Fluorinated building blocks

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A THESIS
entitled

FLUORINATED BUILDING BLOCKS

submitted by

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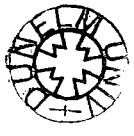
A candidate for the degree of Doctor of Philosophy

Department of Chemistry

2000



Eadem Mutata Resurgo

Acknowledgements

I would like to thank Professor R. D. Chambers and Dr. G. Sandford for all their help and support throughout this project. I would also like to thank Dr. J. Hutchinson for helpful discussions and to EPSRC for funding.

I would also like to mention all the other members of the fluorine group over the past three years for some interesting experiences, namely Ali, Bob, Chris, Christel, Darren, Elodie, Emmanuelle, Hadjar, Mandy, Paul, Phil and Tony.

This research could not have been achieved without the technical staff in the department, namely Dr Alan Kenwright, Mr Ian McKeag and Mrs Catherine Heffernan (NMR); Dr Mike Jones and Miss Lara Turner (Mass Spectroscopy); Dr Tony Royston (Computing); Mrs Jaraka Dostal (Elemental Analysis); Mr Lenny Lauchlan (Chromatography); Mr Ray Hart, Mr Gordon Haswell and Mr Malcolm Richardson (Glass blowing); Mr David Hunter (High Pressure Laboratory); Mr Jimmy Lincoln and Mr Joe Peel (Stores); Mrs Hazel Barker and Mrs Jean Parnaby (Laboratory Hygiene Staff); Mrs Irene Harries, Mrs Carole Hubery and Mrs Anne Carrahar (Secretarial staff) and many others.

Finally I would like to thank my family for all their help and support over the years.

Memorandum

The work described within this thesis was carried out at the University of Durham between October 1997 and September 2000. This thesis is the work of the author, except where acknowledged by reference and has not been submitted for any other degree. The copyright of this thesis lies solely with the author. No quotation from it should be published without prior written consent, and information derived from it should be acknowledged.

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

R. D. Chambers, G. Sandford, J. A. Cooper and C. M. Olivares
Free Radical Chemistry Part 12.
(In preparation for *J. Chem. Soc., Perkin Trans. I*)

and has been presented at:-

I.C.I. Poster Session, University of Durham, December 1999

Graduate Seminar, University of Durham, July 2000

16th International Symposium on Fluorine Chemistry, University of Durham, Durham, England, July 2000.

Abbreviations

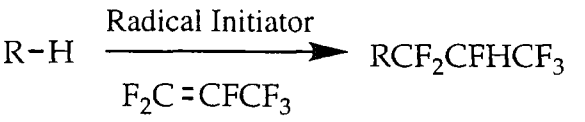
NMR	Nuclear Magnetic Resonance
IR	Infrared
GLC/MS	Gas-liquid Chromatography/Mass Spectroscopy
THF	Tetrahydrofuran
DTBP	Di-*tert*-Butyl Peroxide

Abstract

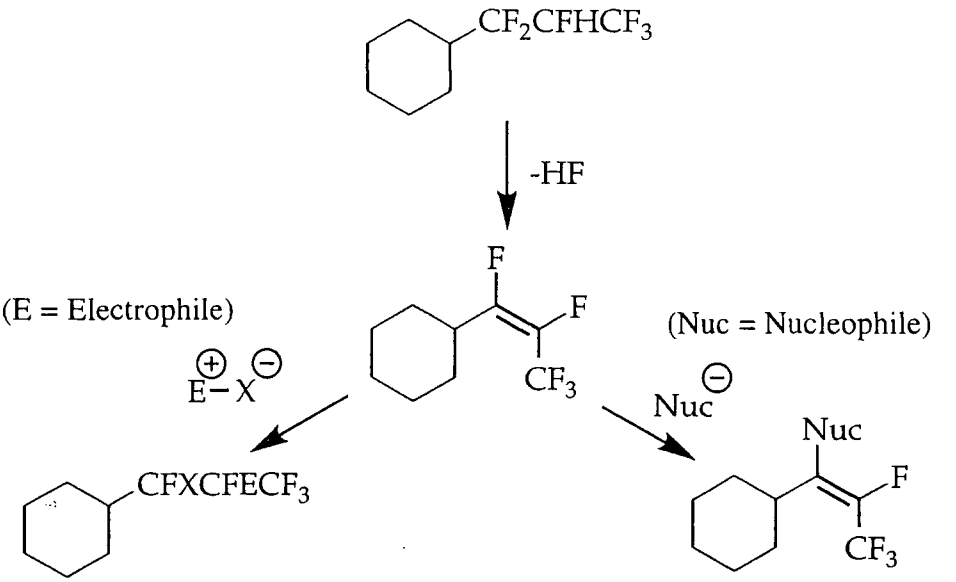
Fluorinated Building Blocks

Julian A Cooper

This work describes the functionalisation of carbon-hydrogen bonds in saturated hydrocarbons via free radical addition to fluorinated alkenes. For example, hexafluoropropene can be added to produce a mono-adduct:-



A range of fluoroalkenes have been used. These adducts can be functionalised by elimination of hydrogen fluoride to give new fluoroalkenes whose chemistry has been investigated.



This has resulted in new fluorinated building blocks.

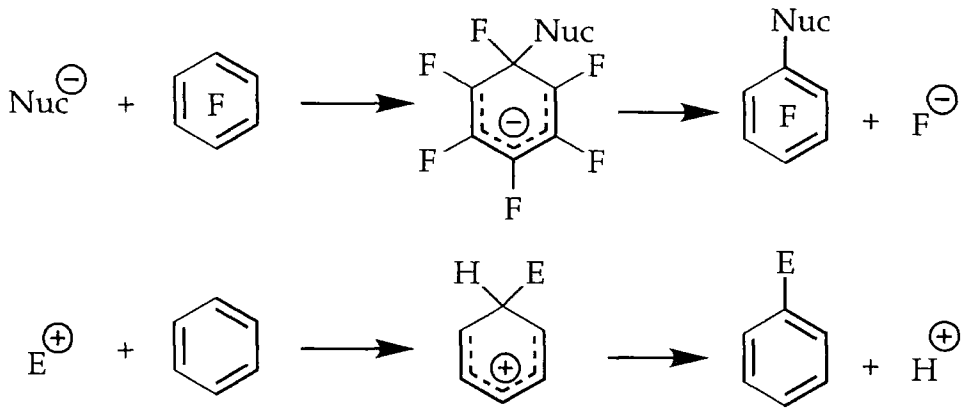
Contents

1. Fluorine in Organic Chemistry

1.1. Introduction

1.1.1. Fluorine in Organic Chemistry

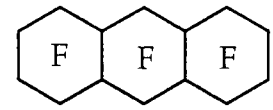
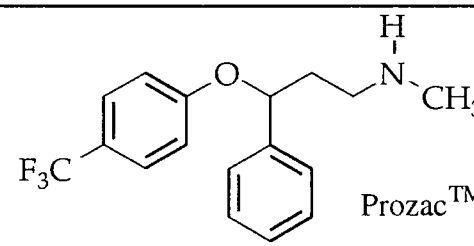
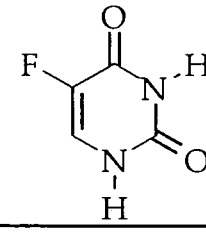
Very few naturally occurring organic compounds contain fluorine and so the field of organofluorine chemistry is almost completely man-made. Fluorine is the most electronegative element and consequently carbon-fluorine bonds are polarised.[1] Therefore fluorine is displaced from organic systems as fluoride ion F^-. This gives a complementary chemistry to hydrocarbon systems, where the proton H^+ acts as a leaving group. For example, fluoroaromatic compounds are attacked by nucleophiles to displace fluoride ion F^- in contrast to non-fluorinated systems which are attacked by electrophiles followed by loss of H^+.



The Van der Waals radius of a fluorine atom is 1.47 Å, which compares to 1.20 Å and 1.75 Å for a hydrogen and a chlorine atom respectively.[1] Therefore when a hydrogen atom is replaced by a fluorine atom, the electronic properties of the molecule are modified with only a small steric disruption. This enables incorporation of fluorine into organic molecules to promote useful biological activity. The carbon-fluorine bond is the strongest single bond to carbon in organic chemistry which imparts chemical and thermal stability to perfluorocarbons.

1.1.2. Applications

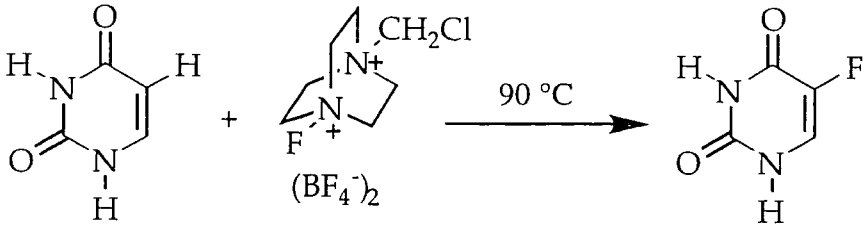
Fluorine has been incorporated into organic molecules which has resulted in a diverse range of applications,[2, 3] some of which are listed below.

Application	Example
Refrigerants	CF_3CH_2F
Fire Extinguishers	CF_3Br
Inert Fluids	
Non-stick Surfaces	$-(CF_2CF_2)_n-$ PTFE (Poly-tetrafluoroethylene)
Anaesthetics	$CF_3CHBrCl$ Fluothane™
Drugs	 Prozac™
Anti-cancer Agent	 5-fluorouracil

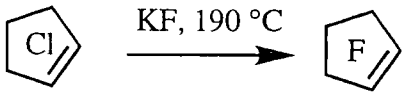
As the table above shows many applications for organofluorine compounds have been found. It is therefore of interest to study methodology for the incorporation of fluorine into organic molecules.

1.1.3. Introduction of Fluorine into Organic Molecules

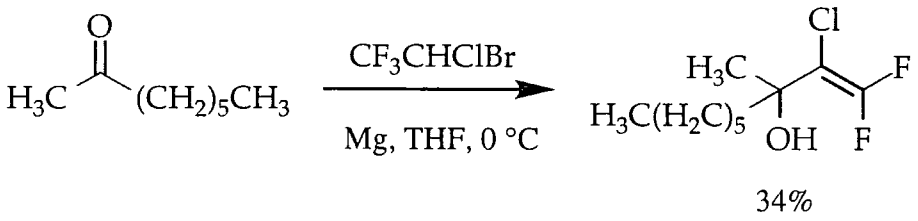
There are essentially two approaches to introducing fluorine into an organic molecule. The first approach concerns the formation of carbon-fluorine bonds by replacing an atom or group by fluorine. A complete discussion of the formation of carbon-fluorine bonds is beyond the scope of the current project and the reader is directed to material in the literature.[4] However, two examples are presented here. For example, Selectfluor™ is a synthetic equivalent[5] for the synthon F^+ and can introduce a fluorine atom at an electron-rich site, as in the synthesis of 5-fluorouracil:-



Carbon-fluorine bonds can also be formed by using a synthetic equivalent for the synthon F^-, for example[1] by using KF:-



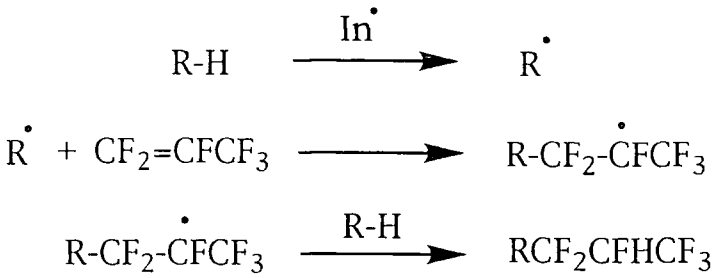
The second approach is the "building block" approach,[6] whereby molecules already containing carbon-fluorine bonds are used to produce new fluorinated molecules via carbon-carbon bond forming reactions. Fluoroalkyl groups can be introduced via electrophilic, nucleophilic or radical processes and has already been extensively reviewed.[7] For example, halothane ($CF_3CHClBr$) can be reacted with a ketone[8] to give a new fluorinated molecule:-



This project concerns the latter of these two approaches whereby fluorinated alkenes are used as building blocks[4] for the synthesis of more complex fluorinated molecules using free radical chemistry.

1.1.4. Aims of Current Project

The current project is concerned with functionalising carbon-hydrogen bonds by means of a free radical initiator. The new radical is then reacted with a fluorinated alkene such as hexafluoropropene and is an ongoing project in this laboratory.[9, 10]

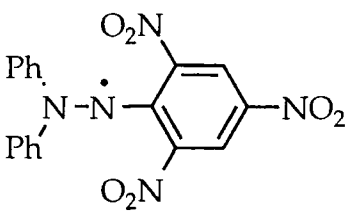


This will lead to new fluorine-containing systems whose chemistry is to be investigated to make new fluorinated building blocks. This chapter aims to give a review of free radical chemistry with fluoroalkenes, and in particular with hexafluoropropene.

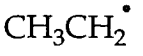
1.2. Free Radical Chemistry

1.2.1. Introduction

A free radical[11] is an uncharged odd electron species, which can typically be formed by homolytic bond cleavage of a substrate upon interaction with a radical initiator. The stability of free radicals varies enormously. For example, the diphenylpicrylhydrazyl radical (DPPH) is very stable:-



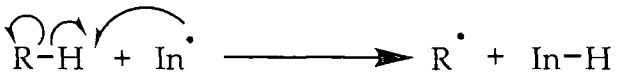
In contrast, some radicals exist only as transient intermediates in a chemical reaction, such as alkyl radicals:-



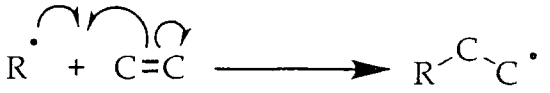
Factors which affect the stability of a radical will be discussed in detail later in this chapter.

1.2.2. Mechanism of Free Radical Addition to Alkenes

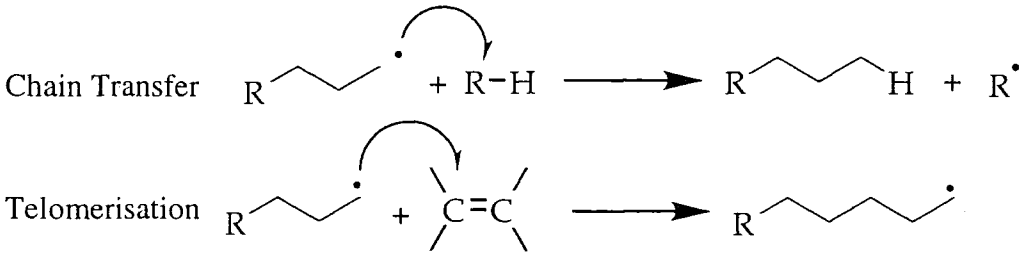
The first step in a free radical process is initiation by means of a radical initiator to give a carbon-centred free radical:-



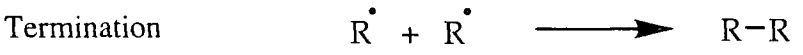
The radical formed then undergoes a series of propagation reactions, the first of which is addition to an alkene to give a new radical:-



The new radical formed undergoes further propagation reactions which are chain transfer and telomerisation:-



Termination of the radical process occurs when two radicals react with one another:-



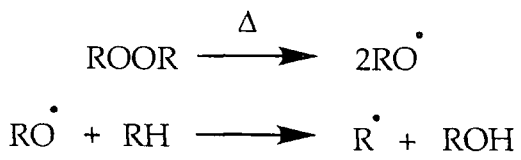
1.2.3. Radical Initiation

A free radical chain reaction can be initiated by a number of methods indicated below, and the reader is directed to reviews[11, 12] on the subject:-

Chemical (Compounds with weak bonds such as peroxides)
γ-rays
UV light
Redox Reactions (e.g. H_2O_2 and Fe^{2+})
Metal Hydrides (e.g. Bu_3SnH)
Thermal (~300 °C)

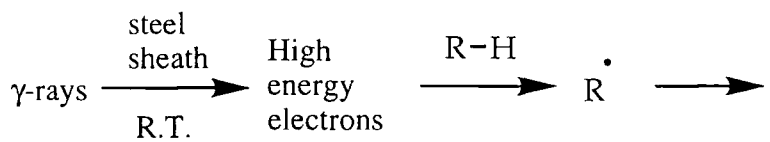
In the current project, chemical and γ-ray initiation were used and so are described more fully here. Chemical initiation is effected by thermal decomposition of compounds with unusually weak bonds, such as the O-O bonds in peroxides. Peroxides

are cleaved homolytically[13] to give radicals which can abstract a hydrogen atom from the substrate.



Dibenzoyl peroxide (DBPO) and di-*tert*-butyl peroxide (DTBP) are commonly used as free radical initiators. These reactions are carried out at 80 °C and 140 °C respectively[14] at which temperature their half-lives are about 4 hours.

The other initiation method used in this project is γ-rays from a cobalt-60 source. This facility is available in Durham and has the advantages that the reaction duration and temperature can be easily varied.[15] The substrate is not cleaved directly because γ-rays pass straight through organic material. Instead, the source is encased in a steel sheath which absorbs radiation and produces secondary electrons. These interact with the organic substrate to produce radical ions to dissociate into radicals as illustrated below:-



The major difference between these two initiation methods is that of temperature, as both involve hydrogen atom abstraction from the substrate. In this project the initiation step to produce a free radical involves hydrogen abstraction, which is discussed in detail below.

1.2.4. Hydrogen Abstraction

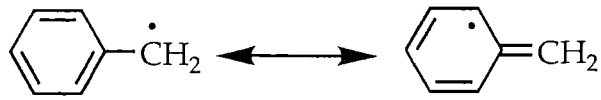
The Hammond Postulate states that in a reaction the transition state is considered to resemble the structure of the stable species nearest in energy. Hydrogen abstraction often has a large activation energy which means that the transition state occurs late in the reaction co-ordinate.[11] Therefore the stability of the radical formed is more important than polar effects when considering the activation energy for the reaction.

