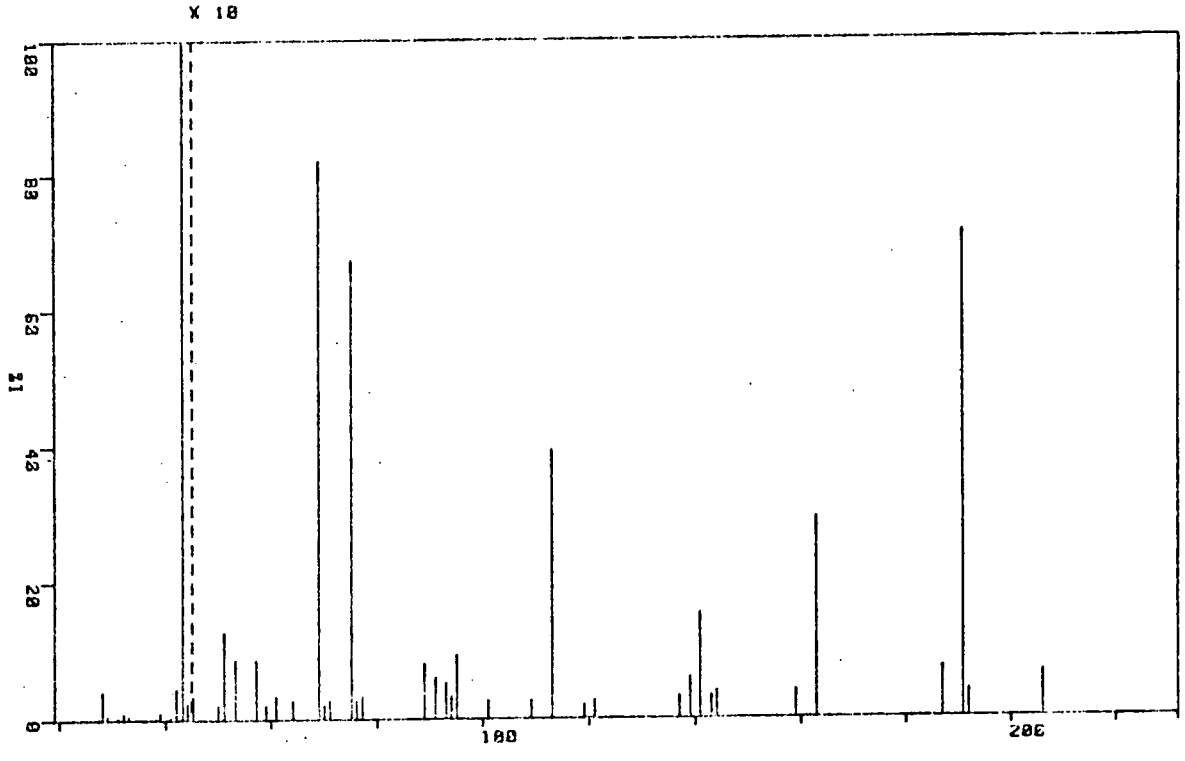
1) 3,4-bistrifluoromethyl-hexa-2,5-dione (106)
2) (Z)-3-trifluoromethyl-1,1,1-trifluoropent-2-en-4-one (110)
3) (E)-3-trifluoromethyl-1,1,1-trifluorohex-2-en-4-one (112)
4) 4,5-bistrifluoromethyl-octa-3,6-dione (114) and 4-trifluoromethyl-4-(2,2,2-trifluoroethyl)-hepta-3,5-dione (113) mixture
5) (E)-3-trifluoromethyl-1,1,1-trifluorohept-2-en-4-one (118)
6) (E)-3-trifluoromethyl-1,1,1-trifluorooct-2-en-4-one (121)
7) (E)-3-trifluoromethyl-1,1,1,5,5,5-hexafluoropent-2-en-4-ol (122)
8) (Z)-3-trifluoromethyl-1,1,1,5,5,5-hexafluoropent-2-en-4-ol (123)
9) Perfluoro-(E)-2-(cyclopent-1'-enyl)-but-2-ene (141)
10) Perfluoro-2,3,4-trimethyl-4-ethylbicyclo[3.3.0]octa-(1,5),(2,3)-diene (142)
11) Perfluorohexamethylcyclopentadiene (145)
12) Perfluoro-1,2,4,6-tetramethylcyclohexene (146)
13) Perfluoro-3,4,5,6-tetramethylocta-3,5-diene (135)
14) Tetrakistrifluoromethylthiophene (162)
15) 3-dimethylsulphuranylhexafluorobutan-2-one (180)
16) 2-*n*-propoxy-1,1,1,4,4,4-hexafluorobut-2-ene isomer mixture (197) & (198)
17) 2-*n*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene isomer mixture (199) & (200)
18) (Z)-2-*sec*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (201)
19) (E)-2-*sec*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (202)
20) 2-*tert*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene isomer mixture (203) & (204)



CJ168 9 29-JLY-80

PEAK NO.	MASS	% INT BASE
2	27.14	0.43
3	28.00	9.70
4	31.84	1.97
5	38.89	0.47
6	41.93	2.65
7	42.98	100.00
8	44.04	3.51
9	45.06	5.12
10	47.07	0.39
11	50.99	0.36
12	57.11	0.39
13	61.02	0.50
14	62.05	1.68
15	68.99	2.25
16	75.12	0.79
17	91.08	0.75
18	95.15	2.11
19	145.22	0.39
20	167.27	0.47
21	215.25	2.97
22	250.29	0.75

CJAC 5 FC.2 EI 206

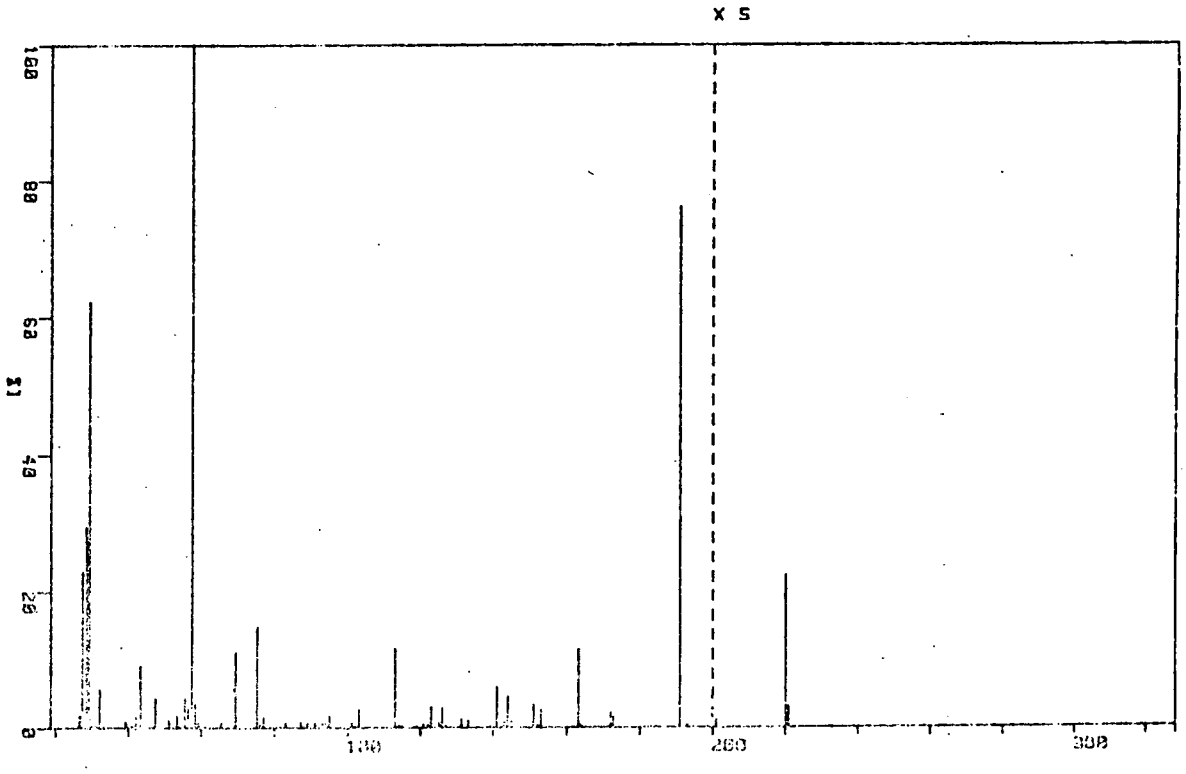


CJAC 5 09-JLY-80

PEAK NO.	MASS	% INT BASE
1	27.25	0.24
2	28.13	4.19
3	28.99	0.59
4	30.91	0.39
5	32.02	0.86
6	33.13	0.51
7	38.08	0.24
8	39.00	1.10
9	40.95	0.37
10	42.04	4.50
11	43.11	100.00
12	44.15	2.35
13	45.16	0.34
14	49.88	0.22
15	50.94	1.27
16	53.07	0.93
17	57.10	0.88
18	59.01	0.24
19	60.98	0.37
20	64.11	0.27
21	68.97	8.20
22	69.93	0.24
23	70.99	0.27
24	75.07	6.78
25	76.07	0.29
26	77.07	0.34
27	88.98	0.86
28	90.95	0.64
29	93.01	0.54
30	94.05	0.34
31	95.06	0.98
32	100.98	0.32
33	109.04	0.27
34	113.02	3.99
35	119.01	0.22
36	120.99	0.29
37	137.03	0.34
38	138.97	0.66
39	140.94	1.54
40	142.97	0.37
41	144.01	0.47
42	159.00	0.42
43	163.00	2.94
44	187.03	0.73
45	190.95	7.15
46	191.99	0.44
47	206.04	0.69

NO.3 MW 220

CJ1852 5

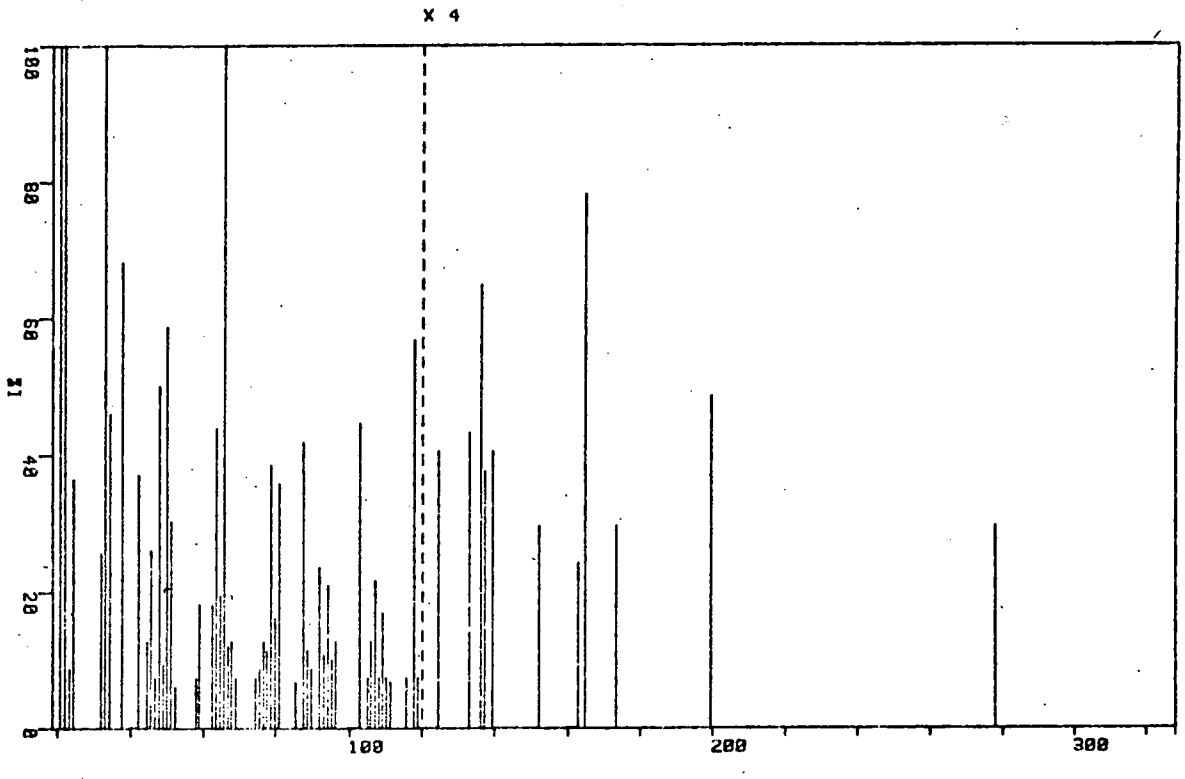


CJ1852. 5 07-JAN-80

PEAK NO.	MASS	% INT BASE
1	26.34	2.05
2	27.27	22.92
3	28.15	29.57
4	29.04	62.28
5	29.87	1.50
7	32.03	5.61
12	42.04	1.63
13	43.11	9.03
15	47.12	4.40
16	50.95	1.14
17	53.09	1.89
19	55.16	4.27
20	56.16	2.90
21	57.15	100.00
22	58.12	3.49
23	59.06	1.08
26	69.05	11.05
27	75.13	14.77
29	77.08	1.63
37	95.04	1.79
40	103.03	2.64
41	112.99	11.57
47	122.99	3.10
49	126.00	2.90
51	130.96	1.27
52	133.01	1.01
54	140.93	5.93
56	142.96	1.27
57	143.98	4.50
58	145.00	1.21
59	150.96	3.36
61	152.99	2.64
62	162.96	11.44
64	171.90	2.22
65	172.94	1.60
66	190.98	76.13
68	200.94	0.29
69	219.90	4.50
70	220.93	0.62

NO.4 MW 278

J1741A 4

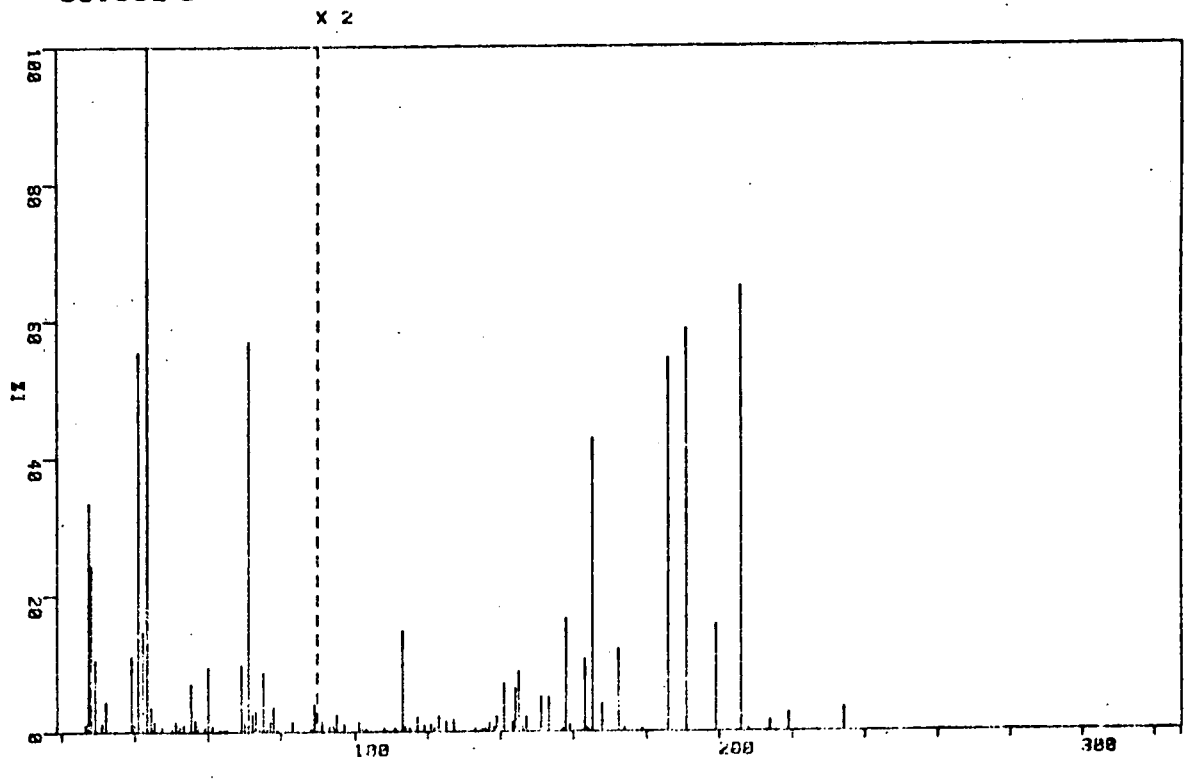


J1741A. 4 08-NOV-71

PEAK NO.	MASS	% INT BASE
1	20.65	64.62
2	21.92	100.00
5	24.30	1.32
6	31.83	0.93
7	33.00	12.67
8	34.23	1.66
9	37.51	2.47
10	41.95	1.34
11	44.31	0.46
12	45.50	0.95
14	47.70	1.81
15	48.77	0.34
16	49.80	2.12
17	50.92	1.10
20	58.74	0.66
21	62.10	0.66
22	63.23	1.59
23	64.38	0.71
24	65.46	3.61
25	66.55	0.44
26	67.64	0.46
30	76.46	0.46
31	77.52	0.42
32	78.56	1.39
33	79.64	0.59
34	80.74	1.29
36	87.34	1.51
37	88.44	0.42
39	91.71	0.85
40	92.87	0.39
41	93.96	0.76
42	95.07	0.37
43	96.15	0.46
44	102.58	1.61
46	105.88	0.46
47	106.97	0.78
49	109.10	0.61
53	117.69	2.05
55	124.28	0.37
56	132.79	0.39
57	135.97	0.59
58	137.11	0.34
59	139.25	0.37
60	152.09	0.27
61	162.68	0.22
62	164.74	0.71
63	173.38	0.27
64	199.49	0.44
65	277.99	0.27

NO.5 MW 234

CJ1932 5

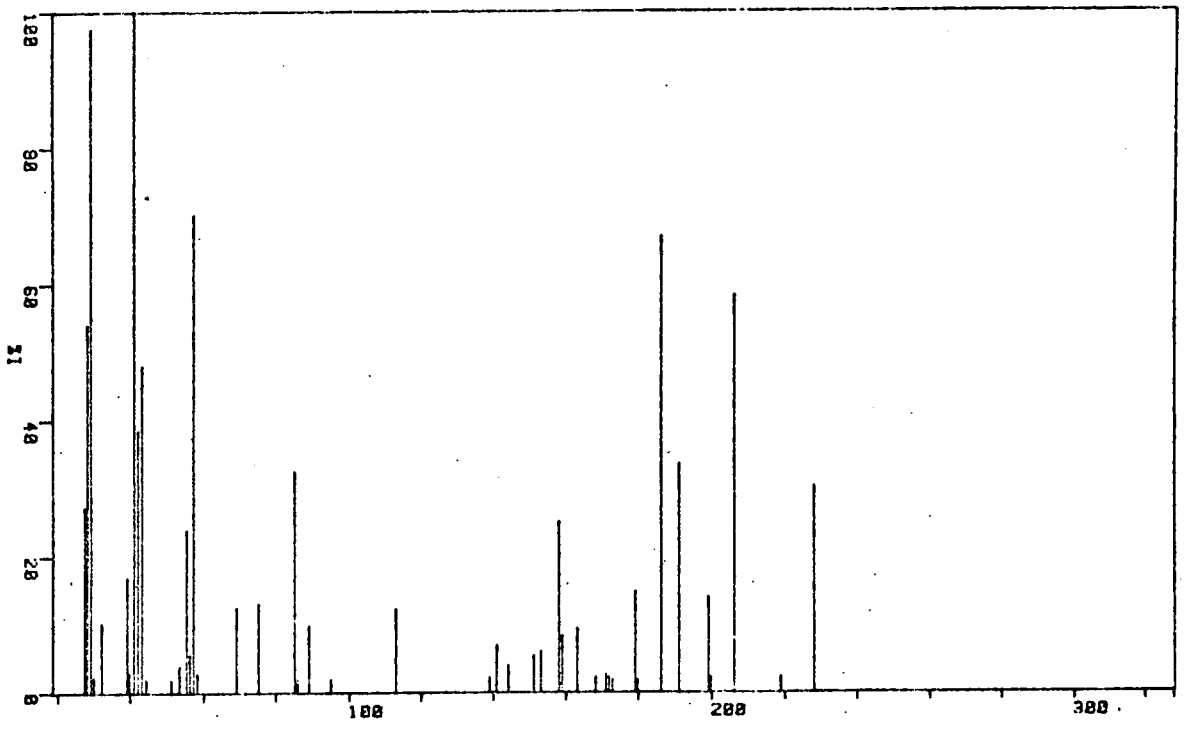


CJ1932. 5 30-JAN-80

PEAK NO.	MASS	% INT BASE			
2	27.25	33.42			
3	28.13	24.31			
4	29.02	10.47			
7	32.01	4.47			
10	39.01	11.00			
11	39.88	2.19			
12	40.94	55.34#			
13	41.04	36.76#			
14	42.05	14.67			
15	43.10	100.00#			
16	43.20	66.10#			
17	44.17	3.61			
24	55.10	6.98			
28	59.89	9.49			
33	68.94	9.76	87	157.93	8.25
35	70.98	56.91	89	162.90	5.32
36	72.03	2.63	93	165.07	21.38
37	73.04	3.11	94	167.59	2.04
39	75.05	8.67	95	172.26	6.06
42	78.03	3.61	98	185.86	27.24
46	88.95	3.99	99	190.81	29.37
60	112.93	7.34	100	198.93	7.84
77	140.85	3.52	101	205.94	32.42
79	143.95	3.16	102	207.83	0.27
80	144.98	4.35	103	213.88	0.86
84	150.89	2.57	104	218.84	1.39
85	152.94	2.51	105	234.18	1.75