The hydrogen atom with the lowest bond dissociation energy (BDE) is abstracted which results in the formation of the most stable radical species. Indeed, the magnitude of the

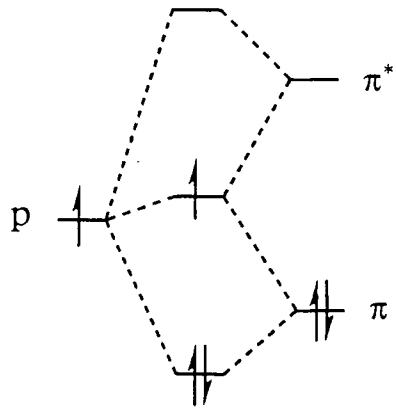
BDE is often taken as a means of radical stability. Some BDEs for hydrocarbons[11] are shown below:-

Substrate	BDE/kcalmol^{-1}
$PhCH_2$-H	85
CH_2=$CHCH_2$-H	86
$(CH_3)_3C$-H	96
$(CH_3)_2CH$-H	99
CH_3CH_2-H	101
CH_3-H	105

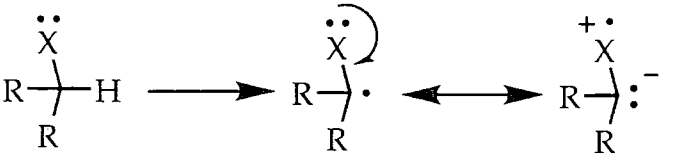
The great stability of the benzyl and allyl radicals results from the delocalisation of the unpaired electron with the π electrons.



From the table above, BDE data shows that radical stability is then in the order tertiary > secondary > primary > methyl. This has been claimed (but is not necessarily correct) to arise from hyperconjugation[11, 16] as the 2p orbital containing the unpaired electron can interact with the π and π^* orbitals of the alkyl group adjacent to the radical centre. These interactions stabilise the electrons in this orbital and slightly destabilise the unpaired electron, the overall result being energetically favourable.

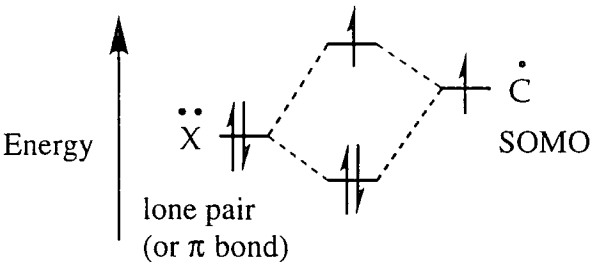


Heteroatoms can also have an effect on radical stability.[1] For example, an alkyl radical can be stabilised by an adjacent atom with a pair of non-bonding electrons via resonance:-



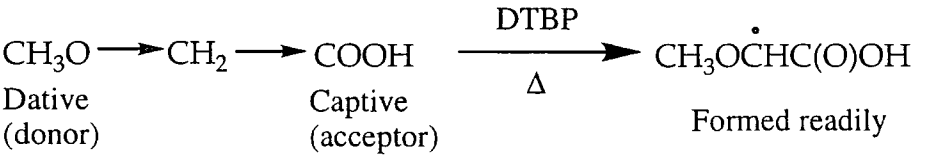
X = O, N, S or Hal

This stabilisation can be explained by Molecular Orbital theory:-

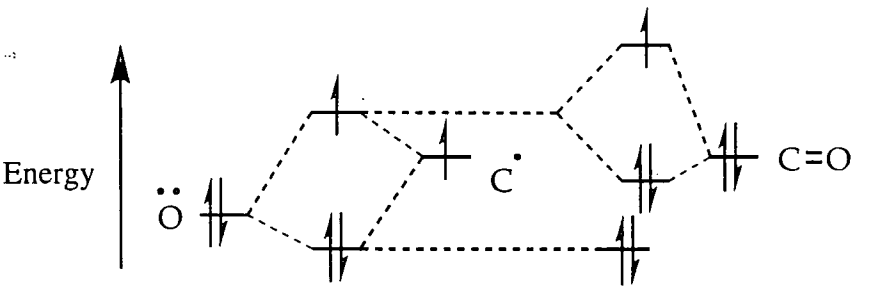


This resonance effect increases the electron density at the reaction centre, stabilising the radical.

Viehe[17] has argued that a combination of electron-withdrawing and electron-donating groups attached to the same carbon atom are especially stabilising. This is termed the Capto-Dative effect.

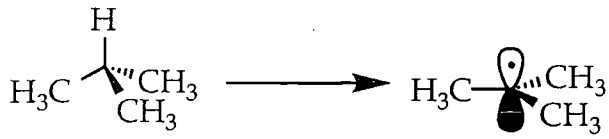


This can be illustrated by MO theory:-



This can be explained by a succession of orbital interactions. The acceptor stabilises the orbital with the unpaired electron as above, which means that it interacts more strongly with the donor than in the absence of the acceptor. This is sometimes referred to as a synergistic effect.

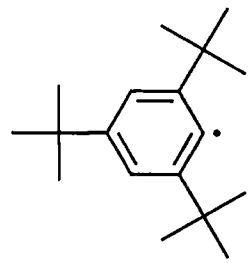
Steric factors can also be important in radical stability. For example, the release of steric compression on radical formation, which increases with more substituents, has a beneficial effect on the stability of the radical.



Release of steric compression

This may help to explain why the BDE for the tertiary radical is lower than that for the secondary or primary alkyl radicals, rather than any hyperconjugation effects claimed earlier.[16]

Hydrogen abstraction can sometimes result in a radical of great kinetic stability, which is usually due to steric crowding around the radical centre. For example, the 2,4,6-tri-*tert*-butylphenyl radical is electronically destabilised but the steric bulk of the *tert*-butyl groups prevents reaction occurring.



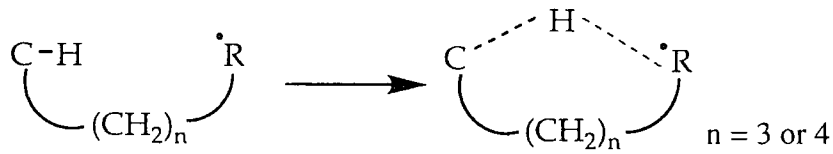
The activation energy of hydrogen abstraction by, for example, trifluoromethyl or methyl radicals shows evidence of an Evans-Polanyi relationship.[18] This gives a direct link between the strength of the carbon-hydrogen bond being broken and the activation energy.

$$E_a = \alpha[BDE(R\text{-}H) + \beta]$$

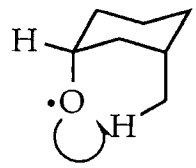
E_a = Activation Energy
α = Constant (depends on the radical)
β = Constant

This confirms the importance of the stability of the radical formed, although this relationship is only valid when polar effects are constant, indicating the importance of polarity. The effect of polarity on radical reactions is discussed later.

Free radicals can also react by intramolecular hydrogen transfer, such as 1,5 and 1,6 hydrogen migrations. These are common, as this allows the C-H-R transition state to be almost linear resulting in a lower activation energy.



When n is 1 or 2 the ring strain is too great but when n is greater than 5, entropy effects make hydrogen abstraction an unlikely event. For example,[11] the alkoxyl radical readily undergoes intramolecular hydrogen atom transfer:-



To conclude, in general the hydrogen atom with the lowest carbon-hydrogen BDE is abstracted preferentially to result in the most stable free radical.

1.2.5. Effects of Fluorine on Radical Stability

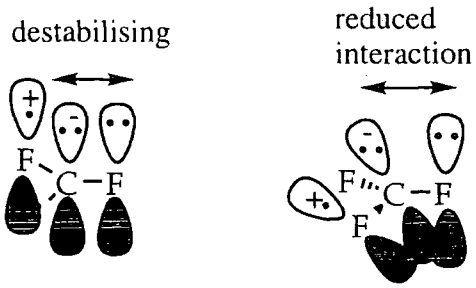
Fluorine atoms are relatively small and consequently the influence of a fluorine atom largely derives from electronic effects which can be sub-divided into σ inductive and π conjugative (resonance) effects.[16] As fluorine is the most electronegative element the σ inductive electron withdrawal is very strong. Fluorine is also a potentially strong π electron donor to carbon π systems, including the singly-occupied molecular orbital (SOMO) of a carbon radical, owing to good overlap with the lone pair 2p orbitals of fluorine with those of carbon.

The net effect of a fluorine substituent on radical stability is a complex interplay of these interactions,[16] and the effect of increasing the number of fluorine atoms is not additive and cannot be derived from understanding the effect of a single fluorine atom.

Fluorine has an effect on the shape of a radical. The methyl radical is planar, but substitution of hydrogen atoms by increasing numbers of fluorine atoms results in increasing loss of planarity.[11, 19]

Planar Pyramidal

It has been suggested[20] that this loss of planarity is as a result of repulsion between the lone pairs of electrons on the fluorine atoms with the unpaired electron on the carbon atom which would otherwise be destabilising.



It has also been argued[16] that rehybridisation has become induced as a result of the higher thermodynamic stability of C-F bonds which are high in p-character.

Molecular Orbital theory predicts that electronegative substituents with lone pairs of electrons should destabilise inductively due to their electronegative nature, and stabilise by resonance owing to their ability to delocalise the odd electron. Fluorine atoms which are α or β relative to a carbon radical centre have been claimed to destabilise inductively,[16] as the electron density at the radical centre is reduced. However, an α-fluorine substituent can give rise to stabilisation from its π-donating resonance interaction with the SOMO. The high electronegativity of fluorine results in the lone pairs of electrons being lower in energy and thus interact more weakly with the SOMO than would the lone pairs on oxygen or nitrogen. As delocalisation is most pronounced for a planar radical, this effect would be expected to be small.

The table below shows BDEs for fluorinated methanes,[21] and it is observed that one or two α-fluorine atoms provide a slight stabilisation owing to the π-electron donation.[22] However, the trifluoromethyl radical is almost tetrahedral in shape so that overlap for π conjugation is very poor, allowing the σ-inductive effect to dominate over any π stabilising effects. This accounts for its lower stability.[23]

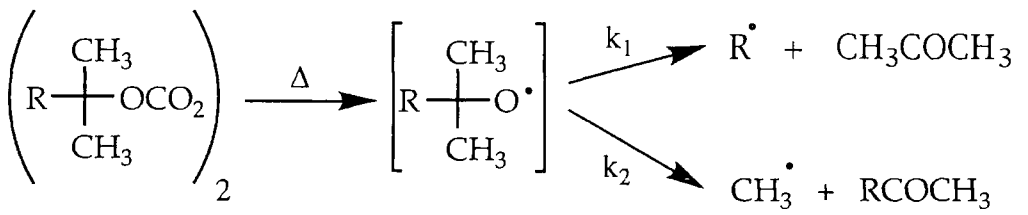
Methane	BDE/kcalmol^{-1}
CH_3-H	104.8 ± 0.2
CH_2F-H	101.2 ± 2
CHF_2-H	103.2 ± 2
CF_3-H	106.7 ± 1

The effect of a β-fluorine atom has been claimed to destabilise inductively as the electron density at the radical centre is reduced.[16] BDEs for fluorinated ethanes are shown below, and some of them are calculated[24] because experimental data is incomplete. It should be noted that for ethane there is a disagreement between the experimental and calculated values, but what is important are the relative values in each table.

Experimental		Calculated	
Ethane	BDE/kcalmol^{-1}	Ethane	BDE/kcalmol^{-1}
CH_3CH_2-H	101.1 ± 1	CH_3CH_2-H	97.7
CF_3CH_2-H	106.7 ± 1	CH_2FCH_2-H	99.6
CH_3CF_2-H	99.5 ± 2.5	CHF_2CH_2-H	101.3
CF_3CF_2-H	102.7 ± 0.5	CF_3CH_2-H	102.0

Even a single β-fluorine atom appears to destabilise relative to hydrogen. Results from high level calculations[25, 26] are consistent with the BDE data presented above.

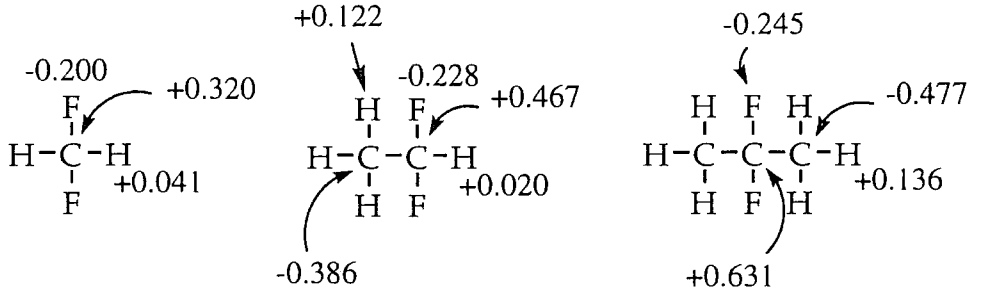
Experimental evidence in support of an order of stability[27] comes from radical fragmentation of a series of fluorinated *tert*-butoxy radicals:-



R	k_1/k_2 (k_{rel})
CH_3	1.0
CH_2F	9.0
CHF_2	10.2
CF_3	0.08

In this experiment the value of k_1/k_2 is greater than unity for CH_2F and CHF_2, indicating that k_1 is faster than k_2. This shows that these radicals form preferentially relative to the CH_3 radical and are therefore more stable. This is in contrast to the CF_3 radical where k_1 is lower than k_2, showing that this radical is less stable than the methyl radical.

One recent study[28] has shown that electrostatics arising from polarised carbon-fluorine bonds provides an explanation for the observed C-H BDEs. The atomic charges on CH_2F_2, CH_3CHF_2 and $CH_3CF_2CH_3$ are illustrated below:-

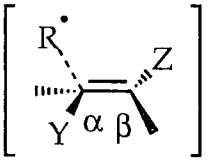


There appears to be a mild electrostatic repulsion between the α-C and α-H atoms of CH_2F_2 and CH_3CF_2H which causes some C-H bond weakening and consequently easier formation of a radical relative to a hydrocarbon system. There is a mild attraction between the α-C and α-H atoms of $CH_3CF_2CH_3$ causing bond strengthening and consequently this radical with β-fluorine atoms does not form so readily.

1.2.6. Free Radical Addition to Alkenes

1.2.6.1. Rate and Polar Effects

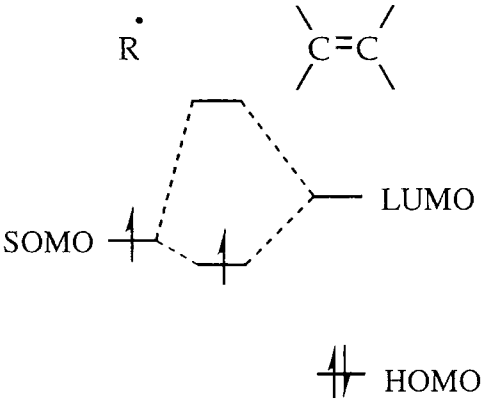
Addition of a radical to an alkene is exothermic[29] as a strong σ bond is formed and a weak π bond is broken overall. The transition state occurs early in the reaction co-ordinate and consequently polar and steric effects are important rather than the stability of the radical formed. The transition state is unsymmetrical and owing to the distance between the attacking radical and the β-carbon substituent Z, it's steric effects are unimportant.[30]



However, the α-substituent Y can exert steric repulsive forces.

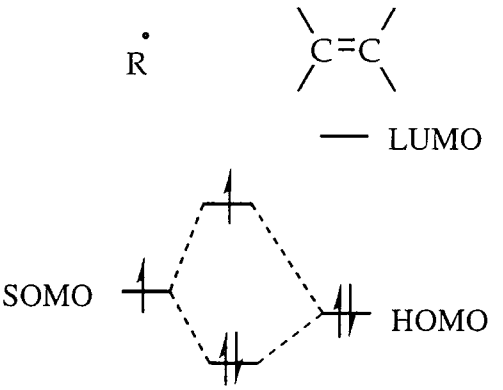
The early transition state and absence of steric β-effects enables the polar effects of free radical addition to be described in terms of Frontier Orbital theory.[30] This states that the energy difference between the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of the reacting species determine rate variations. A small energy difference between these frontier orbitals results in stabilisation of the transition state when the reactants approach one another and consequently a faster rate of reaction. The frontier orbital of a free radical is the singly occupied molecular orbital (SOMO). Therefore, interaction between the SOMO of the free radical and the LUMO and HOMO of the alkene enable polar effects to be interpreted and predicted.

In the MO diagram shown below, the SOMO of the radical is high and so it interacts with the LUMO of the alkene:-



A radical containing electron-donating groups such as a tertiary alkyl radical increases the energy of the SOMO. Electron-withdrawing substituents on the alkene decrease the energy of the LUMO, and this results in a much smaller SOMO-LUMO energy difference and consequently a faster rate of reaction. This is why a *tert*-butyl radical reacts more rapidly with electron-deficient alkenes than with an electron-rich alkene. Therefore alkyl radicals can be termed nucleophilic.

The SOMO of a radical with strongly electron-withdrawing substituents such as fluorine is low in energy so that the SOMO-HOMO interaction becomes important.



The radical is then considered to be electrophilic, for example as in the trifluoromethyl radical.

Free radicals can exhibit nucleophilic or electrophilic behaviour, depending on the SOMO-HOMO and SOMO-LUMO energy difference and therefore by the substituents at the radical centre and on the alkene.

For example,[31] the nucleophilic methyl radical reacts faster with tetrafluoroethene than with ethene, and the electrophilic trifluoromethyl radical reacts faster with ethene. The ratio of addition rates is shown in the table below:-

Radical	$k_{C_2F_4}/k_{C_2H_4}$ (164 °C)
$CH_3^{\bullet}$	9.5
$CF_3^{\bullet}$	0.1

Although polar effects are primarily responsible for the rate of addition of a radical to an alkene, the pyramidal shape of a fluorinated radical may also account for the increased reaction rate. Substantial bending (14-15° from planarity) is required in the transition state for addition of an alkyl radical to an alkene and so a fluorinated system may be at an energetic advantage.[32]

1.2.6.2. Regiochemistry

The regiochemistry of radical addition to an alkene depends on steric and polar effects.[31] As the table below shows,[31] addition of radicals to the alkene CH_2=CHX occurs preferentially at the CH_2 carbon atom (α-site), because the CHX carbon atom (β-site) is sterically hindered towards radical attack. These reactions were all conducted in the gas phase.[31]

$$R^{\bullet} + \overset{\alpha \quad \beta}{CH_2=CH-X}$$

X	$CH_3^{\bullet}$		$CF_3^{\bullet}$		$CCl_3^{\bullet}$	
	$2k_\alpha/k_e$	α:β	$2k_\alpha/k_e$	α:β	$2k_\alpha/k_e$	α:β
H	1	1:1	1	1:1	1	1:1
CH_3	0.7	1:0.15	2.3	1:0.1	4	1:0.07
F	0.9	1:0.20	0.48	1:0.09	0.7	1:0.08
Cl	4.2	1:<0.01	1.3	1:<0.01	2.5	1:<0.01
CF_3	0.9	1:0.33	0.40	1:<0.02	0.9	1:<0.01

k_α = rate with $CHX=CH_2$

k_e = rate with ethene

The orientation is not dictated by polar factors, as the electrophilic trifluoromethyl radical and the nucleophilic methyl radical both add preferentially to the α-site in propene and 3,3,3-trifluoropropene. However, small polar effects can often be observed, as the proportion of methyl radical attack at the β-position is greater with 3,3,3-trifluoropropene than with propene itself.

Steric factors arising from the attacking radical are also important,[31] as can be seen from the addition of branched chain radicals to vinyl fluoride:-

α β
$H_2C=CHF$

Radical	Ratio α:β	$2k_\alpha/k_e$
$CF_3^\bullet$	1:0.1	0.5
$CF_3CF_2^\bullet$	1:0.06	0.6
$(CF_3)_2CF^\bullet$	1:0.02	0.5
$(CF_3)_3C^\bullet$	1:0.005	0.6

The similarity of the $2k_\alpha/2k_e$ values confirms that the large variation in orientations is due to steric hindrance to attack at the β-position, rather than differences in polarity.

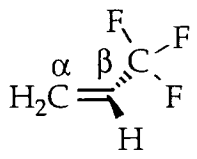
The table below[31] shows the rates and orientations of methyl and three fluoromethyl radicals to fluoroethenes:-

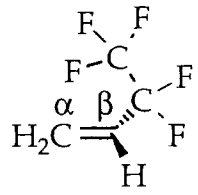
Radical	α β $H_2C=CHF$		α β $H_2C=CF_2$		α β $FHC=CF_2$	
	k/k_e	α:β	k/k_e	α:β	k/k_e	α:β
$CH_3^\bullet$	1.1	1:0.2	-	-	5.8	1:2.1
$CH_2F^\bullet$	0.4	1:0.3	-	1:0.4	-	1:2.0
$CHF_2^\bullet$	0.4	1:0.2	0.1	1:0.1	0.3	1:0.9
$CF_3^\bullet$	0.5	1:0.1	0.2	1:0.04	0.05	1:0.5

For vinyl fluoride, all four radicals attack the α-carbon atom and as the orientation ratios are similar, the electronegative character of the radical appears to be unimportant. The greater steric bulk arising from the fluorine atom explains the results.

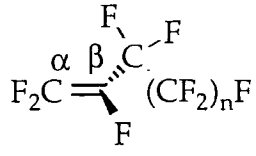
However, polar effects can influence the orientation of addition, as the extent of attack at the β-carbon atom of 1,1-difluoroethene decreases as the radical becomes more electrophilic. This is confirmed by the addition of the nucleophilic methyl radical to trifluoroethene where the orientation of addition is reversed. The total polarity difference between the α and β positions in trifluoroethene is the same as that for vinyl fluoride, but a second fluorine atom on a vinylic site does not double the steric hindrance. Therefore the difference in steric hindrance between the two carbon atoms in trifluoroethene is less than that for vinyl fluoride, so polarity becomes important.

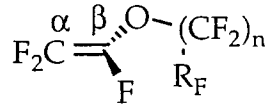
If the X-substituent on an alkene of the type $CH_2=CHX$ is a perfluoroalkyl group, the lone pairs of electrons on the fluorine atoms give rise to stereoelectronic shielding of the β-carbon atom.[33]





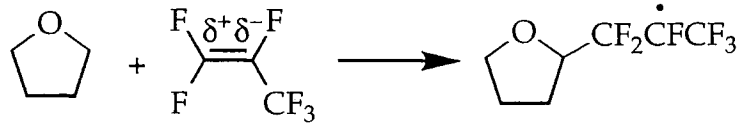
In 3,3,3-trifluoropropene the three fluorine atoms impart some steric shielding at the β-carbon atom. In contrast, the larger number of fluorine atoms in 1-(perfluoroalkyl)ethenes results in high stereoelectronic shielding of the reaction site and consequently radical attack is highly regioselective. This has been termed the "tail effect" by Paleta[34] and is also applicable to perfluorinated systems.[35, 36]



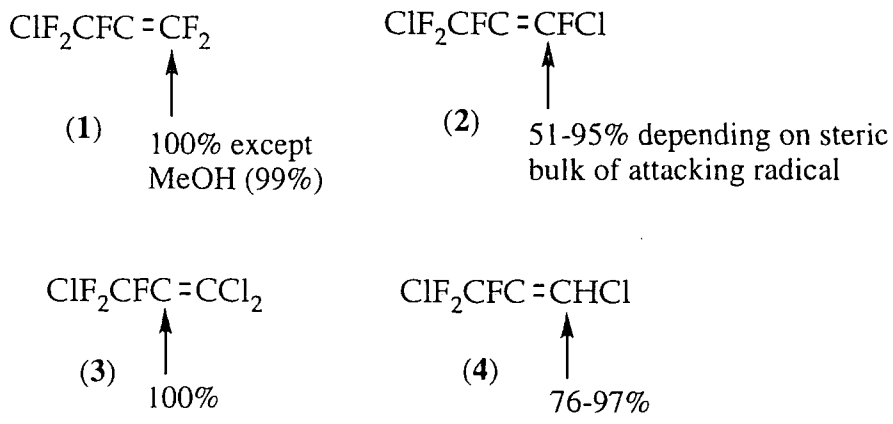


Selectivity of radical addition to perfluoroethenes is high, with little or no attack occurring at the β-carbon atom. In contrast, perfluorovinyl ethers display a lower degree of selectivity, caused by the presence of an oxygen atom near the double bond rather than a CF_2 group so that steric hindrance is reduced.

Addition of nucleophilic radicals such as an ether to hexafluoropropene occurs virtually exclusively at the CF_2 carbon atom, as the steric and electronic effects reinforce each other regarding regiochemistry.[9] Electronically the CF_2 carbon atom is more electrophilic, and sterically is less crowded as the CF carbon atom is directly bonded to the bulky trifluoromethyl group.[37]



The great complexity of factors affecting the orientation of radical addition to alkenes has recently been studied by Paleta.[34] This paper describes reactions of some chlorofluoropropenes with nucleophilic radicals derived from alcohols and ethers. Four chlorofluoropropenes were used, whose structures and orientations of radical attack are summarised below:-



A selection of examples which demonstrates the orientation of addition are shown below:-

$$CH_3\dot{C}HOH + CF_2Cl\text{-}CF{=}CXY \longrightarrow$$

X	Y	Relative amount of attack at CXY (%)
F	F	100
F	Cl	73
Cl	Cl	0
H	Cl	86

Replacement of successive CF_2 fluorine atoms by chlorine atoms in the alkenes shown above resulted in a decrease of the reaction rate. Chlorine is less electronegative than fluorine and so the energy difference between the radical SOMO and the alkene LUMO is greater, which has been explained by Frontier Orbital theory.[30] The complete reversal of orientation of attack at (**3**) compared to (**1**) is due to the steric hindrance associated with the presence of two bulky chlorine atoms, and compound (**2**) exhibits some steric hindrance which accounts for the low regioselectivity.

Alkene (**4**) was found to react with radicals faster than (**2**) and this can also be accounted for by Frontier Orbital theory. Although the CHCl carbon atom is less sterically hindered than the CFCl carbon atom, the latter is more electrophilic.

The better regioselectivity of (**4**) over (**2**) can be accounted for by considering the unshared electron pairs on the CFCl fluorine atom of (**2**). This may result in electronic repulsion of an incoming nucleophilic radical. A hydrogen atom has no unshared electron pairs to cause this repulsion.

These examples above illustrate the complexity of polar, steric and stereoelectronic factors which must be taken into account when rationalising or predicting radical reactions with alkenes.

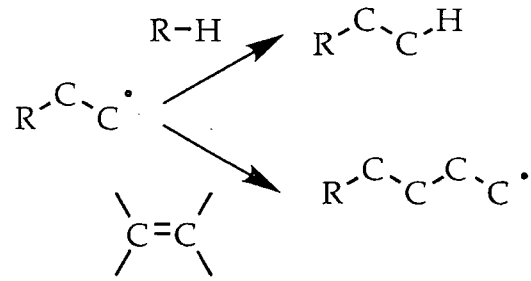
1.2.7. Chain Transfer

As was shown in the overall reaction scheme, chain transfer completes the free radical addition process. Although hydrogen abstraction was discussed in section 1.2.4, hydrogen abstraction by a fluorinated radical is the final step when a substrate-alkene mono-adduct is produced. Fluorinated radicals have been shown to be electron-deficient and therefore have an enhanced rate towards hydrogen atom abstraction compared to alkyl radicals.[16] Some rate constants[38] of hydrogen abstraction are illustrated in the table below, where R represents an alkyl group:-

	k_{rel}			
Substrate	$RCH_2CH_2^{\bullet}$	$RCF_2CF_2^{\bullet}$	$n\text{-}C_4F_9^{\bullet}$	$i\text{-}C_3F_7^{\bullet}$
Cyclohexane	0.014	(1)	1.1	5.6
THF	0.017	(1)	1.1	11
1,4-dioxane	-	(1)	0.8	2.2
t-$BuMe_2SiH$	0.004	(1)	2.6	37
C-H BDE	101.1	101-102	103.3	103.6

The $i\text{-}C_3F_7$ radical is not pyramidal as there is only one fluorine atom at the radical centre, so the high reactivity is due to electrophilic effects. It is more electrophilic than the $n\text{-}C_4F_9$ radical owing to the increased number of β-fluorine atoms and this is indicative of the importance of polar effects in the transition state.

The new radical formed on addition of a radical to a fluoroalkene can either undergo chain transfer or telomerisation.



When hexafluoropropene is used, chain transfer occurs preferentially resulting in the formation of mono-adducts. Some alkenes form telomers, and this is discussed in the next section.

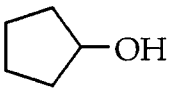
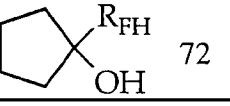
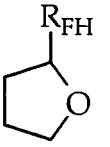
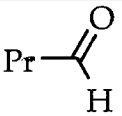
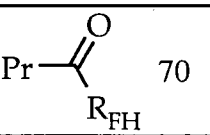
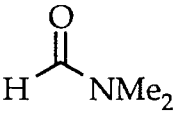
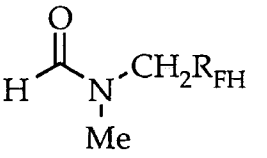
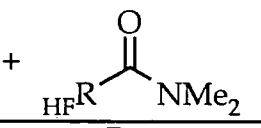
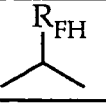
1.3. Radical Additions to Fluoroalkenes

1.3.1. Radical Additions to Fluoropropenes

1.3.1.1. Hexafluoropropene

Radical additions to hexafluoropropene have been extensively reviewed in previous theses from this laboratory[7, 39] so an overview of material described in the literature is presented here. Hexafluoropropene is a useful fluoroalkene to investigate as it is industrially available, cheap and only forms a homopolymer under extreme conditions.[40] As it is very electron-deficient, it reacts readily with nucleophilic radicals to give mono-adducts. In this laboratory, hexafluoropropene has been added to a range of oxygen[10, 37] and nitrogen-containing compounds[41, 42] as well as to hydrocarbons.[9] Reaction with alcohols, aldehydes and ethers is very favourable owing to the nucleophilicity of the radicals, although reaction with amines is complicated by a competing nucleophilic pathway from attack by the lone pair of electrons on the nitrogen atom.[42] Some examples are illustrated below which show the range of substrates that can be functionalised.

Radical Reactions to Hexafluoropropene

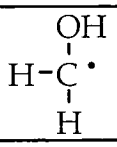
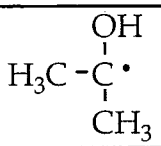
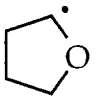
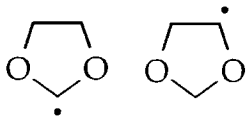
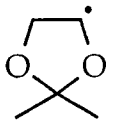
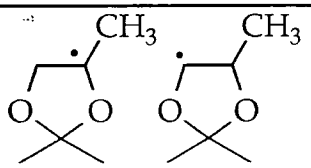
Substrate	Ratio R-H:HFP	Initiator	Products and Yields (%)
	1:1.14	γ-rays[10]	 72
	4:1	γ-rays[37]	 95
	1:1	DBPO[43]	 70
	2.4:1	γ-rays[41]	 50 +  23
	1:1.2	γ-rays[9]	 54

$R_{FH} = CF_2CFHCF_3$

Although much of the work carried out with hexafluoropropene demonstrated that nucleophilic radical attack occurred exclusively at the CF_2 carbon atom, recent work by Paleta[35] has shown that some attack (1-4.5%) does occur at the $CFCF_3$ carbon atom. This is especially when initiation is effected by UV light, which is high in energy. The fact that many of the older papers in the literature do not mention this is most likely because of the improved analytical methods available in the last few years, and in particular the advances in NMR.

Some examples from the literature are given below:-

Orientation of Radical Attack at Hexafluoropropene

Radical	Initiator	Ratio of attack CF_2:$CFCF_3$
	UV,[44] Peroxide[45, 46]	95.5-98:2-4.5
	UV,[44] Peroxide[45, 46]	100:0
	UV[36]	98:2
 92 : 8	UV[35]	99:1
	UV[35]	99:1
 87 : 13	UV[35]	100:0

Quite often with nucleophilic radicals there is no trace of attack at the central carbon atom and this could be due to steric and electronic effects. For example, Haszeldine[44] showed that when hexafluoropropene was reacted with a range of alcohols, reverse-addition was observed for methanol only and not for alcohols of the general formula RCH_2OH or R^1R^2CHOH.

A polar effect can be observed, for example with the addition of thiols.[1] Increasing the electrophilicity of the thioyl radical increases the amount of attack at the central carbon atom.

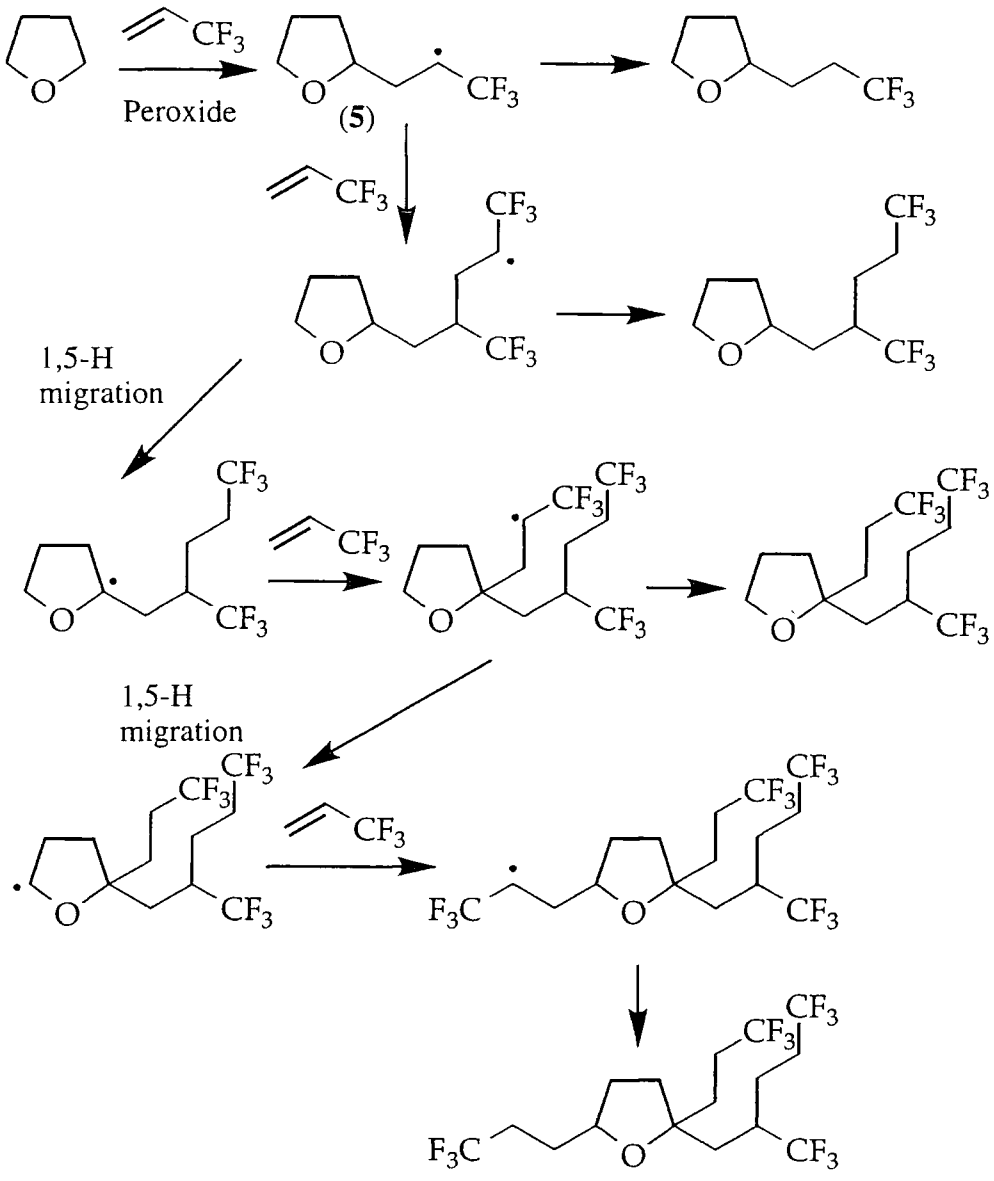
Nevertheless, hexafluoropropene is still a highly efficient method of incorporating fluorine into organic molecules.