NO.6 MW 248

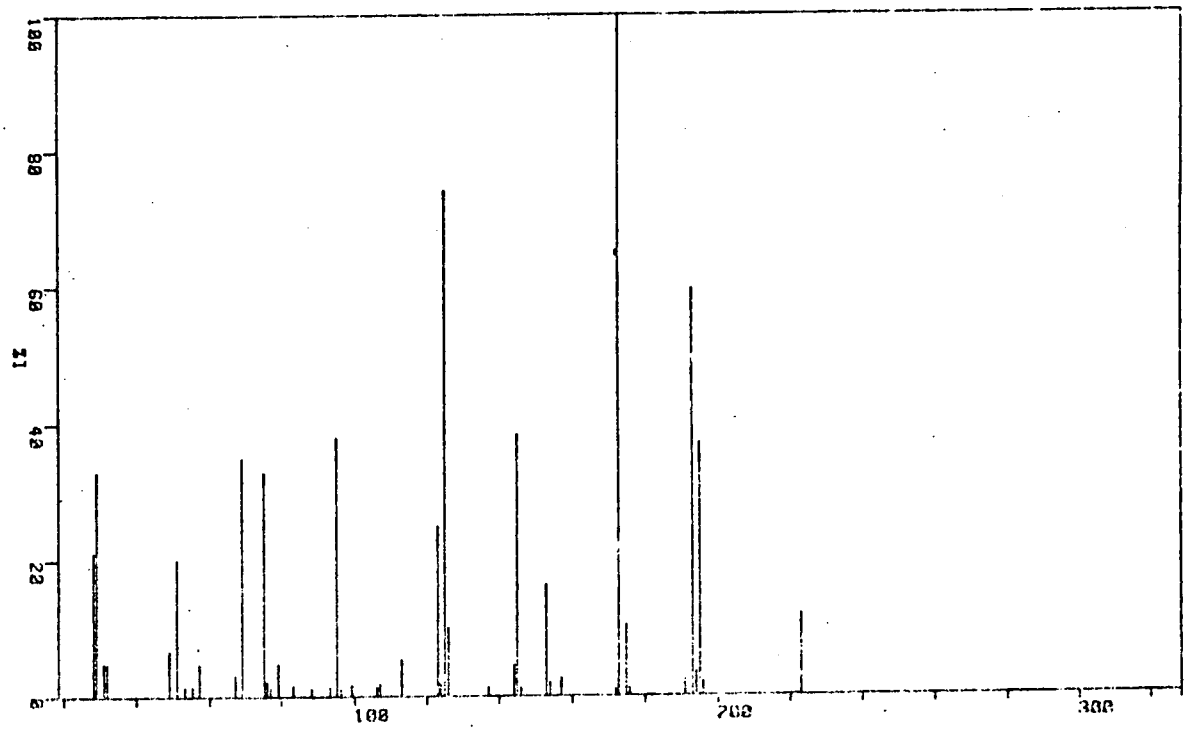
CJ882X 7



CJ882X. 7 30-JAN-80

PEAK NO.	MASS	% INT BASE
1	27.25	27.29
2	28.13	54.17
3	29.02	97.50
4	29.85	2.29
5	32.01	10.21
6	39.00	16.87
7	39.87	3.12
8	40.98	100.00
9	42.07	38.54
10	43.14	48.12
11	44.15	2.08
12	50.91	1.87
13	53.06	3.96
14	55.13	23.96
15	56.13	5.62
16	57.14	70.21
17	58.08	2.92
18	68.96	12.50
19	75.07	13.12
20	85.11	32.50
21	86.02	1.87
22	88.95	9.79
23	94.97	2.08
24	112.95	12.29
25	138.84	2.29
26	140.89	6.87
27	143.93	3.96
28	150.87	5.42
29	152.89	6.04
30	157.91	25.00
31	158.92	8.33
32	162.89	9.37
33	167.97	2.29
34	170.84	2.71
35	171.82	2.29
36	172.82	1.87
37	178.90	14.79
38	179.74	1.87
39	186.02	66.87
40	190.87	33.54
41	198.91	13.96
42	199.76	2.29
43	206.05	58.33
44	218.78	2.29
45	227.99	30.21

CJ2112 5 NO.7 MW 262

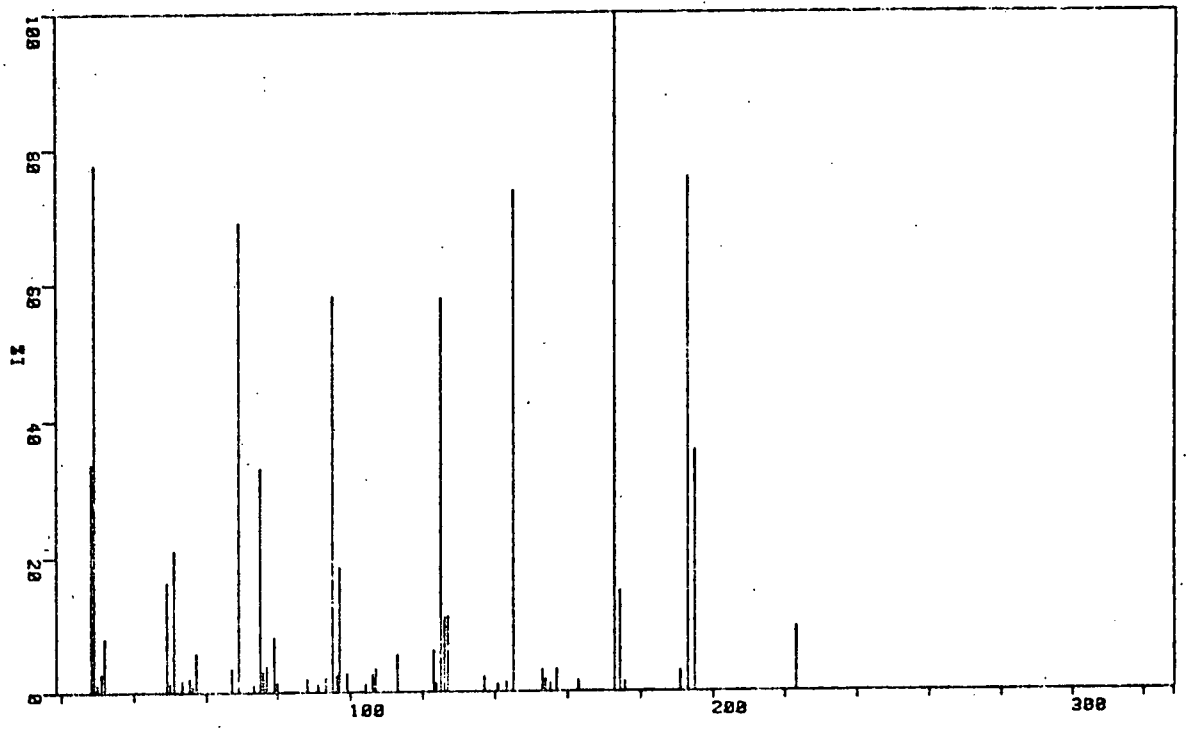


CJ2112. 6 14-MAY-80

PEAK NO.	MASS	% INT BASE
2	28.13	25.67
3	29.00	34.02
6	30.93	4.83
7	32.03	4.67
11	48.98	7.16
12	49.88	0.93
13	50.94	21.00
14	53.08	1.05
15	55.14	1.60
17	57.10	4.73
21	67.08	3.04
22	68.98	35.87
25	75.07	32.13
26	76.09	2.43
27	77.07	1.63
29	78.96	3.90
30	79.90	1.25
32	83.04	1.82
35	88.01	0.96
36	90.95	0.90
37	93.02	1.47
39	95.03	39.23
40	96.05	1.57
41	97.01	1.12
42	98.97	1.69
44	104.04	0.80
45	106.03	1.89
46	107.03	2.21
48	113.00	6.23
49	122.97	23.88
50	124.01	2.01
51	124.99	73.43
52	125.99	10.77
55	136.99	1.21
56	140.93	0.83
58	143.98	4.19
59	144.96	38.94
60	146.00	1.50
62	152.94	16.02
63	154.00	2.01
64	155.07	0.99
66	156.99	2.91
67	162.94	0.99
68	172.88	100.00
69	174.88	10.39
70	175.94	1.25
71	190.91	2.43
73	192.93	60.87#
74	194.79	38.01#
75	196.01	2.21
76	222.92	11.38
77	223.98	0.93

CJ2114 6

NO.8 MW 262

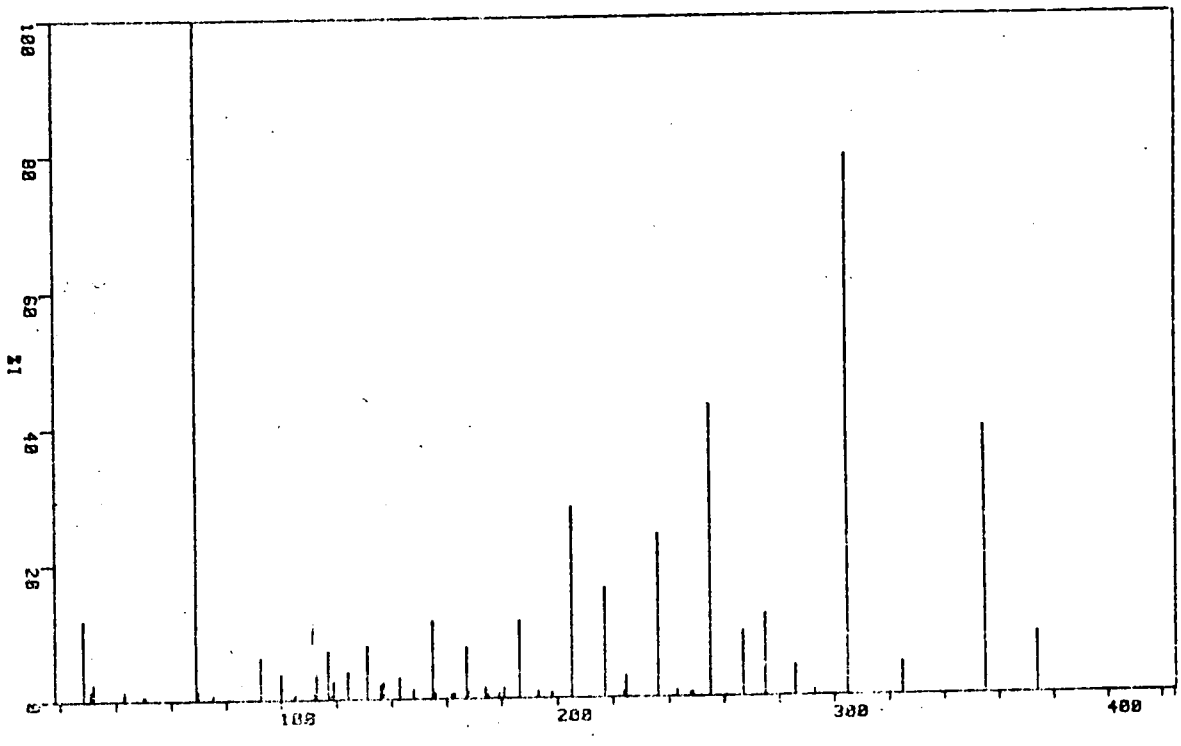


CJ2114. 6 14-MAY-80

PEAK NO.	MASS	% INT BASE			
3	28.13	33.65			
4	28.99	77.61			
6	29.84	1.14			
7	30.93	2.71			
8	32.02	7.93	68	106.03	2.69
18	48.98	16.30	69	107.02	3.41
19	49.89	1.42	71	112.98	5.50
20	50.94	20.95	81	122.97	6.17
22	53.08	1.73	83	123.99	1.39
24	55.14	1.99	84	125.00	57.83
25	56.13	1.27	85	126.00	11.18
26	57.10	5.76	86	126.99	11.26
32	67.08	3.49	90	136.98	2.25
33	68.98	69.14	91	140.93	1.14
36	73.09	1.08	92	142.96	1.42
38	75.08	33.08	94	144.96	73.79
39	76.07	3.07	98	152.94	3.23
40	77.07	3.85	99	154.00	1.94
42	78.96	8.03	100	155.29	1.32
43	79.90	1.37	101	156.93	3.38
50	88.01	1.99	103	162.90	1.65
52	90.94	1.21	111	172.84	100.00#
53	93.01	2.04	112	174.49	14.93#
56	95.03	58.26	113	175.89	1.50
58	96.04	2.40	117	190.86	3.02
59	97.00	18.52	118	192.96	75.72#
61	98.95	2.82	119	194.88	35.54#
65	104.02	1.27	126	222.94	9.50

NO.9 MW 374

CJ483 4

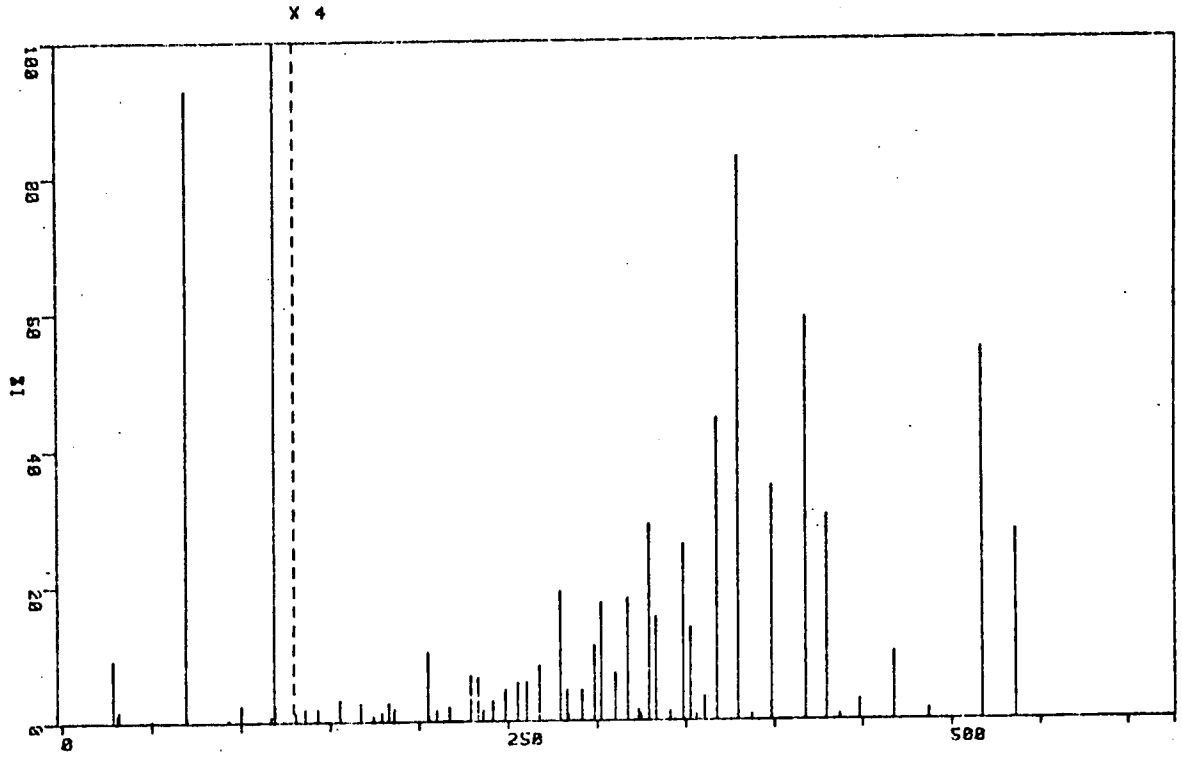


CJ483 4 09-JLY-80

PEAK NO.	MASS	% INT BASE
1	28.13	11.81
2	30.91	1.46
3	32.02	2.57
4	43.11	1.39
5	49.87	0.62
6	50.95	0.62
7	68.97	100.00
8	69.91	1.32
9	75.07	0.62
10	93.01	6.32
11	99.92	3.82
12	105.03	0.90
13	112.02	0.90
14	113.02	3.68
15	117.02	7.15
16	118.01	0.56
17	118.96	2.64
18	124.01	4.10
19	130.94	7.85
20	136.01	2.15
21	136.99	2.50
22	142.97	3.26
23	147.98	1.46
24	155.00	11.46
25	156.01	0.90
26	161.96	0.62
27	163.00	0.90
28	167.00	7.57
29	167.96	1.11
30	174.00	1.67
31	175.00	0.62
32	178.89	0.76
33	180.94	1.60
34	186.20	11.39
35	192.95	1.04
36	197.92	0.83
37	205.01	28.19
38	216.99	16.11
39	223.96	0.83
40	224.92	3.26
41	236.05	24.10
42	242.89	1.04
43	247.93	0.62
44	248.68	0.69
45	254.95	42.85
46	266.96	9.58
47	274.86	12.01
48	285.91	4.51
49	292.91	0.90
50	304.95	79.37
51	324.52	4.79
52	354.97	39.44
53	373.94	9.10

NO.10 MW 536

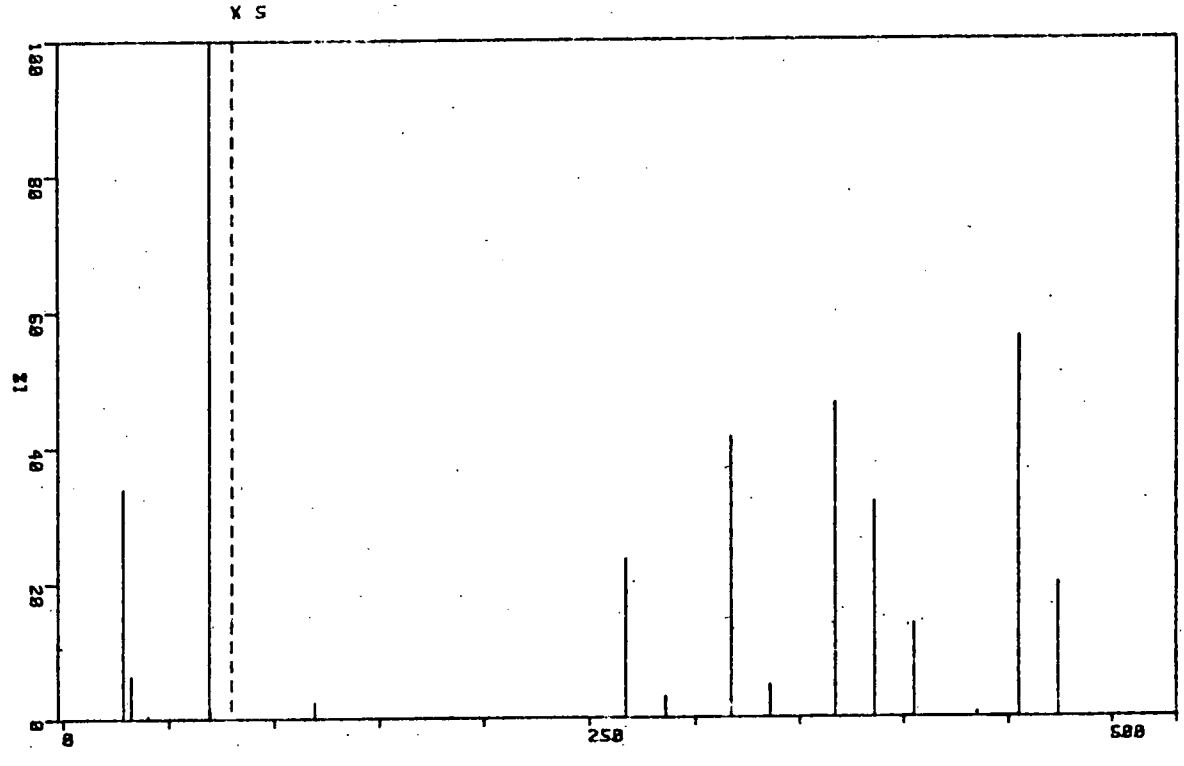
CJ486 5



CJ486 5 09-JLY-80

PEAK NO.	MASS	% INT BASE
1	28.13	9.04
2	30.90	1.16
3	32.02	1.72
5	68.97	92.85
6	69.91	1.13
8	99.91	2.47
10	118.96	100.00
11	119.91	2.44
22	204.99	2.56
26	228.98	1.72
27	232.98	1.66
30	248.00	1.16
31	254.96	1.42
32	259.96	1.45
33	267.01	2.01
34	279.05	4.74
35	282.95	1.13
37	290.96	1.16
38	298.12	2.79
39	301.98	4.36
40	309.97	1.77
41	317.00	4.48
44	329.01	7.24
45	333.00	3.81
47	348.05	6.48
48	352.00	3.43
51	367.01	11.08
52	378.97	20.70
54	397.99	8.60
55	417.00	14.77
56	428.92	7.56
57	436.57	0.26
58	447.98	0.76
59	466.94	2.47
60	486.85	0.41
61	517.07	13.60
62	536.00	6.98

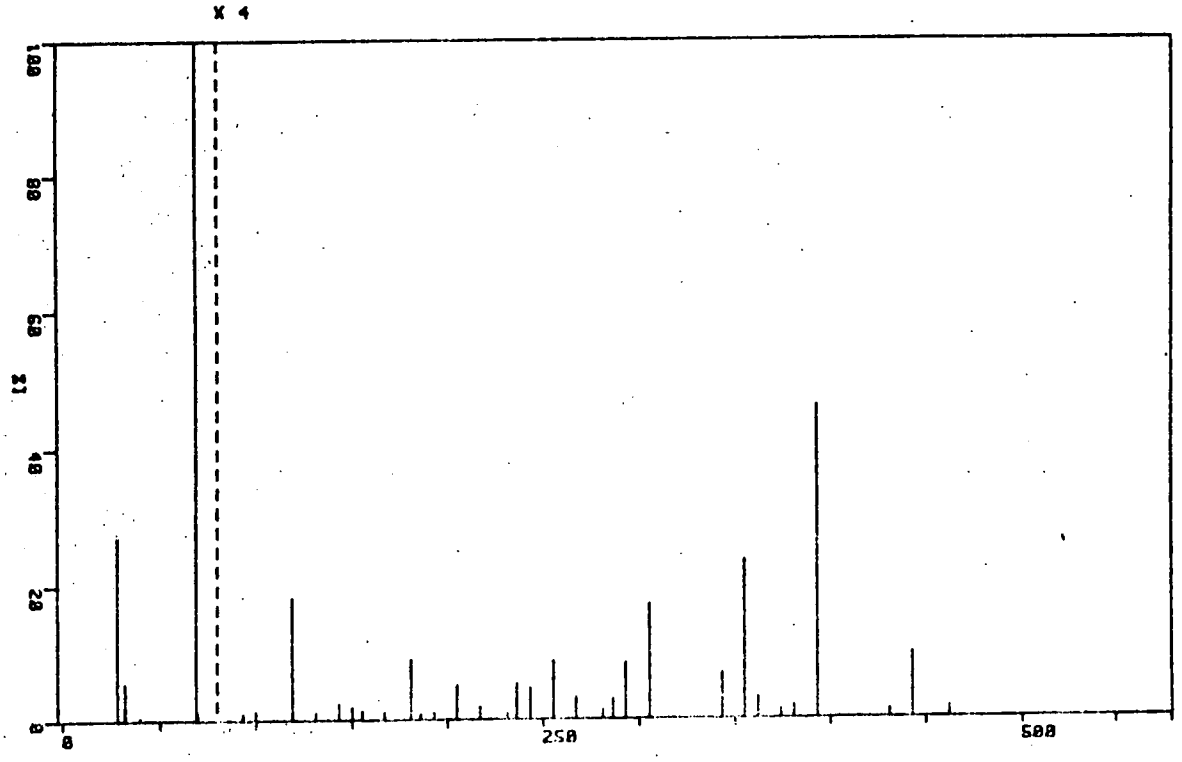
CJ1155 S NO.11 MW 474



CJ1155 5 16-SEP-80

PEAK NO.	MASS	% INT BASE
1	28.13	33.87
2	32.02	6.32
3	39.85	0.50
4	68.99	100.00
5	69.94	1.05
6	119.06	0.50
7	267.10	4.71
8	286.06	0.61
9	317.13	8.31
10	336.02	1.00
11	367.07	9.31
12	385.98	6.37
13	404.96	2.77
14	455.08	11.25
15	474.00	3.99