1.3.1.2. 3,3,3-Trifluoropropene

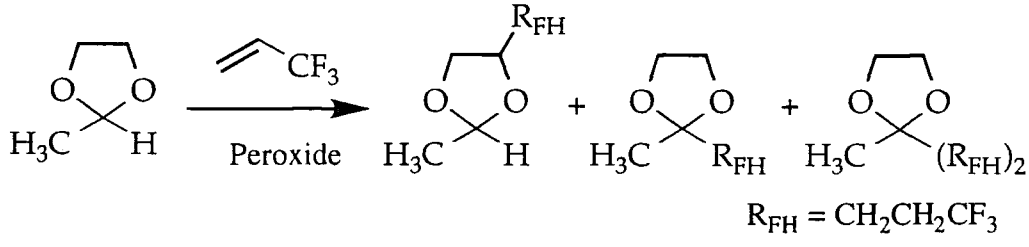
In contrast to hexafluoropropene, telomerisation of 3,3,3-trifluoropropene competes successfully over chain transfer and consequently can be reacted with a range of telogens. The telomer length can be controlled by varying the ratio of the two reactants and a range of initiators can be employed. Although addition of HBr to alkenes is normally ionic, the need for UV initiation confirmed the radical mechanism.

Telogen	Initiator	Telomer Structure
$(CH_3)_2C(OH)H$	γ-rays at 90 °C[47]	$(CH_3)_2C(OH)[CH_2CHCF_3]_nH$
CBr_4	DBPO[48]	$Br_3C(CH_2CHCF_3)_nBr$ n = 1-3
CF_3I	UV, 5 days[49]	$CF_3(CH_2CHCF_3)_nI$ n = 1 or 2
HBr	UV[49]	$CF_3CH_2CH_2Br$

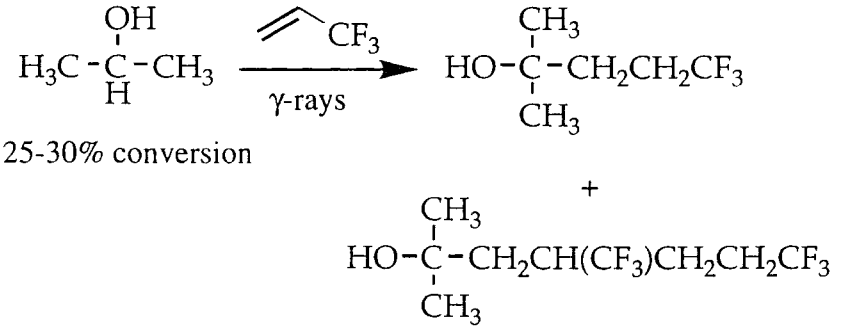
Although 3,3,3-trifluoropropene forms telomers readily, attempts have been made to isolate mono-adducts by employing stringent conditions. Bergstrom showed that 3,3,3-trifluoropropene could be added to tetrahydrofuran and mono-adduct could be isolated by using a large excess of substrate.[50] However, no yield was given. As the following reaction scheme shows, the newly-formed radical (**5**) reacts readily with another molecule of alkene. This, combined with 1,5-hydrogen migrations, produces a mixture of adducts of varying molecular weights.



This illustrates just how complex these reactions are, even when a large excess of substrate is used. A similar reaction using diethyl ether has been performed earlier in this laboratory,[51] but γ-ray initiation even using a vast deficiency of alkene gave a viscous liquid of high molecular weight (M > 500). 3,3,3-Trifluoropropene has also been reacted with 2-methyl-1,3-dioxolane[52] to give a mixture of adducts and telomers, but no yields were reported:-



Russian workers have successfully reacted 3,3,3-trifluoropropene with iso-propanol[47] to give mono- and di-adducts:-

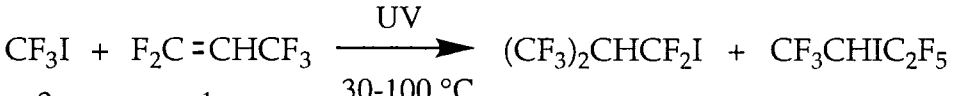


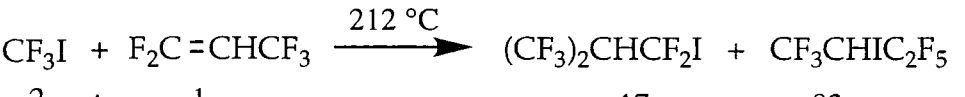
Although yields were not given, the formation of a large amount of higher molecular weight telomers was avoided by carrying it out as a continuous process so that the total alkene concentration remained very low at all times. This forced chain transfer to compete over telomerisation.

No examples were found in the literature with any hydrocarbons as the telogen.

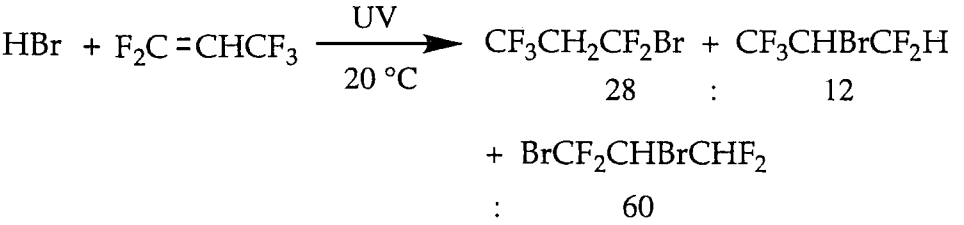
1.3.1.3. 1,1,3,3,3-Pentafluoropropene

Haszeldine[53] has shown that CF_3I can be successfully reacted with 1,1,3,3,3-pentafluoropropene to give a mixture of mono-adducts. The formation of higher molecular weight telomers did not occur.

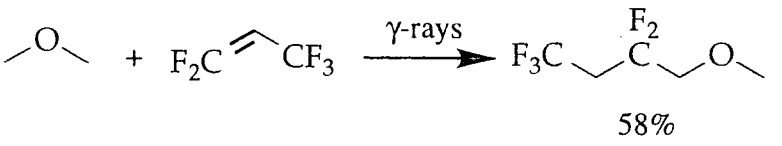




Attack of the trifluoromethyl radical occurred predominantly at the less sterically-hindered CF_2 carbon atom. Bromine atoms[53] have also been added to give a mixture of products:-



The only example found in the literature where 1,1,3,3,3-pentafluoropropene is added to a molecule via carbon-hydrogen bond functionalisation[51] was that of dimethyl ether, carried out earlier in this laboratory:-



This reaction was regioselective and no telomer formation was reported. However, the relatively low yield was due to the low reactivity of the alkene as a large quantity of unreacted starting material was recovered. Despite the fact that reaction of 1,1,3,3,3-pentafluoropropene appeared to be selective and would open up new synthetic possibilities, this has not yet been fully investigated.

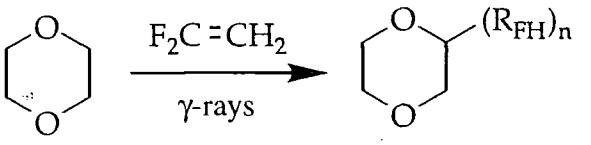
1.3.2. Radical Additions to Fluoroethenes

1.3.2.1. 1,1-Difluoroethene

Telomers of 1,1-difluoroethene can be formed using a variety of telogens.[54]

Telogen	Initiator	Telomer Structure
CF_2Br_2	190 °C[55]	$CF_2Br(C_2H_2F_2)_nBr$
Cl_3C-H	DTBP[56]	$Cl_3C(C_2H_2F_2)_nH$ n > 3
CF_3I	UV[57]	$CF_3(CH_2CF_2)_nI$ n = 1
CF_3S-SCF_3	UV[58]	$CF_3S(C_2H_2F_2)_nSCF_3$ n = 1-6

Reaction of 1,1-difluoroethene with an ether via functionalisation of a carbon-hydrogen bond was investigated in this laboratory,[59] but high molecular weight products resulted:-



n = 250 on average

$R_{FH} = CF_2CH_2$

There do not appear to be any examples in the literature where a hydrocarbon molecule is reacted with 1,1-difluoroethene.

1.3.2.2. Chlorotrifluoroethene

Chlorotrifluoroethene forms telomers readily and consequently has been extensively investigated using a range of telogens and initiators. A few examples are given below, and for a more detailed summary the reader is directed to a recent review.[54]

Telogen	Initiator	Telomer Structure
Alkane R-H	DBPO[60]	$R(CF_2CFCl)_nH$ n = 1-3
CH_3OH	H_2O_2[61]	$CH_2OH(CF_2CFCl)_nH$ n = 3-5
C_2F_5I	DBPO[62]	$C_2F_5(CF_2CFCl)_nI$ n = 1-3
CCl_4	CuCl[63]	$CCl_3(CF_2CFCl)_nCl$ n = 1

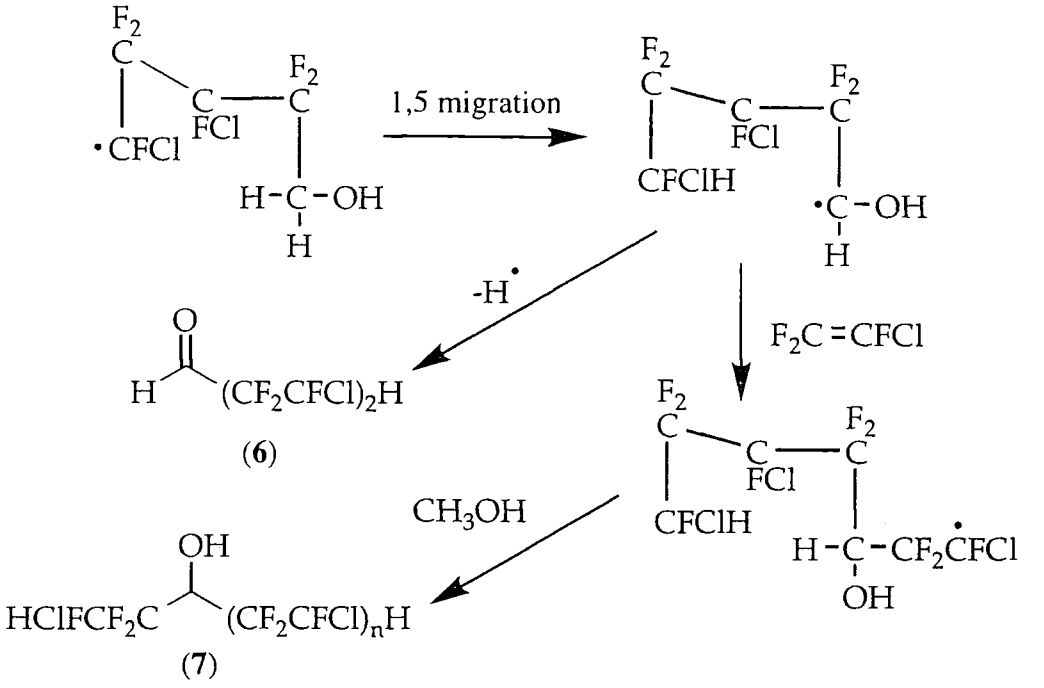
Despite the fact that telomer formation occurs readily, there has been much investigation on the addition of chlorotrifluoroethene to organic molecules by functionalisation of carbon-hydrogen bonds. Alcohols, diols, aldehydes, ethers and amines have all been investigated and some examples are described below.

Addition to Alcohols

Addition of chlorotrifluoroethene to various alcohols such as methanol[64] have been investigated:-

$$CH_3OH \xrightarrow[\text{DTBP, UV or } \gamma\text{-rays}]{F_2C=CFCl} CH_2OH(CF_2CFCl)_nH$$

A mixture of telomers of varying molecular weights resulted with radical attack occurring preferentially at the CF_2 carbon atom owing to the steric bulk of chlorine. Although all three methods of initiation gave a complex mixture of products, initiation using UV gave a high proportion of products where n = 1 or 2 as shown in the table (overleaf). When UV or γ-rays were used, some mono-adduct resulting from radical attack at the CFCl carbon atom was observed, but no telomers resulted from this mode of addition. However, two more products were reported in these reactions which resulted from 1,5-migration of an α-hydrogen atom in one of the telomer radicals:-



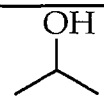
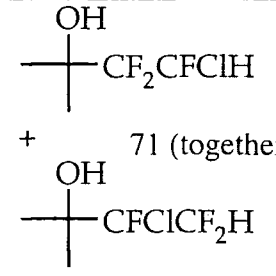
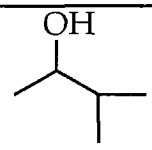
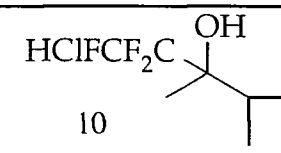
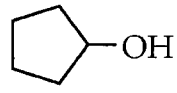
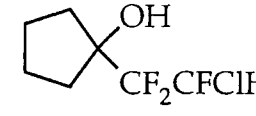
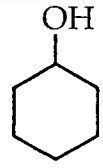
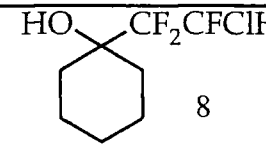
Ratio			Product Yields (%) (with respect to CTFE)					
R-H:CTFE	Initiator	T/°C	n = 1	R/A	n = 2	n = 3	(**6**)	(**7**)
7.8:1	DTBP	140	1.0	0	1.8	1.5	1.1	0.9
4.8:1	γ-rays	20	7.5	0.3	7.4	9.3	0.3	4.2
3.4:1	UV	65	13.0	1.9	1.3	0.5	0.6	0.8
23.5:1	UV	20	27.0	2.9	9.4	2.4	0	3.5
21:1	UV	20	35.9	3.7	12.8	2.0	0	2.8

R/A = Reverse Addition (attack at CFCl)

Comparison of the results from the table is difficult as the reactant ratios are different for each experiment. However, a large excess of telogen at a low temperature (20 °C) appears to favour mono-adduct formation. All of the reactions were reported to give a distillation residue which consisted of higher molecular weight telomers.

Addition to ethanol[65] and 1-propanol[66] gave entirely similar products to those obtained with methanol, including the ketone (**6**) and tri-adduct (**7**). In the case of ethanol a yield of 24-31% was achieved using a large excess of substrate (5.4:1) with γ-ray initiation, which is a good yield considering the problems of telomerisation.

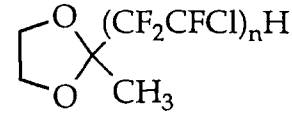
Secondary alcohols have also been added to chlorotrifluoroethene[67, 68] and a summary of the mono-adducts produced is given below:-

Alcohol	Ratio R-H:CTFE	Initiator	Product and Yield (%)
	1.9:1	UV	 71 (together)
	1.8:1	γ-rays	 10
	2.4:1	UV	 18
	1.3:1	γ-rays	 8

The addition of chlorotrifluoroethene to 2-propanol was reported to have been performed in a flow system, thus allowing a low steady concentration of alkene to avoid telomerisation. This accounted for the unexpectedly high yield, but also resulted in some reverse-addition product (about 5%). For the remaining secondary alcohols, no reverse-addition compounds were reported which may be a reflection of the increased steric bulk surrounding the carbon-centred radical. In all of the reactions with alcohols except for methanol and ethanol, a trace quantity of products arising from reduction of the C-Cl bond to a C-H bond was also observed.

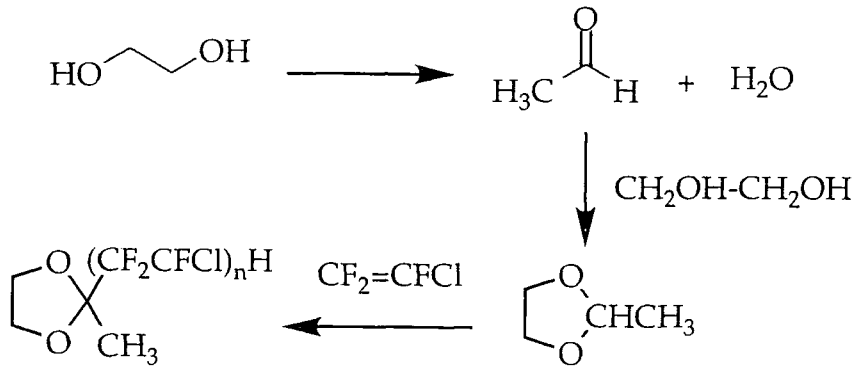
Addition to Diols

Addition of chlorotrifluoroethene to ethane-1,2-diol[69] by UV radiation only occurred if acetone was used as a photosensitiser. The major product was unexpectedly a substituted 1,3-dioxolane:-



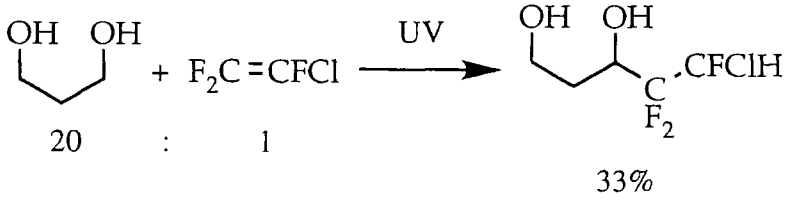
n = 1 33%
n = 2 4%

This was thought to arise from cleavage of the 1,2-dihydroxyethyl radical to give acetaldehyde and water. The aldehyde is acetylated with the 1,2-diol starting material to give the dioxolane, which then reacted with chlorotrifluoroethene:-