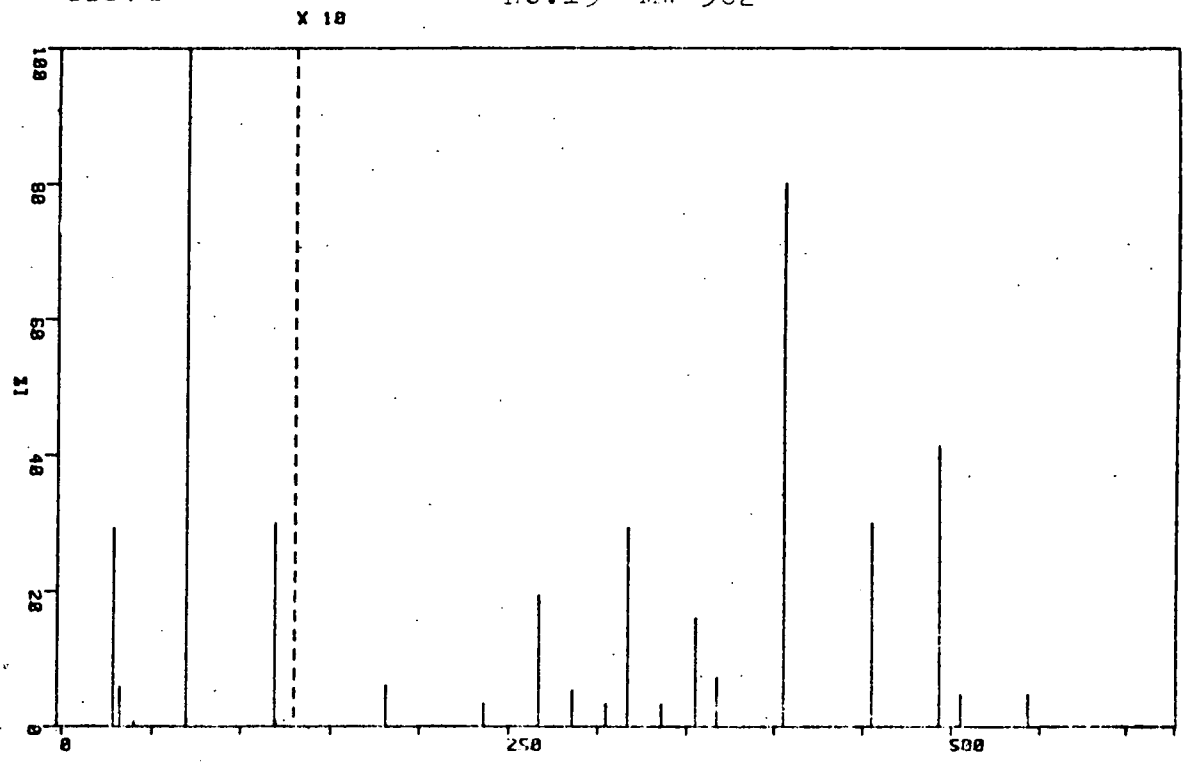
CJ1151 5 NO.12 MW 462



CJ1151 5 16-SEP-80

PEAK NO.	MASS	% INT BASE
1	28.13	27.15
2	29.01	0.25
3	32.02	5.49
4	39.84	0.53
5	69.00	100.00
6	69.93	1.09
7	93.06	0.31
8	99.96	0.36
9	119.01	4.57
10	131.03	0.31
11	143.05	0.64
12	149.99	0.50
13	155.11	0.33
14	167.09	0.31
15	181.03	2.23
16	186.08	0.25
17	193.08	0.31
18	205.08	1.31
19	217.10	0.53
20	231.10	0.25
21	236.09	1.34
22	243.06	1.14
23	255.10	2.14
24	267.08	0.81
25	281.05	0.39
26	286.06	0.75
27	293.07	2.09
28	305.15	4.32
29	343.03	1.73
30	355.09	5.90
31	362.04	0.84
32	374.04	0.39
33	380.96	0.47
34	393.03	11.56
35	430.97	0.39
36	443.05	2.45
37	462.01	0.42

CJ64 S NO.13 MW 562

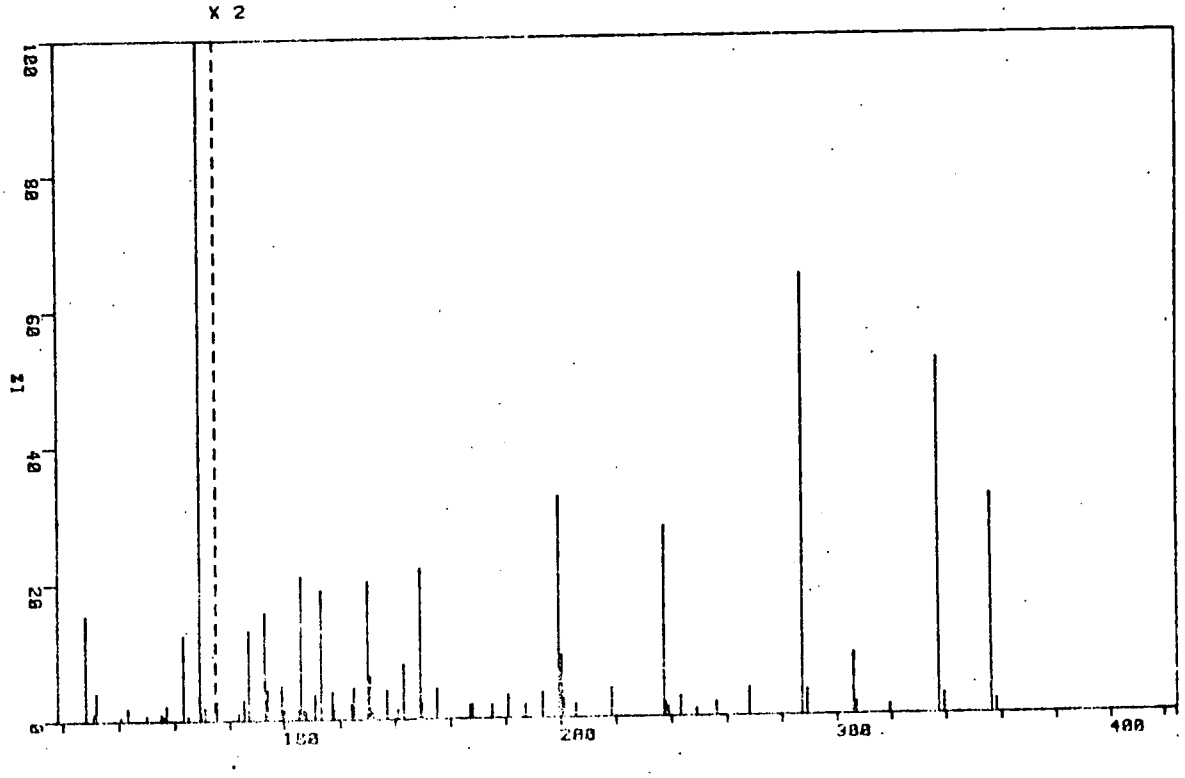


CJ64 5 16-SEP-80

PEAK NO.	MASS	% INT BASE
1	28.13	29.33
2	32.02	5.90
3	39.84	0.68
4	68.99	100.00
5	69.94	1.15
6	119.01	30.01
7	119.97	0.68
8	181.03	0.64
9	236.14	0.38
10	267.10	1.95
11	286.06	0.55
12	305.02	0.38
13	317.11	2.97
14	336.05	0.38
15	354.99	1.66
16	366.96	0.76
17	405.00	8.02
18	455.05	3.01
19	493.03	4.16
20	504.98	0.47
21	543.05	0.47

NO.14 MW 356

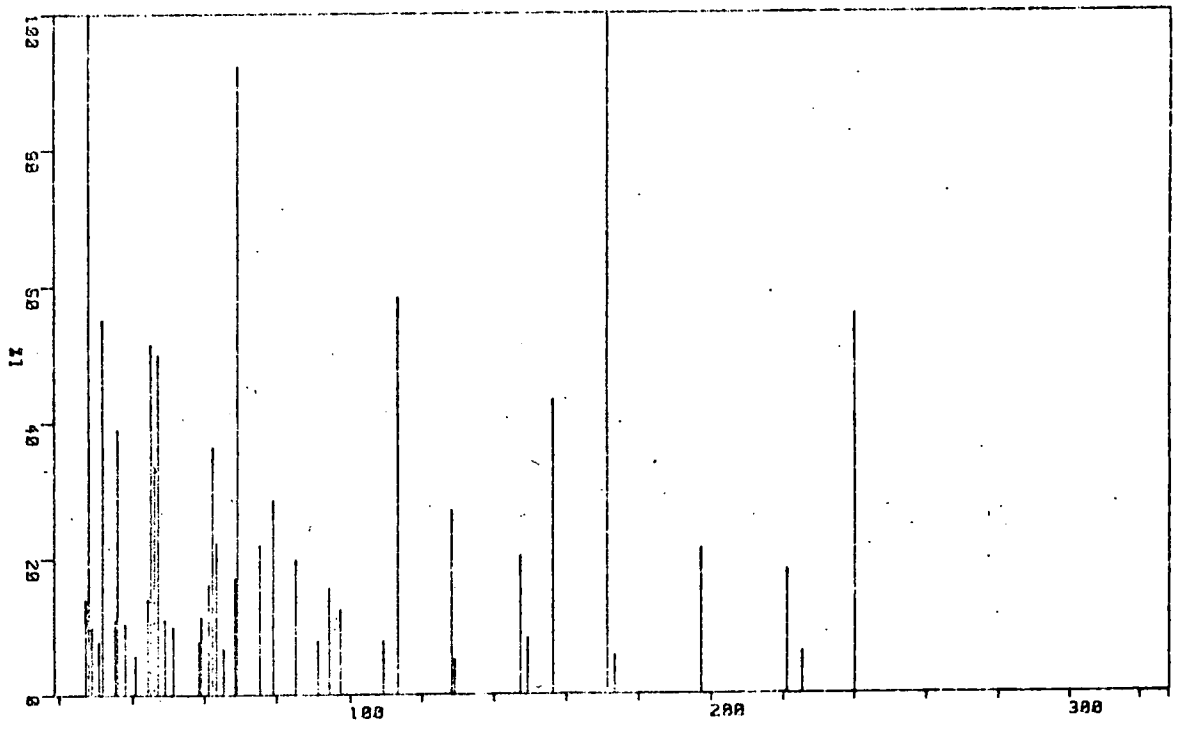
CJ167 12



CJ167 12 24-OCT-79

PEAK NO.	MASS	% INT BASE
1	28.12	15.50
2	30.91	1.18
3	32.02	4.15
5	43.17	1.87
7	55.19	0.97
9	57.17	2.28
10	63.07	12.53
12	69.01	100.00
13	69.97	1.31
14	71.09	1.87
15	75.10	1.45
17	85.21	1.59
18	87.06	6.64
19	93.08	7.89
20	94.07	2.28
21	99.01	2.56
24	106.07	10.59
27	111.02	1.87
28	113.06	9.48
29	117.09	2.08
31	124.09	1.18
32	125.08	2.35
33	129.98	10.10
34	131.03	3.25
36	137.06	2.15
38	143.08	4.01
39	149.01	11.00
40	150.00	1.25
41	155.11	2.28
42	167.10	1.04
43	168.05	1.11
44	175.07	1.04
45	181.06	1.80
46	187.07	1.18
47	193.07	1.87
48	199.02	16.26
49	200.03	4.64
50	201.06	1.59
51	205.07	1.04
52	218.07	2.15
53	237.05	13.98
54	238.05	1.04
56	243.08	1.59
58	256.11	1.11
59	268.07	2.08
60	287.08	32.32
61	288.97	1.87
62	306.01	4.57
63	307.14	0.97
65	337.06	26.09
66	338.97	1.52
67	356.12	16.12
68	357.97	1.04