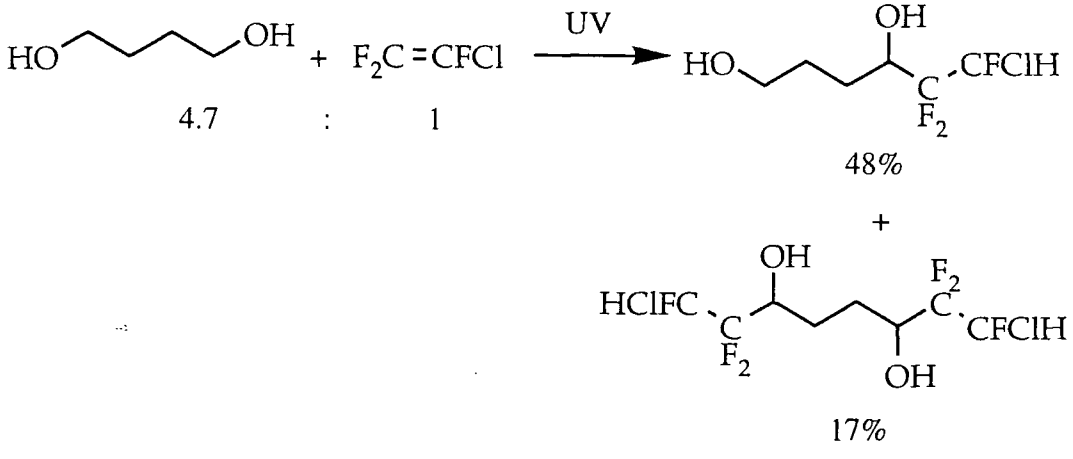


n = 1 or 2

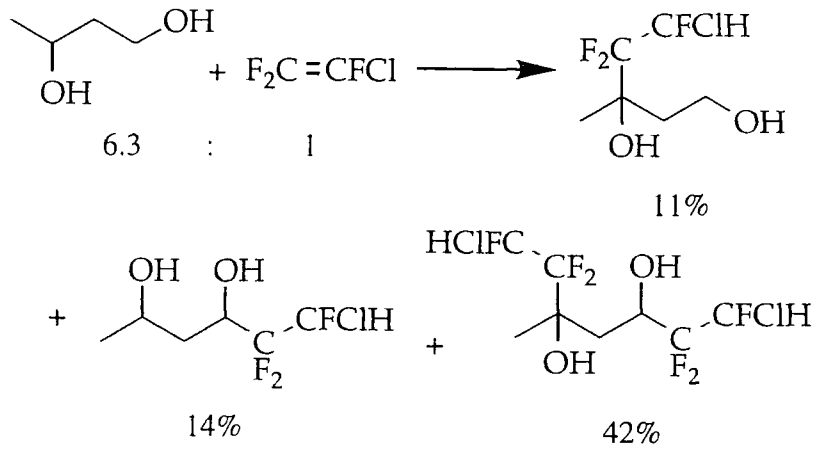
In contrast, 1,3-propanediol added to chlorotrifluoroethene[69] in the expected manner:-



1,4-Butanediol[69] gave some di-adduct as well as mono-adduct:-

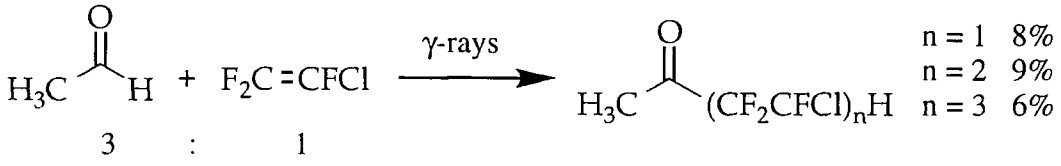


However, addition to 1,3-butanediol[69] gave mainly the di-adduct. This resulted from 1,5-hydrogen migration to give a new radical centre which reacted with another molecule of chlorotrifluoroethene:-



Addition to Aldehydes

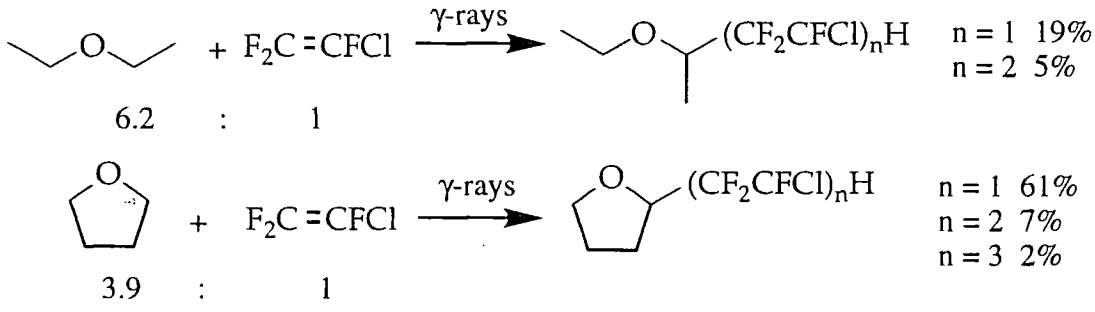
Acetaldehyde has been successfully added to chlorotrifluoroethene[65] to give a mixture of adducts:-



The low yields were attributed to the formation of higher molecular weight telomers.

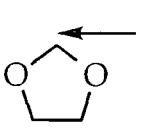
Addition to Ethers

Diethyl ether and tetrahydrofuran[70] have been added to chlorotrifluoroethene:-

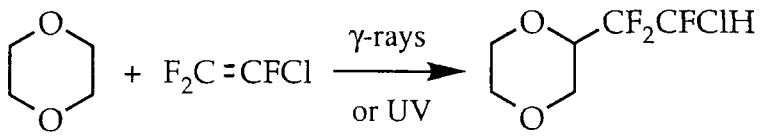


Again, higher molecular weight telomers formed, thus lowering the yield of mono- and di-adducts.

1,3-Dioxolanes have been added to chlorotrifluoroethene,[71] but a complex mixture of mono-, di- and tri-adducts resulted. Although the dioxolane radical is formed preferentially at the carbon atom directly between the two oxygen atoms, some molecules have a radical formed at one of the other carbon atoms:-

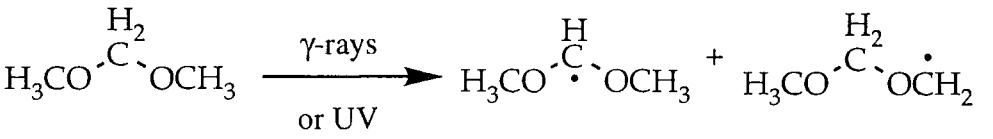


1,4-Dioxane has also been added to chlorotrifluoroethene[72] to give a mono-adduct:-



For this reaction no yield was given and it is assumed that higher molecular weight telomers also resulted.

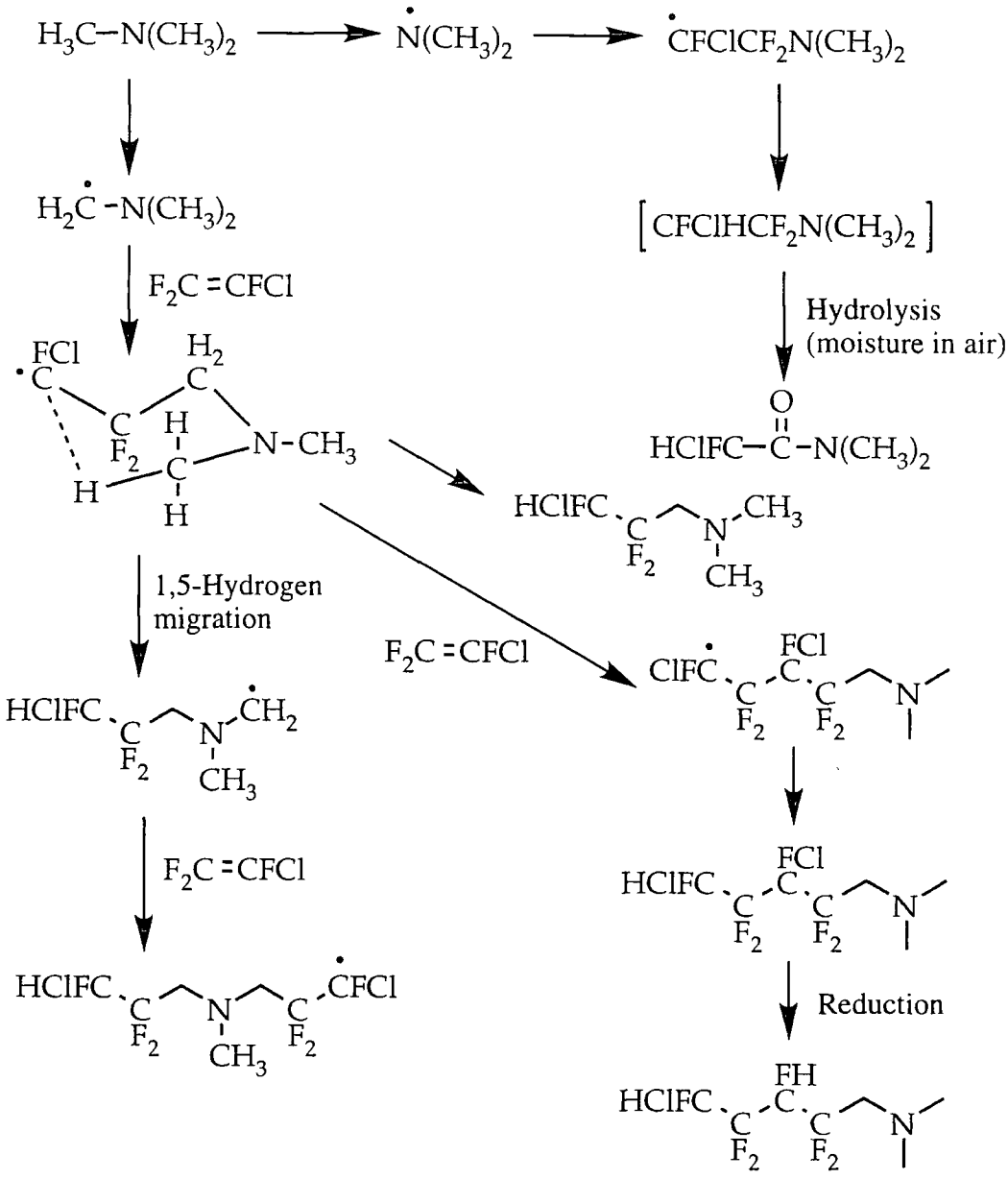
Reaction with formaldehyde dimethyl acetal[73] gave a complex mixture of products as two radical centres were formed:-



Although the formation of a secondary radical is preferred over a primary radical, the statistical distribution of carbon-hydrogen bonds results in there being nearly equal quantities of each radical. Owing to the complexity of the reaction mixture product yields were not determined.

Addition to Amines

A number of tertiary amines have been reported to add to chlorotrifluoroethene[74] but complex mixtures of products resulted. For example, trimethylamine[75] gave the expected mono-adduct, two isomers of di-adduct, one di-adduct with C-Cl to C-H bond reduction and an amide. It was further complicated by the fact that when trimethylamine is irradiated using γ-rays or UV light, a nitrogen-carbon bond can cleave to form a nitrogen-centred radical in addition to the expected carbon-centred radical.



Owing to the complexity of the reaction, yields were not determined. There do not appear to be any examples in the literature where a carbon-hydrogen bond of a hydrocarbon is functionalised and reacted with chlorotrifluoroethene.

1.3.2.3. 1,1-Dichlorodifluoroethene

1,1-Dichlorodifluoroethene has been reacted with various telogens to give 1:1 adducts as shown in the table below. Unlike chlorotrifluoroethene, higher molecular weight telomers do not form.

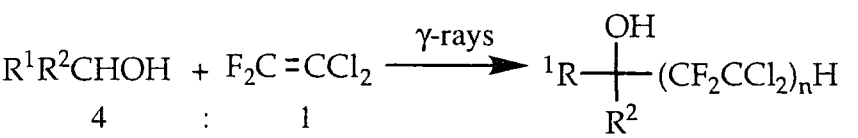
Telogen	Initiator	Telomer Structure
Cl_3C-Br	UV[76]	Cl_3C-CF_2CCl_2-Br (28%)
RSH	Peroxide[77]	RS-CF_2CCl_2-H

Reaction with CF_3OF,[78] R_fOBr[79] and ICl[80] have also been reported, but there still remains some controversy as to whether they are radical or ionic processes. The reaction with bromotrichloromethane is complicated by the fact that further decomposition occurs.

Muramatsu and co-workers have investigated the addition of 1,1-dichlorodifluoroethene to various organic substrates via functionalisation of carbon-hydrogen bonds[81-83] as discussed below.

Addition to Alcohols

1,1-Dichlorodifluoroethene has been added to a range of alcohols[82] to give a mixture of mono-adduct, di-adduct and higher molecular weight telomers.

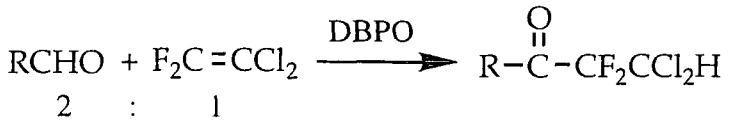


		Yields (%)	
R^1	R^2	n = 1	n = 2
H	H	4	2
H	CH_3	10	2
H	C_2H_5	10	4
CH_3	CH_3	15	7

No compounds resulting from the reverse mode of addition were reported, and the very low yields resulted as higher molecular weight telomers were also produced.

Addition to Aldehydes

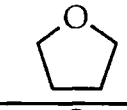
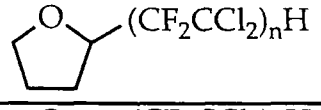
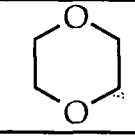
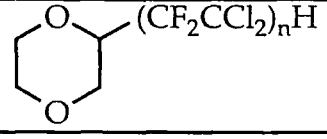
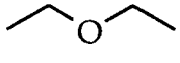
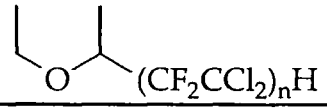
1,1-Dichlorodifluoroethene has been successfully added to a range of aldehydes[81] using peroxide initiation. In contrast to the reactions with alcohols, yields of the mono-adducts were significantly higher with a smaller quantity of higher molecular weight telomers formed.



R	Yield (%)
CH_3	38
C_2H_5	42
n-C_3H_7	43
i-C_3H_7	15

Addition to Ethers

1,1-Dichlorodifluoroethene has also been added to ethers[83] resulting in product mixtures. The large differences in yield depending on the ether used are difficult to account for.

Ether	Ratio R-H:Alkene	Initiator	Products	Yields (%) n = 1	n = 2
	2:1	γ-rays		65	4
	2:1	γ-rays		5	3
	2:1	γ-rays		15	14

As with the other organic substrates used, higher molecular weight telomers were also produced.

It can be concluded that although 1,1-dichlorodifluoroethene does produce higher molecular weight telomers, the reaction products are not complex mixtures as when chlorotrifluoroethene is used. It appears that hydrocarbon molecules have not yet been investigated as a possible telogen.

1.3.2.4. 1-Chloro-2,2-difluoroethene

There is very little information in the literature concerning radical additions to 1-chloro-2,2-difluoroethene. One example reported by Haszeldine[84] is the radically-induced addition of trifluoromethyl iodide:-

$$F_2C{=}CHCl \;+\; CF_3I \xrightarrow{UV} CF_3CF_2CHClI \;+\; CF_3CHClCF_2I$$
$$1 \;:\; 2 \qquad\qquad 9 \;:\; 1$$
$$75\%$$

It was reported that there was only a small quantity of higher molecular weight telomers produced.

Addition of HBr has also been accomplished:-

$$F_2C{=}CHCl \;+\; HBr \xrightarrow{UV} CF_2BrCH_2Cl$$
$$1 \;:\; 2 \qquad\qquad 97\%$$

Although reaction of HBr with alkenes usually proceeds via an ionic mechanism, in this instance reaction only occurred in the presence of UV light. This confirmed the radical process.

Addition of CCl_3Br via homolytic cleavage of the C-Br bond has also been achieved,[58] although product mixtures resulted together with some olefinic by-products:-

$$F_2C{=}CHCl \;+\; CCl_3Br \xrightarrow{UV} CF_2BrCHClBr \;+\; CCl_3CF_2CHClBr$$
$$39\% \qquad\qquad 21\%$$
$$+ \text{ by-products}$$

This is the extent of radical reactions of 1-chloro-2,2-difluoroethene reported in the literature. There appear to be no examples of it being added to an organic substrate via functionalisation of a carbon-hydrogen bond.

1.3.2.5. Bromotrifluoroethene

There is very little information in the literature concerning radical additions to bromotrifluoroethene, although it has been reacted with various telogens to produce telomers as summarised below:-

Telogen	Initiator	Telomer Structure
Cl_3C-Br	UV[76]	Cl_3C-CF_2CFBr_2 (97%) + Cl_3C-CFBr-CF_2Br (3%)
Cl_3C-F	UV[85]	$Cl_2CF(CF_2CFBr)_nCl$ n = 1-13
Br_3CX (X=F or Br)	UV[86]	$XCBr_2(CF_2CFBr)_nBr$ n = 1,2
F_3CS-SCF_3	UV[58]	$F_3CS(CF_2CFBr)_nSCF_3$ n = 1-3

There are no examples in the literature of addition to an organic molecule by functionalisation of a carbon-hydrogen bond.

1.3.2.6. 1-Bromo-2,2-difluoroethene

There is even less information in the literature concerning radical reactions with 1-bromo-2,2-difluoroethene. The only reported examples concerned the addition of CF_3O-X (X = Cl or F), but there remains some controversy as to whether the mechanism is radical or ionic.[78]

1.4. Conclusions

- Organic compounds containing fluorine have a wide range of applications, so therefore it is of interest to study new methodology for the introduction of fluorine.

- A carbon-hydrogen bond can be functionalised to produce a free radical which readily reacts with a fluorinated alkene.

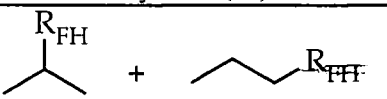
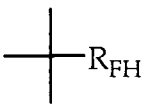
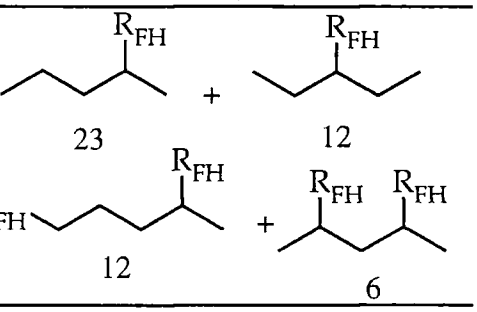
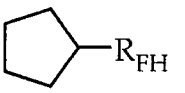
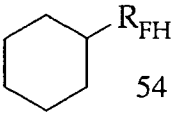
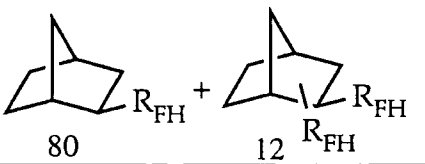
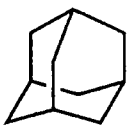
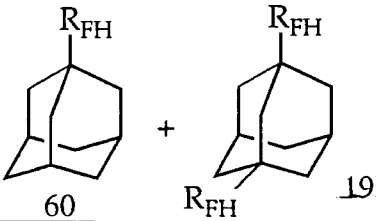
- A range of substrates can be reacted with various fluoroalkenes, so there is considerable scope for making new fluorinated building blocks.