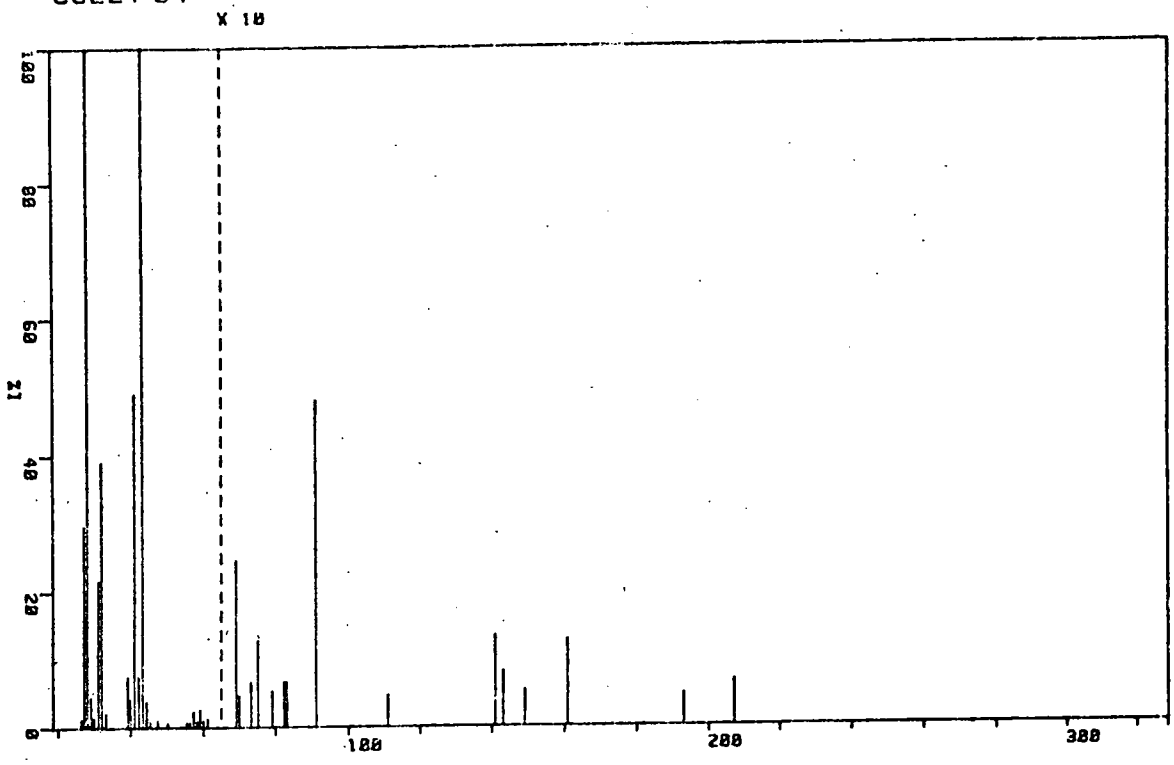
CJDMSO 5 NO.15 MW 240



CJDMSO 5 15-JLY-80

PEAK NO.	MASS	% INT BASE
2	27.14	5.73
3	28.01	100.00
4	28.88	4.03
5	30.75	3.18
6	31.83	22.51
7	35.00	4.46
8	35.98	15.92
9	37.92	4.25
10	40.89	2.34
11	44.03	5.73
12	45.05	21.02
13	46.05	13.80
14	47.05	20.38
15	48.99	4.46
16	50.99	4.03
17	58.07	3.18
18	59.02	4.67
19	61.02	6.58
20	62.08	14.86
21	63.08	9.13
22	65.14	2.76
23	68.14	7.01
24	69.02	37.58
25	75.15	8.92
26	79.06	11.68
27	85.16	8.07
28	91.17	3.18
29	94.21	6.37
30	97.20	5.10
31	109.19	3.18
32	113.19	23.78
33	128.18	11.04
34	129.20	2.12
35	147.25	8.28
36	149.26	3.40
37	156.26	17.62
38	171.22	40.76
39	173.27	2.34
40	197.26	8.70
41	221.23	7.43
42	225.31	2.55
43	240.26	22.72

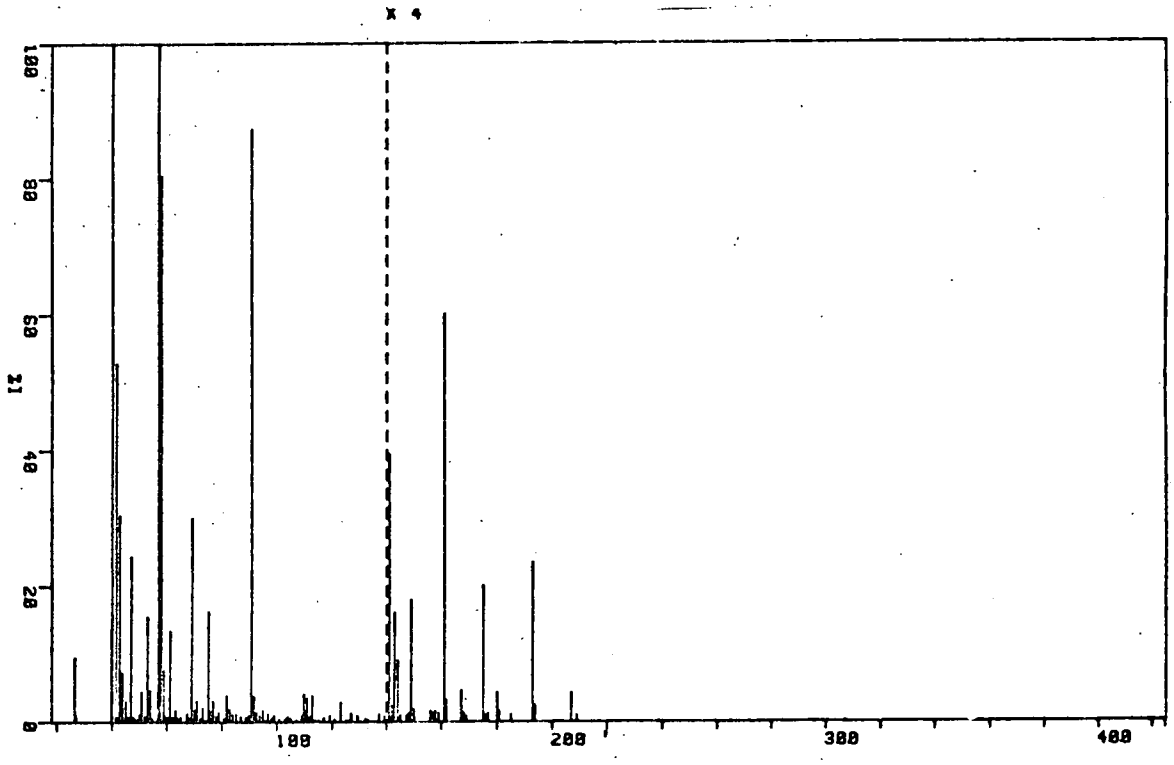
CJ227 34 NO.16 MW 222



CJ227 34 17-SEP-80

PEAK NO.	MASS	% INT BASE
1	26.33	0.76
2	27.25	17.05
3	28.13	100.00
4	28.24	0.27
5	29.01	2.61
6	29.84	0.85
7	30.93	12.43
8	32.02	22.37
9	33.12	1.25
10	39.00	4.27
11	39.85	2.47
12	40.98	28.11
13	42.08	4.27
14	43.14	57.22
15	44.18	2.20
16	45.19	0.51
17	47.13	0.63
18	49.91	0.37
19	55.19	0.42
20	56.17	0.42
21	57.13	1.37
22	58.08	0.51
23	59.02	1.51
24	59.96	0.63
25	60.99	0.73
26	68.97	1.44
27	70.00	0.29
28	73.10	0.42
29	75.05	0.76
30	78.96	0.34
31	82.02	0.42
32	83.07	0.42
33	83.14	0.29
34	90.93	2.76
35	110.94	0.27
36	140.96	0.78
37	142.99	0.49
38	148.95	0.32
39	160.95	0.76
40	193.03	0.29
41	207.07	0.42

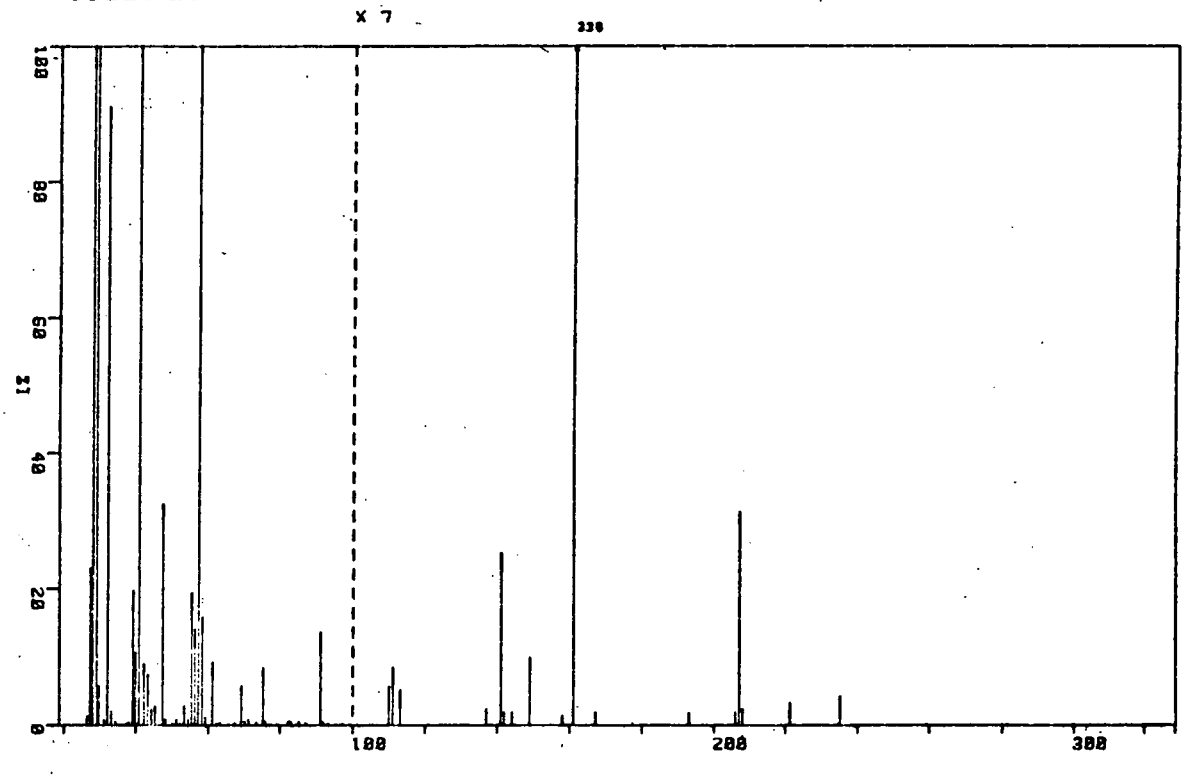
CJ229 33 NO.17 MW 236



CJ229 33 17-SEP-80

PEAK NO.	MASS	% INT BASE			
1	26.31	9.40			
4	39.86	13.97			
5	40.36	100.00			
6	41.53	52.82			
14	43.14	30.50			
17	44.14	7.25			
19	45.16	3.13			
24	47.11	24.42			
29	50.94	4.42			
34	53.09	15.58			
38	54.13	4.62			
43	56.56	4.40			
44	56.80	100.00			
45	57.87	80.42			
46	58.74	7.69			
52	61.00	13.46			
54	63.06	1.76			
60	68.97	30.06			
61	69.96	1.86			
62	71.02	3.17			
64	73.07	2.17	105	113.01	3.83
68	75.07	16.29	111	123.00	2.93
69	76.06	1.64	121	140.93	9.91
70	77.03	3.05	123	142.96	4.05
74	81.98	3.83	124	143.96	2.27
75	83.04	1.88	128	148.92	4.47
85	90.92	87.20	135	160.91	15.04
88	91.97	3.76	140	174.99	5.05
91	95.03	1.68	146	192.93	5.89
102	109.88	4.05	148	206.95	1.10
103	110.93	3.52	149	208.92	0.27

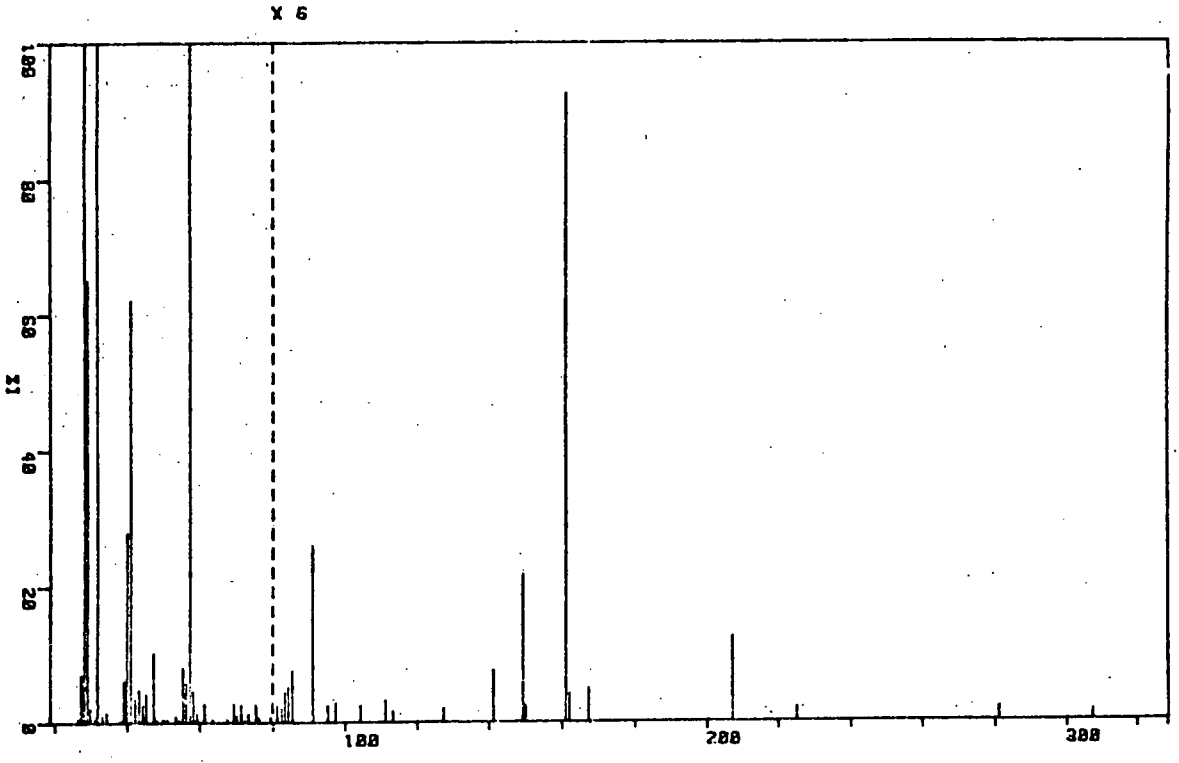
CJ226 26 NO.18 MW 236



CJ226 26 16-SEP-80

PEAK NO.	MASS	% INT BASE
2	27.25	23.00
5	28.13	100.00
6	29.04	100.00
8	29.86	5.69
10	32.02	91.06
12	33.13	2.08
17	39.01	19.68
18	39.85	10.62
21	40.99	100.00
22	42.08	8.99
23	43.13	7.45
24	44.16	2.27
25	45.18	2.76
26	47.13	32.50
31	53.12	2.81
33	55.18	19.46
34	56.18	14.02
37	57.17	100.00
38	58.13	15.80
40	61.03	9.23
45	69.01	5.79
49	75.15	8.42
58	90.95	13.55
68	141.00	3.61
73	161.05	48.40
76	206.07	0.32
77	207.09	4.47
78	208.09	0.34
79	221.12	0.49
80	235.13	0.66

CJ226 30 NO.19 MW 236

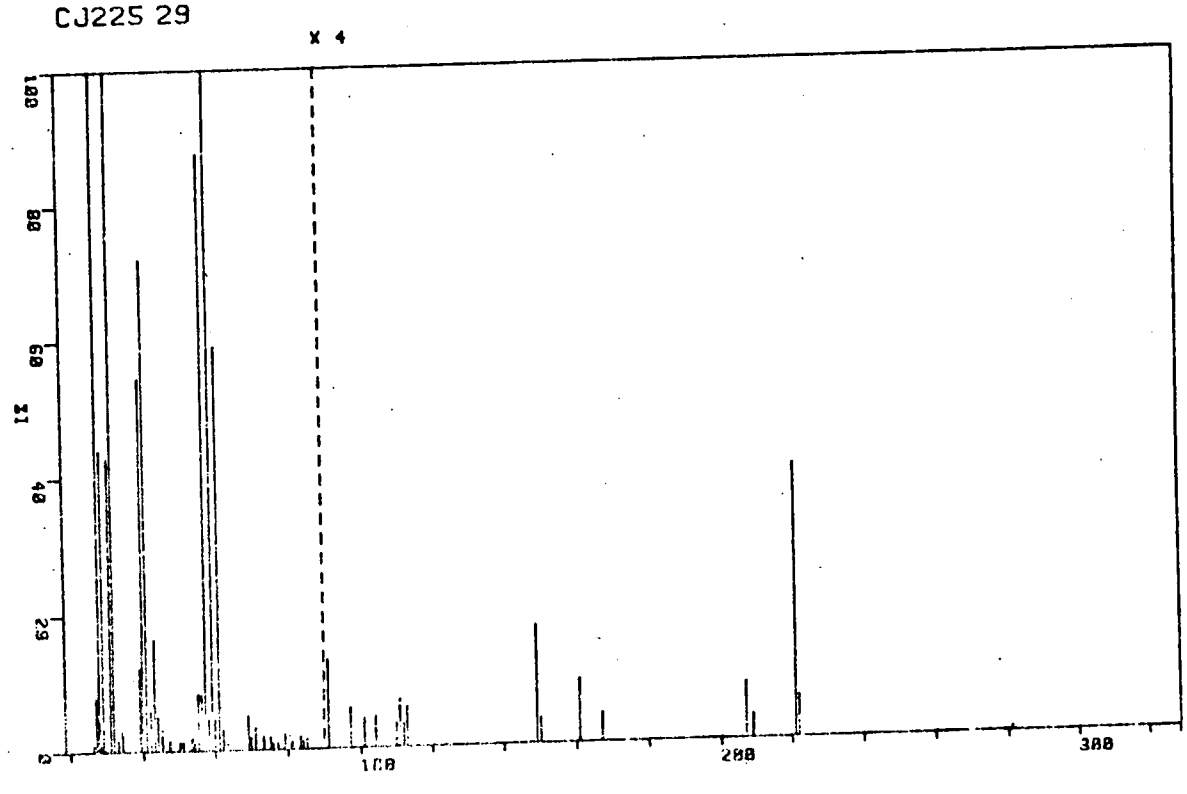


CJ226 30 16-SEP-80

PEAK NO.	MASS	% INT BASE
2	27.26	4.96
3	28.13	100.00
5	29.03	46.20
6	29.86	1.44
9	32.02	100.00
11	34.17	1.03
13	39.01	4.27
14	39.84	19.88
15	41.00	44.13
16	42.09	2.42
17	43.14	3.37
18	44.14	1.81
19	45.19	2.95
20	47.14	7.28
26	55.19	5.64
27	56.18	4.03
28	57.17	71.04
29	58.13	3.22
30	59.05	0.93
31	61.04	1.93
34	69.04	1.93
35	70.01	0.76
36	71.08	1.81
38	73.13	0.90
39	75.15	1.86
46	85.19	0.90
47	91.01	3.10
54	141.10	0.93
55	149.06	2.59
57	161.06	10.94
60	207.12	1.51
61	225.12	0.24
62	281.09	0.27
63	307.35	0.22

NO.20 MW 236

CJ225 29



CJ225 29 17-SEP-80

PEAK NO.	MASS	% INT BASE
2	27.25	1.93
4	28.13	100.00
6	29.02	10.82
8	30.93	10.53
10	32.02	100.00
11	33.13	0.42
12	34.16	0.71
13	39.01	3.00
14	39.84	13.41
15	40.99	17.73
16	42.08	1.44
17	43.12	4.03
18	44.13	1.25
19	45.18	0.78
20	47.13	0.37
23	53.11	0.46
25	55.17	2.05
26	56.17	2.00
27	57.15	21.51
28	58.11	1.12
29	59.03	24.57
30	59.96	1.10
31	61.03	14.55
32	62.09	0.76
33	69.01	1.22
34	69.98	0.46
35	71.06	0.81
36	73.12	0.51
37	75.11	0.46
40	78.97	0.56
43	83.10	0.44
45	85.16	0.37
46	90.97	0.81
47	97.13	0.37
51	111.02	0.44
53	113.11	0.37
54	149.01	1.07
55	150.08	0.24
56	160.99	0.58
57	167.10	0.27
58	207.10	0.51
58	209.14	0.22
60	221.11	2.47
61	222.08	0.39

APPENDIX IV

DEPARTMENTAL COLLOQUIA AND FIRST YEAR INDUCTION COURSE FOR POST-GRADUATES

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing

(a) all research colloquia, research seminars and lectures arranged by the Department of Chemistry during the period of the writer's residence as a post-graduate student;

(b) all research conferences attended and papers read out by the writer of the thesis, during the period when the research for the thesis was carried out; and

(c) details of the first-year induction course.