- Very little work has been carried out on the functionalisation of hydrocarbons to produce new fluorinated building blocks.

2. Addition of Cyclohexane to Fluoropropenes

2.1. Introduction

The functionalisation of hydrocarbons is a field that is continually expanding and a variety of approaches have been taken.[87-89] Additions of hydrocarbons to hexafluoropropene have been documented in the literature[9, 90-94] as a relatively straightforward approach to functionalise carbon-hydrogen bonds. Some examples are illustrated below.

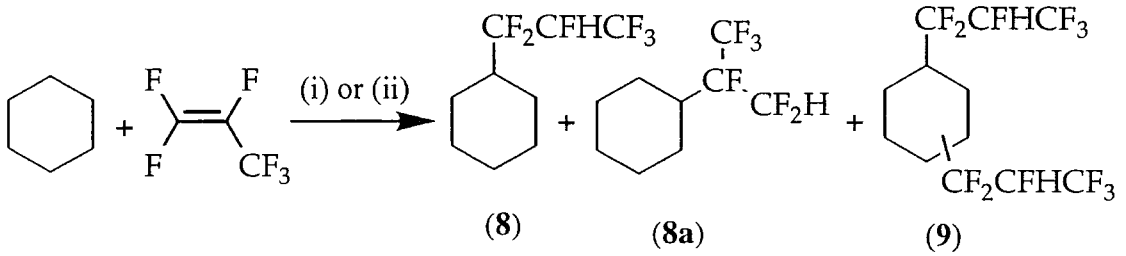
Hydrocarbon	Ratio R-H:HFP	Initiator	Products and yields (%)
	1:2	γ-rays[9]	 21 2
	1:2	γ-rays[9]	 42
		300 °C[91]	 23 12 12 6
	3:1	UV[90]	 43
	3:1	280 °C[91]	 54
	1:1.3	γ-rays[9]	 80 12
	1:1.2	DTBP[9]	 60 19

$R_{FH} = CF_2CFHCF_3$

Despite all the work carried out with hexafluoropropene, there does not appear to be any work in the literature concerning the addition of hydrocarbons to other fluorinated propenes. The work in this chapter describes radical additions to hexafluoropropene, 1,1,3,3,3-pentafluoropropene and 3,3,3-trifluoropropene.

2.2. Addition of Cyclohexane to Hexafluoropropene

Cyclohexane was added to hexafluoropropene using γ-ray and DTBP initiation to give 1-cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**), a trace of 2-cyclohexyl-1,1,1,2,3,3-hexafluoropropane (**8a**) and a mixture of isomers of the di-adduct 1,1,2,3,3,3-hexafluoro-1-[x-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl]propane (x=2,3, 4) (**9**).



(**8**) (**8a**) (**9**)

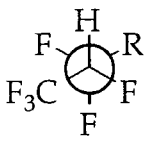
	Initiator and Conditions	Ratio R-H:HFP	Alkene Conv (%)	Yields (%) (**8**)	(**9**)
(i)	γ-rays, R.T, 14 days	1:1.5	89	68	25
(ii)	DTBP, 140 °C, 24 hrs	1:1.2	98	73	22

Fractional distillation separated the major product, 1-cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**) from the di-adduct isomers (**9**). GLC/MS showed a trace of 2-cyclohexyl-1,1,1,2,3,3-hexafluoropropane (**8a**), resulting from radical attack at the central carbon atom of hexafluoropropene. Higher molecular weight telomers did not form.

The preparation of 1-cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**) is documented in the literature.[9] However, the NMR spectral data are described here in some detail as it assists with the characterisation of subsequent compounds prepared during the course of this work.

The resonances on the fluorine NMR spectrum for 1-cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**) were assigned by their relative integration. The resonance for the trifluoromethyl fluorine atoms occurred at -74.8 ppm, characteristic for a CF_3 group[95] and the CFH fluorine resonance occurred at -211.9 ppm. The CF_2 fluorine

atoms are diastereotopic and consequently consisted of an AB system at -118.84 and -118.12 ppm which can be illustrated with the aid of a Newman projection:-



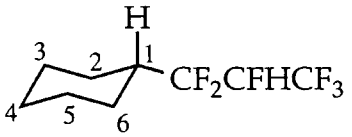
R = Cyclohexyl

The proton-decoupled carbon NMR spectrum of (**8**) gave three signals at high frequency which were assigned to the hexafluoropropyl carbon atoms according to their coupling to the fluorine atoms. The CF_3 carbon atom resonance occurred at 121.0 ppm as a quartet ($^1J_{C-F}$ 293) of a doublet ($^2J_{C-F}$ 26) because it is directly bonded to three fluorine atoms and adjacent to a CF carbon atom.

The resonance due to the carbon atom adjacent to the cyclohexyl group occurred at 119.7 ppm. It consisted of two doublets with one-bond coupling constants resulting from coupling to two non-equivalent fluorine atoms ($^1J_{C-F}$ 252 and $^1J_{C-F}$ 242), and a doublet resulting from two-bond coupling to the CFH fluorine atom ($^2J_{C-F}$ 25).

The CFH carbon atom resonance occurred at 84.7 ppm and gave a doublet ($^1J_{C-F}$ 195) of a multiplet, resulting from one-bond coupling to one fluorine atom. The splitting from coupling to the other fluorine atoms was not resolved, and complicated by the presence of the AB system.

The remaining carbon atom resonances occurred at low frequency and on the basis of chemical equivalency, there would be expected to be four resonances for the six carbon atoms but in fact there were six. This is because pairs of ring carbon atoms (C-2, C-6 and C-3, C-5) are actually magnetically inequivalent despite their chemical equivalency and this is due to subtle asymmetric effects.[96]



(**8**)

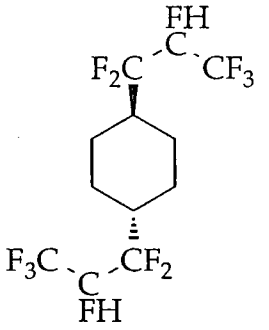
In ^{13}C NMR, the detection of a carbon atom is only possible if a ^{13}C nucleus is present, which has a probability of 1.1%. When C-2 is observed by NMR and is therefore a ^{13}C nucleus, C-6 will predominantly be a ^{12}C atom (98.9%). This induces chirality at C-1 which potentially leads to different chemical shifts for C-2 and C-6. For a mono-substituted cyclohexane such as cyclohexanol, this effect is very small and the two resonances coincide to the resolution limit of the spectrometer. However, if the sidegroup contains a chiral centre as in the hexafluoropropyl group (CF_2CFHCF_3), the molecule is diastereomeric and the signals for C-2 and C-6 can often be resolved from each other. Sometimes the chiral centre at C-1 can have two separate resonances, but was not observed in this system.

The resonances for C-1, C-2 and C-6 were assigned according to their coupling to the fluorine atoms. The other carbon atom resonances were singlets, with C-4 being assigned to the lowest frequency shift as it is furthest away from the electron-withdrawing fluoroalkyl group.

The resonance due to the hydrogen atom on the fluoroalkyl side-chain occurred at 4.82 ppm as a doublet ($^2J_{H\text{-}F}$ 41) of a doublet ($^3J_{H\text{-}F}$ 14) of a quartet ($^3J_{H\text{-}F}$ 7.0) of a doublet ($^3J_{H\text{-}F}$ 6.6), which also confirmed the structure as (**8**).

A trace amount (<1% by fluorine NMR) of adduct arising from attack at the central carbon atom of hexafluoropropene was also observed which was previously unreported.[9] The proton-decoupled carbon NMR spectrum of (**8**) gave a resonance of low relative intensity at 112.3 ppm. This was a triplet ($^1J_{C\text{-}F}$ 250) of doublets ($^2J_{C\text{-}F}$ 32), assigned to the CF_2H carbon atom of (**8a**). The hydrogen NMR spectrum of (**8**) gave a resonance of low relative intensity at 5.98 ppm. This was a triplet ($^1J_{H\text{-}F}$ 53) of doublets ($^2J_{H\text{-}F}$ 6.8), assigned to the CF_2H hydrogen atom and confirmed the structure as 2-cyclohexyl-1,1,1,2,3,3-hexafluoropropane (**8a**).

When the mixture of di-adducts (**9**) was allowed to stand, a white solid crystallised out which had earlier been shown to be 1,1,2,3,3,3-hexafluoro-1-[4-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl]propane (**9a**) by X-ray crystallography.[9] The NMR data was in agreement with earlier work.



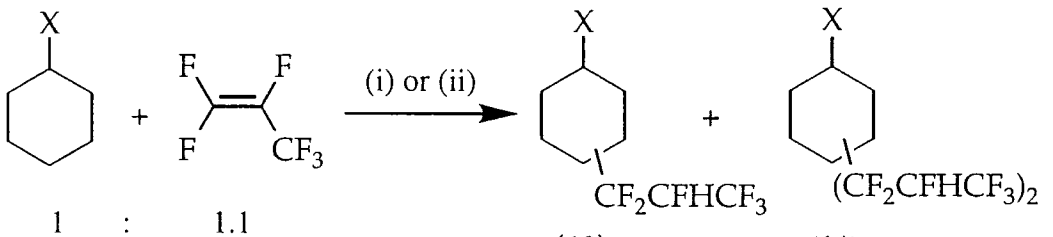
(**9a**)

This is a highly symmetric molecule, dominated by a centre of inversion *i*. GLC/MS showed that the liquid di-adducts consisted of a mixture of isomers in the ratio of 1:11:26:15:14:5 which could not be separated individually.

2.3. Investigation of Cyclohexane Derivatives

2.3.1. Addition to Hexafluoropropene

A range of cyclohexane derivatives were reacted with hexafluoropropene in an attempt to produce adducts and to establish a reactivity order. The reactions using γ-rays were all repeated using acetone as a photosensitizer but had no effect unless otherwise stated.



1 : 1.1

(10) (11)

(i) γ-rays, R.T, 14 days (with or without acetone)
(ii) DTBP, 140 °C, 24 hours

The products and conversions were determined by GLC/MS, and incorporation of hexafluoropropene was confirmed by fluorine NMR.

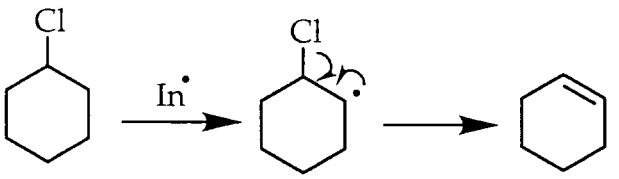
	Conversion of RX (%)		
	γ-rays		DTBP
X	**(10)**	**(11)**	**(10)**
NO_2	0	0	-
I	0	0	-
CH_3	29	10	-
Cl	6	0	-
Br	0	0	3
$BrCH_2$	3[a]	0	7
$BrCH_2CH_2$	10[a]	0	10

[a] = acetone

Attempted addition of nitro- and iodocyclohexane to hexafluoropropene gave no trace of addition products. This could have been due to electronegative effects, or radical inhibition which is discussed in section 2.3.2. DTBP was not used as a method of initiation with these substrates owing to their complete lack of reactivity using γ-rays.

Reaction with methylcyclohexane gave a mixture of mono- and di-adduct isomers. The increased nucleophilicity and stability of the tertiary carbon radical centre did not overcome the statistical advantage of there being a greater number of secondary carbon atoms present. Initiation using DTBP was not carried out as this has been investigated earlier in this laboratory[97] and the same worker also characterised the mixtures of isomers. The low conversion was surprising so a competition experiment with cyclohexane was performed as described in section 2.3.3.

Reaction with chlorocyclohexane only gave a low conversion, as chlorine withdraws electron density making it more difficult to react with the electron-deficient hexafluoropropene. Earlier work in this laboratory[7] using DTBP as the initiator gave cyclohexene as the major product with only a trace quantity of the desired mono-adduct. This resulted from free-radically-induced dehydrochlorination:-



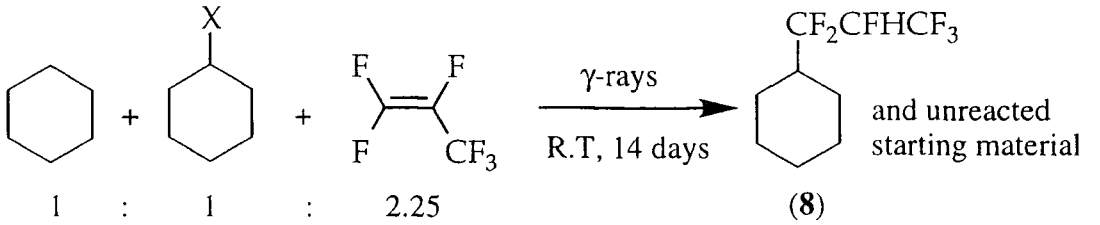
Reaction with bromocyclohexane using γ-ray initiation gave no trace of adducts, but was repeated with DTBP initiation as a comparison to the other bromine-containing cyclohexane derivatives. With the advantage of a much higher reaction temperature, a low conversion resulted.

Reaction using bromomethyl- and bromoethylcyclohexane using γ-rays both gave no trace of reaction unless acetone was used as a photosensitizer. Reaction using DTBP as initiator had a small effect, but in both cases selectivity was poor.

Owing to the poor conversions and low selectivites, none of the above reactions had their products fully characterised.

2.3.2. Test for Radical Inhibition

The lack of reactivity for some of the cyclohexane derivatives could be accounted for by the electronegative nature of the substituent X. However, radical inhibition can also occur[13, 98] and this possibility was investigated by means of competition experiments. A small excess of hexafluoropropene was reacted with an equimolar ratio of cyclohexane and the cyclohexane derivative in question as shown below. After reaction, the ratio of unreacted cyclohexane to 1-cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**) was determined by GLC/MS. Earlier it was shown that cyclohexane could be added quantitatively to hexafluoropropene, and in this experiment conversion of cyclohexane would be expected to be complete if no radical inhibition occurred.

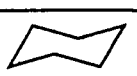
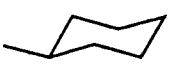


X	Product Ratio C_6H_{12}:(**8**)
I	16.3:1
NO_2	10.5:1
Br	4.6:1
$BrCH_2$	2.8:1
$BrCH_2CH_2$	0.7:1

In all cases, complete conversion of cyclohexane did not occur and this was attributed to inhibition. With iodocyclohexane for example, the small proportion of 1-cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**) indicated that inhibition was occurring. However, trace impurities such as iodine could be present which is a known radical inhibitor.[11] This has demonstrated that competition reactions are required to overcome the possibility of impurities which could act as inhibitor, and has illustrated the uncertainties associated with the comparison of absolute rate measurements.

2.3.3. Competition Reaction

The reactivity of methylcyclohexane was compared to that of cyclohexane itself by means of a competition experiment. An equimolar mixture of methylcyclohexane and cyclohexane was reacted with a deficiency of hexafluoropropene using γ-ray initiation and the reaction mixture analysed before and after reaction by GLC/MS.

	Ratio prior to reaction (R_1)	Ratio after reaction (R_2)
	45.89	27.57
	53.54	50.40

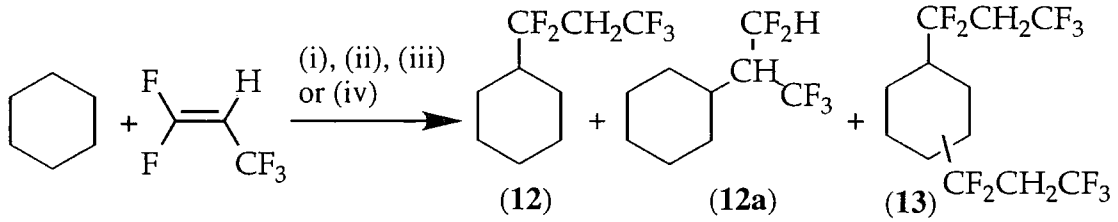
Although the data could not be quantified, reaction occurred faster with cyclohexane than with methylcyclohexane which cannot be explained by electron

inductive effects. The competition reaction confirmed that there was no trace of inhibitor present in the initial experiment as the cyclohexane reacted.

A tertiary radical site is very stable and it is possible that it was too stable to react. There is also steric hindrance associated with such a system. Methylcyclohexane contains five potential secondary radical sites which accounted for the product mixtures, but not for the lack of reactivity.

2.4. Addition of Cyclohexane to 1,1,3,3,3-Pentafluoropropene

Cyclohexane was added to 1,1,3,3,3-pentafluoropropene using γ-ray and peroxide initiation to give 1-cyclohexyl-1,1,3,3,3-pentafluoropropane (**12**), the reverse-addition compound 2-cyclohexyl-1,1,1,3,3-pentafluoropropane (**12a**) and a mixture of isomers of the di-adduct 1,1,3,3,3-pentafluoro-1[x-(1,1,3,3,3-pentafluoropropyl)-cyclohexyl]propane (x=2,3,4) (**13**).



(**12**) (**12a**) (**13**)

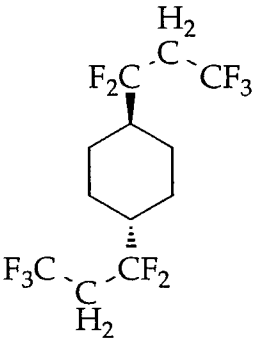
	Initiator and Conditions	Ratio R-H:PFP	Alkene Conv (%)	Product Ratio (**12**):(**12a**):(**13**)	Yield (%) (**12**)
(i)	γ-rays, R.T, 14 days	0.5:1	15	24:1:0	14
(ii)	γ-rays, R.T, 28 days	0.67:1	84	21:1:1.2	82
(iii)	DTBP, 140 °C, 24 hrs	6.6:1	97	10:1:0.6	66
(iv)	DTBP, 140 °C, 24 hrs	1.5:1	99	10:1:1.7	53

1,1,3,3,3-Pentafluoropropene is less reactive than hexafluoropropene so a much longer exposure to γ-rays was required for conversion to be quantitative. Although initiation using DTBP at 140 °C achieved complete conversion, the selectivity was poorer. In all cases high molecular weight material was not formed.

A resonance in the proton-decoupled carbon NMR spectrum of (**12**) at 38.2 ppm consisted of six lines from coupling to five fluorine atoms was assigned to the CH_2 carbon atom on the fluoroalkyl side-chain. A triplet at 44.1 ppm ($^2J_{C-F}$ 23) was assigned to the CH ring carbon atom which confirmed the structure as (**12**). The hydrogen NMR spectrum of (**12**) gave 6 lines ($^3J_{H-F}$ 10 and $^3J_{H-F}$ 10) at 2.8 ppm with no other resonances present apart from the ring hydrogen atoms which also confirmed the structure.

A triplet ($^2J_{H-F}$ 54) of doublets ($^3J_{H-H}$ 4.4) of low relative intensity at 5.7 ppm in the hydrogen NMR spectrum of (**12**) was attributed to (**12a**), arising from radical attack at the central carbon atom of 1,1,3,3,3-pentafluoropropene. This was assigned to the CF_2H hydrogen atom.

In experiment (iv) the larger proportion of di-adduct isomers (**13**) formed allowed their characterisation. When the di-adduct mixture was allowed to stand, a white solid precipitated out. This was shown by NMR to be 1,1,3,3,3-pentafluoro-1[4-(1,1,3,3,3-pentafluoropropyl)cyclohexyl]propane (**13a**). The proton-decoupled carbon NMR spectrum of (**13a**) showed only two resonances at low frequency which could be assigned to the ring carbon atoms. A triplet at 43.0 ppm ($^2J_{C-F}$ 30) was assigned to the CH ring carbon atoms, and a triplet at 24.1 ppm ($^3J_{C-F}$ 4.5) was assigned to the CH_2 ring carbon atoms. There were only two resonances due to the ring carbon atoms and not three as for the hexafluoropropyl di-adduct (**9a**). In this system there was no chiral centre on the fluoroalkyl side-chain and so all of the CH_2 ring carbon atoms were magnetically equivalent.



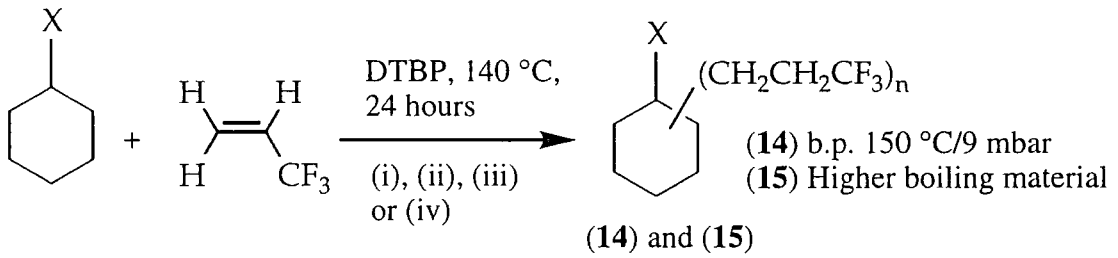
(**13a**)

GLC/MS showed the remaining liquid di-adduct isomers (**13**) to be in the ratio of 1.5:4:1:2.5 and could not be separated from each other.

The reactivity of 1,1,3,3,3-pentafluoropropene was very different to that of hexafluoropropene. The selectivity was poorer because the central carbon atom is less sterically hindered as a fluorine atom has been replaced by a hydrogen atom. The CF_2 carbon atom is less electrophilic and therefore less susceptible to attack by a nucleophilic radical, accounting for the lower reactivity. The radical formed on addition to cyclohexane is still fairly electrophilic and abstracted a hydrogen atom in preference to reacting with another molecule of electron-deficient alkene.

2.5. Addition of Cyclohexane to 3,3,3-Trifluoropropene

3,3,3-Trifluoropropene was investigated as another potential route to introduce fluorine into organic molecules. Initiation using γ-rays gave no trace of reaction, but with DTBP higher molecular weight telomers were produced.



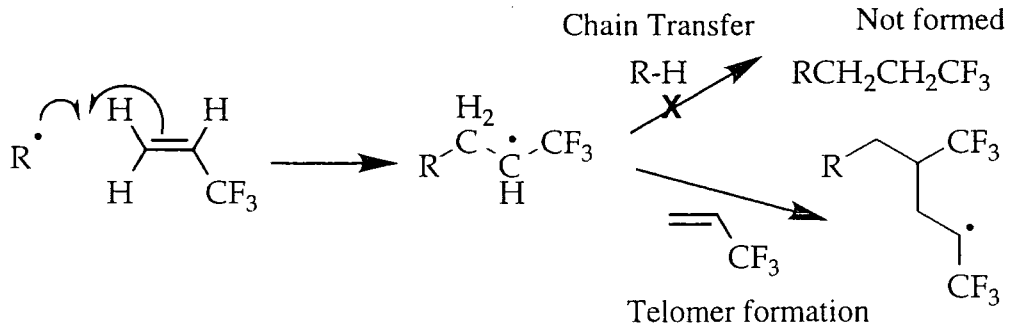
The product was complex and is expressed in terms of material which distilled at 150 °C/9 mbar (**14**) and higher molecular weight material which did not distill under those conditions (**15**).

		Reactant Ratio	Conversion (%)		Product Ratio
	X	RX:Alkene:DTBP	Substrate	Alkene	(**14**):(**15**)
(i)	H	0.5:1:0.0006	68	100	1:2.2
(ii)	H	2:1:0.15	26	96	1:2.8
(iii)	H	10:1:0.38	10	60	1:1
(iv)	OH	2:1:0.16	60	90	1:1

Even with a large excess of R-H higher molecular weight material formed and a mono-adduct could not be isolated. Reaction using cyclohexanol was carried out, as a radical centre next to oxygen is easier to form and chain transfer may have been able to compete over telomerisation. Although the relative quantity of distillation residue was reduced, the runaway telomerisation process still occurred.

Fluorine NMR of the products gave resonances around -70 ppm, indicating the presence of trifluoromethyl groups. Mass spectral data of the distillation residue showed it to fragment with the loss of $-CH_2CH_2CF_3$ groups with a molecular weight of around 1700 amu.

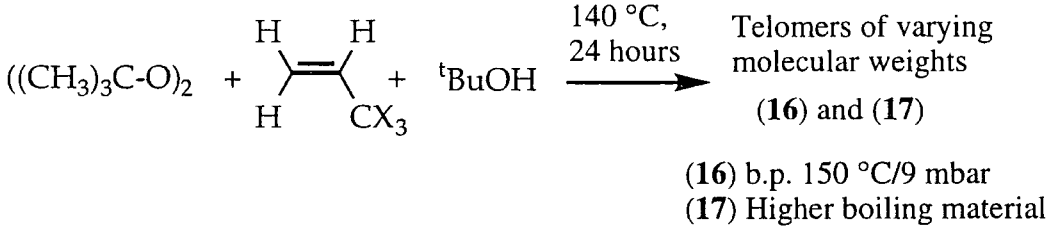
In this system telomerisation occurred in preference to chain transfer:-



3,3,3-Trifluoropropene is much less sterically hindered than hexafluoropropene and is therefore more susceptible to attack by a radical. The radical formed upon addition of one molecule of 3,3,3-trifluoropropene to cyclohexane is far less electrophilic than that in the hexafluoropropene system as described in section 2.2. Therefore it is less likely to react with a nucleophilic C-H site in another molecule of cyclohexane.

In the reactions described above, DTBP breaks down into two molecules of *tert*-butoxy radicals which abstract a hydrogen atom from molecules of R-H. Owing to the high reactivity of 3,3,3-trifluoropropene it was considered a possibility that the *tert*-butoxy radicals reacted directly with the alkene instead.

DTBP was reacted directly with 3,3,3-trifluoropropene and as before, the products are expressed as material which distilled at 150 °C/9 mbar (**16**) and that which did not (**17**).



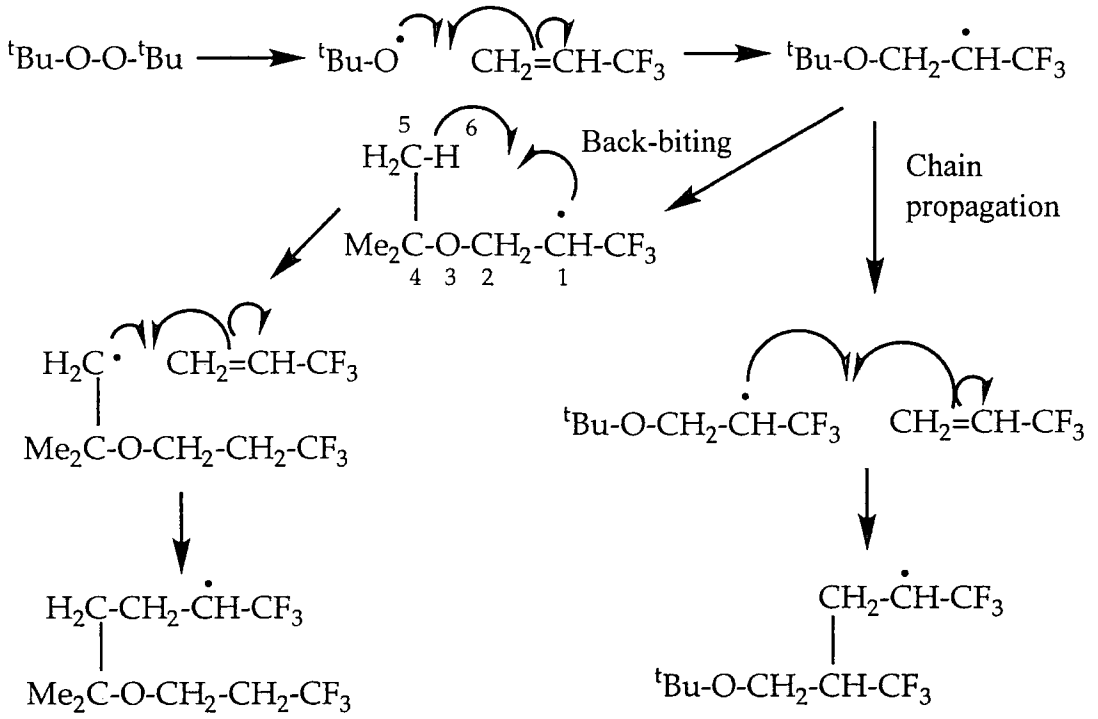
(**16**) b.p. 150 °C/9 mbar
(**17**) Higher boiling material

	X	Reactant Ratio Alkene:DTBP:^{t}BuOH	Conv (%) Alkene	Product Ratio (**16**):(**17**)
(i)	H	1:0.08:0	0	0
(ii)	F	1:0.08:0	78	1:0.4
(iii)	F	1:0.5:0	92	1:0.5
(iv)	F	1:0.08:0.64	91	1:1.2

Propene (X=H) was used as a comparison to 3,3,3-trifluoropropene and no reaction occurred. The *tert*-butoxy radicals formed on decomposition of the DTBP molecules added to a molecule of alkene which in turn reacted further to give telomers of *tert*-butanol. As with the reactions using cyclohexane, fluorine NMR of the products gave resonances around -70 ppm, and mass spectral data showed extensive

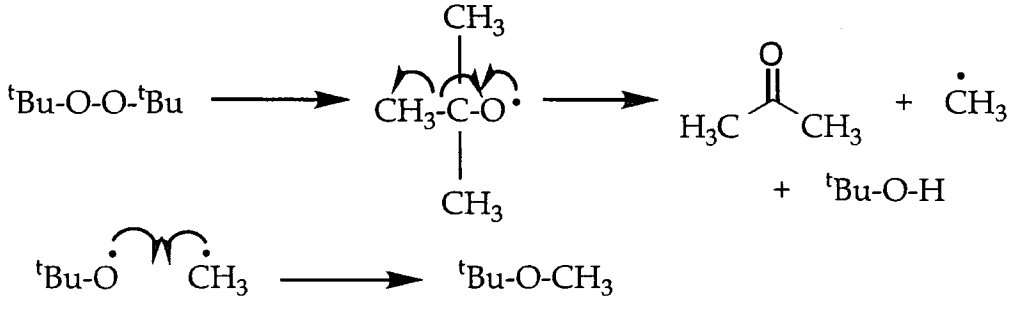
fragmentation with loss of $CH_2CH_2CF_3$ groups and a molecular mass of around 1700 amu. A carbon NMR spectrum gave a multiplet at 126 ppm arising from trifluoromethyl carbon atoms, as well as resonances in the region of 20-40 ppm which were too complex to assign. Hydrogen NMR showed multiplets at 1.7-1.8 ppm and at 2.0-2.2 ppm with a sharp CH_3 resonance at 1.2 ppm. There was also a trace of alkenic hydrogen atoms in the region of 5.2-5.4 ppm, illustrating how unselective the reaction was.

On the basis of the steric requirement of the *tert*-butyl group, the radical was likely to attack at the CH_2 carbon atom of 3,3,3-trifluoropropene. Therefore a possible mechanism is as follows:-



Back-biting process proceeds through a 6-membered ring transition state, and this together with 1,5-hydrogen shifts resulted in a complex mixture of products.

In experiments (ii) and (iii), acetone and *tert*-butanol were detected as byproducts by GLC/MS, whose formation was considered to arise as follows:-



Experiment (iii) was an attempt to product 1:1 adducts but telomerisation still occurred. Although it appeared to contain an equimolar quantity of radicals, the radicals formed slowly over time as the reaction vessel was heated and consequently all of the 3,3,3-trifluoropropene had reacted long before all the radicals were formed. This accounted for the similar product distribution as for experiment (ii).

Experiment (iv) gave a different product distribution as the radicals formed could easily abstract a hydrogen atom from a molecule of *tert*-butanol. Therefore the average molecular weight of the distillation residue would be expected to be lower than for experiments (ii) and (iii), which was confirmed by GPC analysis as shown in the table below.

Although a full discussion of GPC is beyond the scope of this thesis, a brief summary of the principles is described here. Conventional Calibration involves comparison of its retention volume and refractive index to a polystyrene standard of a known molecular weight to give an estimate of the molecular weight. This entails a number of approximations which are documented in the literature.[99] The Universal Calibration plot compares the intrinsic viscosity to that of a standard and generally gives more accurate results than Conventional Calibration does, although experimentally is more difficult to achieve. The standard may be very different to the polymer in question so the margin for error is large.

	M_n	M_w	P_d	Calibration
(ii)	1550	4240	2.74	Universal
(ii)	1100	1960	1.78	Conventional
(iii)	840	1370	1.43	Conventional
(iv)	880	1850	2.10	Conventional

M_n is the number average molecular weight, which is the average molecular weight taking all of the molecules into account. M_w is the weight average molecular weight and takes into consideration the fact that although small molecules are numerous (and could outnumber the larger molecules), their contribution to the total mass is negligible. P_d is the polydispersity and is a measure of the range of molecular weights present, so a value of 1.00 indicates that all the molecules are the same length. High values of polydispersity indicate a range of molecular sizes.

The material produced consisted of telomers rather than long chain polymers. Increasing the amount of DTBP decreased the length of the chains, which was expected owing to the larger number of radicals around. Adding *tert*-butanol also had a significant effect on decreasing the size of the molecules.

Although 3,3,3-trifluoropropene was not a successful route to new fluorinated building blocks, it is a potential route to partially fluorinated telomers and polymers.

2.6. Conclusions

- Carbon-hydrogen bonds in saturated hydrocarbons can be functionalised by producing a free radical and reacting the radical with hexafluoropropene. This gave a fluoroalkylated mono-adduct with the potential for further functionalisation.

- Cyclohexane derivatives with an electron-withdrawing group gave a low and unselective conversion when reacted with hexafluoropropene. In some systems this was attributed to radical inhibition.

- Addition of a hydrocarbon to 1,1,3,3,3-pentafluoropropene occurred less readily than to hexafluoropropene, and the degree of selectivity depended on the method of initiation. The mono-adduct formed also has the potential for further functionalisation.

- 3,3,3-Trifluoropropene telomerised readily and reacted directly with *tert*-butoxy radicals. Mono-adducts could not be isolated, even using a large excess of R-H.

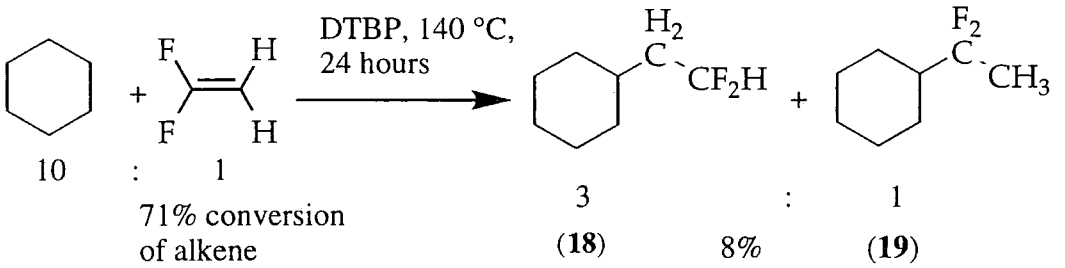
3. Addition of Cyclohexane to Fluoroethenes

3.1. Introduction

This chapter describes addition of the cyclohexyl radical to a range of fluoroethenes, some of which contain bromine or chlorine. Radical reactions of the fluoroethenes investigated in this chapter have been reviewed in chapter 1, and no examples of reaction with hydrocarbon radicals appear to exist in the literature.

3.2. Addition of Cyclohexane to 1,1-Difluoroethene

Cyclohexane was added to 1,1-difluoroethene using DTBP initiation to give a mixture of 2-cyclohexyl-1,1-difluoroethane (**18**) and 1-cyclohexyl-1,1-difluoroethane (**19**) which could not be separated from each other.



The two compounds (**18**) and (**19**) were formed by the cyclohexyl radical attacking either of the two carbon atoms in 1,1-difluoroethene. The remainder of the crude reaction mixture was shown by GLC/MS to be higher molecular weight telomers, which accounted for the low yield. The mixture was complex and preparative scale GLC was required to isolate (**18**) and (**19**). When an excess of 1,1-difluoroethene was used telomerisation occurred with both DTBP and γ-ray initiation.