Events in (a) which were attended are marked *

Research Colloquia, Seminars and Lectures

1. University of Durham Chemistry Colloquia

Academic Year 1977 - 1978

* 19 Oct. Dr. B. Heyn (U. of Jena, D.D.R.), "Sigma-organo molybdenum complexes as alkene polymerisation catalysts".

* 27 Oct. Professor R.A. Filler (Illinois Institute of Technology, U.S.A.), "Reactions of organic compounds with xenon fluorides".

2 Nov. Dr. N. Boden (U. of Leeds),"N.m.r. spin-echo experiments for studying structure and dynamical properties of materials containing interacting spin Y_2-pairs".

* 9 Nov. Dr. A.R. Butler (U. of St. Andrews), "Why I lost faith in linear free energy relationships",

7 Dec. Dr. P.A. Madden (U. of Cambridge), "Raman studies of molecular motions in liquids".

* 14 Dec. Dr. R.O. Gould (U. of Edinburgh), "Crystallography to the rescue in ruthenium chemistry".

* 25 Jan. Dr. G. Richards (U. of Oxford), "Quantum Pharmacology".

* 1 Feb. Professor K.J. Ivin (Queens U. Belfast), "The olefin metathesis reaction, mechanism of ring opening polymerisation of cycloalkenes".

* 3 Feb. Dr. A. Hartog (Free U., Amsterdam), "Surprising recent studies in organomagnesium chemistry".

* 22 Feb. Professor J.D. Birchall (Mond Division, I.C.I.), "Silicon in the biosphere".

* 1 Mar. Dr. A. Williams (U. of Kent), "Acyl group transfer reactions".

3 Mar. Dr. G. van Koten (U. of Amsterdam), "Structure and reactivity of aryl-copper cluster compounds".

15 Mar. Professor G. Scott (U. of Aston), "Fashioning plastics to match the environment".

22 Mar. Professor H. Vahrenkamp (U. of Freiburg, Germany), "Metal-metal bonds in organometallic complexes".

19 Apr. Dr. M. Barber (UMIST), "Secondary ion mass spectra of surfaces and adsorbed species".

16 May Dr. P. Ferguson (C.N.R.S., Grenoble), "Surface plasma waves and adsorbed species on metals".

18 May Professor M. Gordon (U. of Essex), "Three critical points in polymer chemistry".

22 May Professor D. Tuck (U. of Windsor, Ontario), "Electrochemical synthesis of inorganic and organometallic compounds".

24 & 25 May Professor P. von Schleyer (U. of Erlangen, Nürnberg)

* I "Planar tetra-coordinate methanes, perpendicular ethenes and planar allenes".

* II "Aromaticity in three dimensions".

* III "Non-classical carbo-cations".

21 June Dr. S.K. Tyrlik (Acad. of Sci., Warsaw), "Dimethylglyoxime cobalt complexes - catalytic black boxes".

23 June Professor G. Metescu (Case Western Reserve U., Ohio), "A concerted spectroscopy approach to the characterisation of ion and ion-pairs: facts, plans and dreams".

8 Sept. Dr. A. Diaz (I.B.M., San Jose, California), "Chemical behaviour of electrode surface bonded molecules".

15 Sept. Professor W. Siebert (Marburg, W. Germany), "Boron heterocycles".

22 Sept. Professor T. Fehlner (Notre Dame, U.S.A.), "Ferraboranes: synthesis and photochemistry".

Academic Year 1978 - 1979

* 12 Dec. Professor C.J.M. Stirling (U. of Bangor), "Parting is such sweet sorrow - the leaving group in organic chemistry".

* 31 Jan. Professor P.D.B. de la Mare (U. of Auckland, New Zealand), "Some pathways leading to electrophilic substitution".

14 Feb. Professor B. Dunnel (U. of British Columbia), "The application of n.m.r. to the study of motions of molecules in solids".

* 14 Mar. Dr. J.C. Walton (U. of St. Andrews), "Pentadienyl radicals".

* 28 Mar. Dr. A. Reiser (Kodak Ltd.), "Polymer photography and the mechanism of cross-link formation in solid polymer matrices".

* 25 Apr. Dr. C.R. Patrick (U. of Birmingham), "Chlorofluorocarbons and stratospheric ozone: an appraisal of the environmental problem".

* 1 May Dr. G. Wyman (European Research Office, U.S. Army), "Excited state chemistry of indigoid dyes".

* 2 May Dr. J.D. Hobson (U. of Birmingham), "Nitrogen-centred reactive intermediates".

8 May Professor A. Schmidpeter (Inst. of Inorg. Chem., Munich U.), "Five-membered phosphorus heterocycles containing dicoordinate phosphorus".

* 9 May Professor G. Maier (Lahn Giessen U.), "Tetra-tert-butyltetrahedrane".

9 May Dr. A.J. Kirkby (U. of Cambridge), "Structure and reactivity in intramolecular and enzymic catalysis".

16 May Dr. J.F. Nixon (U. of Sussex), "Some recent developments in platinum-metal phosphine complexes".

* 23 May Dr. B. Wakefield (U. of Salford), "Electron transfer in reaction of metals and organometallic compounds with polychloropyridine derivatives".

* 13 June Professor I. Ugi (U. of Munich), "Synthetic uses of super nucleophiles".

* 25 Sept. Professor R. Soulen (Southwestern U., Texas), "Applications of HSAB theory to vinylic halogen substitution reactions and a few copper coupling reactions.

Academic Year 1979 - 1980

* 21 Nov. Dr. J. Müller (U. of Bergen), "Photochemical reactions of ammonia".

28 Nov. Dr. B. Cox (U. of Stirling), "Macrobicyclic cryptate complexes: dynamics and selectivity".

* 5 Dec. Dr. G.C. Eastmand (U. of Liverpool), "Synthesis and properties of some multicomponent polymers".

12 Dec. Dr. C.I. Ratcliffe, "Rotor motions in solids".

18 Dec. Dr. K.E. Newman (U. of Lausanne), "High pressure multinuclear n.m.r. in the elucidation of mechanism of fast simple inorganic reactions".

30 Jan. Dr. M.J. Barrow (U. of Edinburgh), "The structures of some simple inorganic compounds of silicon and germanium - pointers to structural trends in group IV".

* 6 Feb. Dr. J.M.E. Quirke (U. of Durham), "Degradation of chlorophyll - a in sediments".

* 23 Apr. B. Grievson B.Sc. (U. of Durham), "Halogen radio-pharmaceuticals".

* 14 May Dr. R. Hutton (Waters Associates), "Recent developments in multi-milligram and multi-gram scale preparative high performance liquid chromatography".

21 May Dr. T.W. Bentley (U. of Swansea), "Medium and structural effects on solvolytic reactions".

* 10 July Professor D. Des Marteau (U. of Heidelberg), "New developments in organonitrogen fluorine chemistry".

2. Durham University Chemical Society

Academic Year 1977 - 1978

13 Oct. Dr. J.C. Young and Mr. A.J.S. Williams (U. of Aberystwyth), "Experiments and considerations touching colour".

* 20 Oct. Dr. R.L. Williams (Metropolitan Police Forensic Science Dept.), "Science and Crime".

* 3 Nov. Dr. G.W. Gray (U. of Hull), "Liquid crystals - their origins and applications".

24 Nov. Mr. G. Russel (Alcan), "Designing for social acceptability".

1 Dec. Dr. B.F.G. Johnson (U. of Cambridge), "Chemistry of binary metal carbonyls".

* 2 Feb. Professor R.A. Raphael (U. of Cambridge), "Bizarre reactions of acetylenic compounds".

* 16 Feb. Professor G.W.A. Fowles (U. of Reading), "Home winemaking".

2 Mar. Professor M.W. Roberts (U. of Bradford), "The discovery of molecular events at solid surfaces".

* 9 Mar. Professor H. Suschitzky (U. of Salford), "Fruitful fissions of benzofuroxans".

4 May Professor J. Chatt (U. of Sussex), "Reactions of coordinated dinitrogen".

* 9 May Professor G.A. Olah (Case Western Reserve U., Ohio), "Electrophilic reactions of hydrocarbons".

Academic Year 1978 - 1979

* 10 Oct. Professor H.C. Brown (Purdue U.). "The tool of increasing electron demand in the study of cationic processes".

* 19 Oct. Mr. F.C. Shenton (Public Analyst, Co. Durham), "There is death in the pot".

* 26 Oct. Professor W.J. Albery (Imperial College, London), "Photogalvanic cells for solar energy conversion".

* 9 Nov. Professor A.R. Katritsky (U. of East Anglia), "Some adventures in heterocyclics".

* 16 Nov. Dr. H.C. Fielding (Mond Division, I.C.I.), "Fluorochemical surfactants and textile finishes".

23 Nov. Dr. C. White (Sheffield U.), "The magic of chemistry".

18 Jan. Professor J.C. Robb (Birmingham U.), "The plastics revolution".

8 Feb. Mr. C.G. Dennis (Vaux Ltd.), "The art and science of brewing".

* 1 Mar. Professor R. Mason (Govt. Scientific Advisor), "The Scientist in defence policy".

10 May Professor G. Allen (Chairman SRC), "Neutron scattering for polymer structures".

Academic Year 1979 - 1980

18 Oct. Dr. G. Cameron (U. of Aberdeen), "Synthetic polymers - twentieth century polymers".

25 Oct. Professor P. Gray (U. of Leeds), "Oscillatory combustion reactions".

* 1 Nov. Dr. J. Ashby (I.C.I. Toxicological Laboratory), "Does chemically-induced cancer make chemical sense?".

* 8 Nov. Professor J.H. Turnbull (R.M.C. Shrivenham), "Luminescence of drugs".

* 15 Nov. Professor E.A.V. Ebsworth (U. of Edinburgh), "Stay still, you brute: the shape of simple silyl complexes".

* 24 Jan. Professor R.J.P. Williams (U. of Oxofrd), "On first looking into biology's chemistry".

14 Feb. Professor G. Gamlen (U. of Salford), "A yarn with a new twist - fibres and their uses".

* 21 Feb. Dr. M.L.H. Green (U. of Oxford), "Synthesis of highly reactive organic compounds using metal vapours".

28 Feb. Professor S.F.A. Kettle (U. of E. Anglia), "Molecular shape, structure and chemical blindness".

* 6 Mar. Professor W.D. Ollis (U. of Sheffield), "Novel molecular rearrangements".

Research Conferences Attended

IXth International Symposium On Fluorine Chemistry, Avignon, 3 - 7 September 1979.

3rd Annual Congress of the Chemical Society, Durham, 9 - 11 April 1980.

First Year Induction Course

In each part of the course, the use and limitations of the various services available are explained by the people responsible for them.

Departmental organisation	Dr. E.J.F. Ross
Safety matters	Dr. M.R. Crampton
Electrical appliances and infrared spectroscopy	Mr. R.N. Brown
Chromatography and microanalysis	Mr. T.F. Holmes
Library facilities	Mr. W.B. Woodward (Keeper of science books)
Atomic absorptiometry and inorganic analysis	Mr. R. Coult
Mass spectrometry	Dr. M. Jones
N.m.r. spectroscopy	Dr. R.S. Matthews
Glassblowing techniques	Mr. W.H. Fettis and Mr. R. Hart

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