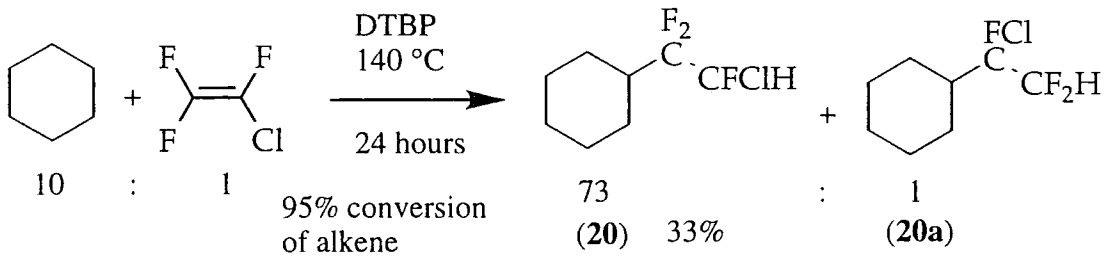
The fluorine NMR spectrum of (**18**) and (**19**) consisted of a singlet at -95 ppm and a multiplet at -113 ppm in the ratio of 1:3 respectively. The multiplet at -113 ppm was nearer to the CF_2H region, hence its assignment to (**18**) as the major product.[95] The carbon atom resonances were assigned with the aid of an HSQC spectrum, which enabled carbon atoms with different numbers of hydrogen atoms directly attached to be distinguished from each other.

Radical attack occurred mainly at the CH_2 carbon atom as it is sterically least hindered, although polar factors directed some attack to the CF_2 carbon atom. The two effects are in opposition and as neither completely dominated over the other, a product mixture resulted.

3.3. Addition of Cyclohexane to Chlorofluoroethenes

3.3.1. Chlorotrifluoroethene

Cyclohexane was added to chlorotrifluoroethene using DTBP initiation to give 2-chloro-1-cyclohexyl-1,1,2-trifluoroethane (**20**). When an excess of chlorotrifluoroethene was used telomerisation occurred with both DTBP and γ-ray initiation.



GLC/MS of the crude reaction mixture also showed the presence of higher molecular weight material which accounted for the low yield.

The proton-decoupled carbon NMR spectrum of (**20**) gave a resonance at 119.4 ppm (td, $^{1}J_{C\text{-}F}$ 251, $^{2}J_{C\text{-}F}$ 24) assigned to the CF_2 carbon atom, and a resonance at 97.4 ppm (dt, $^{1}J_{C\text{-}F}$ 250, $^{2}J_{C\text{-}F}$ 37) assigned to the CFCl carbon atom. The CH ring carbon atom had a shift of 40.7 ppm as a triplet ($^{3}J_{C\text{-}F}$ 22) from coupling to two equivalent fluorine atoms, which confirmed the structure as (**20**).

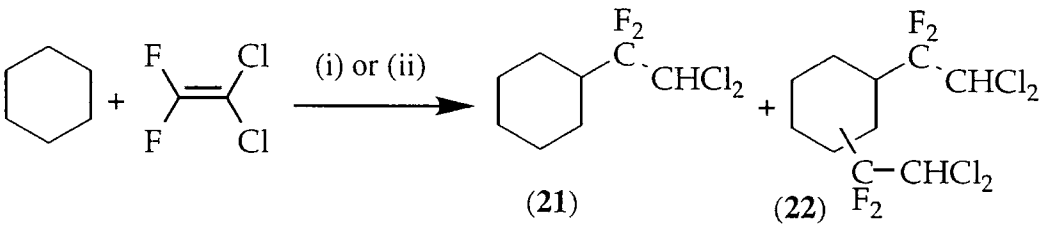
The hydrogen NMR spectrum of (**20**) gave a CFClH hydrogen atom resonance at 6.2 ppm as a doublet ($^{2}J_{H\text{-}F}$ 48) of two doublets from coupling to two non-equivalent fluorine atoms as further proof of the orientation of addition. As the CF_2 fluorine atoms are diastereotopic different coupling constants for coupling to the hydrogen atom would be expected. However, the two fluorine atoms were averaged out as a result of rapid carbon-carbon bond rotation and consequently the two coupling constants of the AB system appeared to be the same ($^{3}J_{H\text{-}F}$ 6.4).

A triplet ($^{2}J_{H\text{-}F}$ 54) of doublets ($^{3}J_{H\text{-}F}$ 6) of very low relative intensity at 5.8 ppm in the hydrogen NMR spectrum of (**20**) was attributed to the reverse-addition compound 1-chloro-1-cyclohexyl-2,2-difluoroethane (**20a**), arising from radical attack at the CFCl carbon atom.

The nucleophilic cyclohexyl radical attacked the more electrophilic and less sterically bulky CF_2 carbon atom of a chlorotrifluoroethene molecule. By using a large excess of cyclohexane chain transfer was made to compete successfully over telomerisation.

3.3.2. 1,1-Dichlorodifluoroethene

Cyclohexane was added to 1,1-dichlorodifluoroethene using γ-ray and DTBP initiation to give 2,2-dichloro-1-cyclohexyl-1,1-difluoroethane (**21**) and an isomer of di-adduct (**22**).



(**21**) (**22**)

	Initiator and Conditions	Ratio R-H:Alkene	Product Ratio (**21**):(**22**)	Yield (%) (**21**)
(i)	γ-rays, R.T, 14 days	1.5:1	1:1	24
(ii)	DTBP, 140 °C, 24 hrs	2.5:1	6:1	40

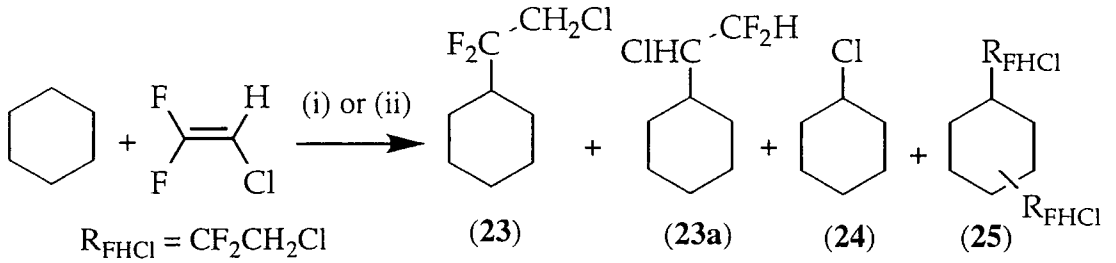
GLC/MS of the crude reaction mixture showed the presence of mono-adduct (**21**) (M=217) and an isomer of the di-adduct (**22**) (M=350) with no trace of reverse-addition compound observed. Although the conversion of the alkene appeared to be high based on the amount of volatile material collected, fluorine NMR of the recovered cyclohexane showed that unreacted alkene had partially dissolved. This accounted for the low isolated yield, and therefore a conversion of the alkene based on the quantity of volatile material recovered would not have been accurate.

The mode of addition of (**21**) was determined from the proton-decoupled carbon NMR spectrum, which gave two triplets with a two-bond coupling constant from coupling to fluorine. A triplet at 40.1 ppm ($^2J_{C\text{-}F}$ 23) was assigned to the CH ring carbon atom, and a triplet at 69.4 ppm ($^2J_{C\text{-}F}$ 35) was assigned to the $CHCl_2$ carbon atom. If the reverse mode of addition had occurred there would only have been one carbon atom with two-bond coupling, as the fluorine atoms would be on the end of the side-chain. The hydrogen NMR spectrum of (**21**) gave a triplet at 5.8 ppm ($^3J_{H\text{-}F}$ 9.2) assigned to the $CHCl_2$ hydrogen atom, and the three-bond coupling constant confirmed the structure.

No trace of radical attack at the CCl_2 carbon atom was observed owing to the large steric requirement of two chlorine atoms.

3.3.3. 1-Chloro-2,2-difluoroethene

Cyclohexane was added to 1-chloro-2,2-difluoroethene using γ-ray and DTBP initiation to give 2-chloro-1-cyclohexyl-1,1-difluoroethane (**23**) as the major product. The reverse-addition compound 1-chloro-1-cyclohexyl-2,2-difluoroethane (**23a**), chlorocyclohexane (**24**) and di-adduct isomers (**25**) were observed by GLC/MS.



	Initiator and Conditions	Ratio R-H:Alkene	Product Ratio (**23**):(**23a**):(**24**):(**25**)	Yield (%) (**23**)
(i)	γ-rays, R.T, 14 days	0.67:1	30:1.5:1:34	0 (dec)
(ii)	DTBP, 140 °C, 24 hrs	4:1	45:3:1:5	49

The recovered cyclohexane was shown by fluorine NMR to contain unreacted 1-chloro-2,2-difluoroethene which accounted for the relatively low isolated yield. The products from the γ-ray reaction decomposed on distillation.

The mode of addition of the major product (**23**) was proved by the hydrogen NMR spectrum, which gave a triplet at 3.6 ppm ($^3J_{H-F}$ 13) and by the relative integration accounted for two hydrogen atoms. This resonance was assigned to the CH_2Cl hydrogen atoms, showing that the cyclohexyl ring was adjacent to the CF_2 carbon atom. The proton-decoupled carbon NMR spectrum of (**23**) gave two triplets with two-bond coupling constants at 41.1 ppm ($^2J_{C-F}$ 35) and 43.0 ppm ($^2J_{C-F}$ 23) which confirmed the structure.

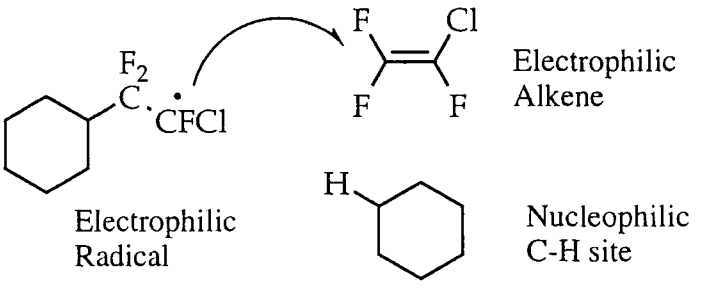
The formation of chlorocyclohexane (**24**) was attributed to the initially-formed cyclohexyl radical either abstracting a chlorine atom directly from a molecule of 1-chloro-2,2-difluoroethene or from a molecule of addition product. The selectivity of the mode of addition was marginally better with γ-ray initiation, and the relatively large quantity of di-adduct isomers (**25**) resulted because an excess of alkene was used.

Attack occured predominantly at the CF_2 fluorine atom and this was again due to the steric bulk of the chlorine atom as well as the electrophilicity of the CF_2 carbon atom.

3.3.4. Discussion of Results for Chlorofluoroethenes

For the reactions with 1,1-dichlorodifluoroethene and 1-chloro-2,2-difluoroethene chain transfer occurred with ease and preparation of the mono-adducts (**21**) and (**23**) did not require a large excess of cyclohexane. However, with chlorotrifluoroethene a large excess of cyclohexane was required to isolate the mono-adduct (**20**) and telomerisation still occurred. This is because an alkene is more reactive when it has a greater number of fluorine atoms directly attached to it.[1] Repulsion of the lone pairs of electrons on the fluorine atoms with the π electrons of the carbon-carbon double bond causes this destabilisation, and hence greater reactivity. In the present work, the greater number of fluorine atoms on chlorotrifluoroethene causes it to be very reactive. In the reactions with 1,1-dichlorodifluoroethene and 1-chloro-2,2-difluoroethene, fluorine NMR showed the presence of unreacted alkene in the recovered cyclohexane. The low reactivity was responsible for the low yields, and a larger amount of DTBP and a longer reaction time may have improved the conversion.

Although the reaction with chlorotrifluoroethene was a competition between hydrogen atom abstraction (chain transfer) and telomerisation, the observed result was not consistent with an electrophilic site attacking a nucleophilic site. The result could only be explained by the alkene reactivity, which overcame any effect of the electrophilicity or nucleophilicity of the radical centres.

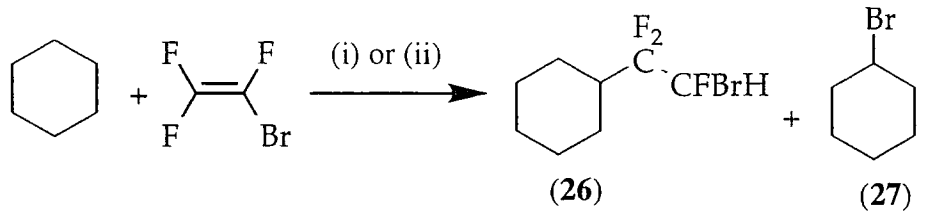


Attack occurred predominantly at the CF_2 fluorine atom in all three systems due to the steric bulk of the chlorine atom and also because the CF_2 carbon atom is more electrophilic. Partial attack occurred at the CHCl carbon atom of 1-chloro-2,2-difluoroethene and this could have been due to the reduced steric hindrance compared to CFCl on a chlorotrifluoroethene molecule. However, the CFCl carbon atom would be expected to be much more electrophilic than the CHCl carbon atom. With chlorotrifluoroethene, the lone pairs of electrons on the CFCl fluorine atom can repel an incoming nucleophilic radical and this effect has been discussed by Paleta[34] on the effects of chlorine on a series of chlorofluoropropenes. The steric bulk of two chlorine atoms on 1,1-dichlorodifluoroethene is quite considerable which prohibited attack at the CCl_2 carbon atom.

3.4. Addition of Cyclohexane to Bromofluoroethenes

3.4.1. Bromotrifluoroethene

Cyclohexane was added to bromotrifluoroethene using γ-ray and DTBP initiation to give 2-bromo-1-cyclohexyl-1,1,2-trifluoroethane (**26**) and bromocyclohexane (**27**).



(**26**) (**27**)

	Initiator and Conditions	Ratio R-H:Alkene	Product Ratio (**26**):(**27**)	Yield (%) (**26**)
(i)	γ-rays, R.T, 14 days	2:1	0.5:1	22
(ii)	DTBP, 140 °C, 24 hrs	4:1	1.5:1	35

GLC/MS showed the mono-adduct (**26**) (M=244/246) and bromocyclohexane (**27**) (M=162/164) with no reverse-addition compound observed and only trace amounts of baseline material. Fluorine NMR of the recovered cyclohexane showed that the alkene partially dissolved, which accounted for the low isolated yield.

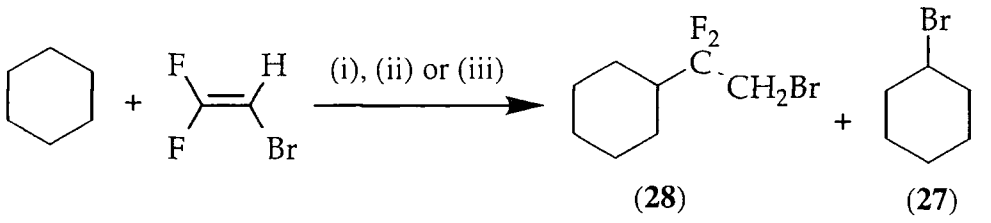
With γ-ray initiation, GLC/MS showed (**26**) and (**27**) which made up 24% and 48% respectively of the crude reaction mixture after the cyclohexane was removed. Two other unidentified compounds with longer retention times which made up 9% and 15% were also observed. The DTBP-initiated reaction did not contain these impurities.

The mode of addition of (**26**) was determined from the hydrogen NMR spectrum, with a resonance at 6.40 ppm consisting of a doublet ($^1J_{H\text{-}F}$ 47) of a doublet ($^2J_{H\text{-}F}$ 11) of a doublet ($^2J_{H\text{-}F}$ 11). This was not a doublet of triplets because the CF_2 fluorine atoms are diastereotopic. The proton-decoupled carbon NMR spectrum also confirmed the structure as (**26**) with a resonance at 40.7 ppm consisting of a triplet ($^2J_{C\text{-}F}$ 22), assigned to the CH ring carbon atom.

No trace of radical attack occurred at the CFBr carbon atom owing to the steric bulk of the bromine atom.

3.4.2. 1-Bromo-2,2-difluoroethene

Cyclohexane was added to 1-bromo-2,2-difluoroethene using γ-ray and DTBP initiation to give 2-bromo-1-cyclohexyl-1,1-difluoroethane (**28**) and bromocyclohexane (**27**).



(**28**) (**27**)

	Initiator and Conditions	Ratio R-H:Alkene	Product Ratio (**28**):(**27**)	Yield (%) (**28**)
(i)	γ-rays, 20 °C, 14 days	4.4:1	4:1	36
(ii)	DTBP, 140 °C, 24 hours (1)	17:1	4:1	19
(iii)	DTBP, 140 °C, 24 hours (2)	5:1	5.6:1	22

GLC/MS showed the mono-adduct (**28**) (M=226/228) and bromocyclohexane (**27**) (M=162/164) with no reverse-addition compound observed and only trace amounts of baseline material. Again, fluorine NMR of the recovered cyclohexane showed that the alkene partially dissolved, which accounted for the low isolated yield.

The mode of addition of (**28**) was determined from the proton-decoupled carbon NMR spectrum. Two triplets with two-bond coupling constants at 41.8 ppm ($^2J_{C-F}$ 22) and at 30.8 ppm ($^2J_{C-F}$ 34) confirmed the structure as (**28**). The hydrogen NMR spectrum of (**28**) gave a triplet at 3.5 ppm ($^2J_{H-F}$ 14) and with a relative integration of 2 was assigned to the CH_2Br hydrogen atoms.

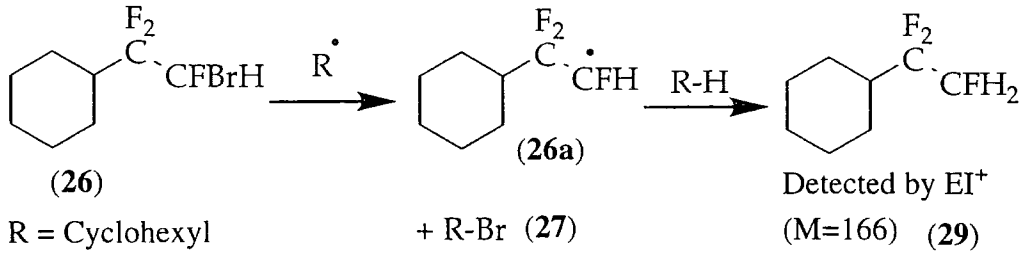
No radical attack occurred at the CHBr carbon atom, again owing to the steric bulk of the bromine atom.

3.4.3. Discussion of Results for Bromofluoroethenes

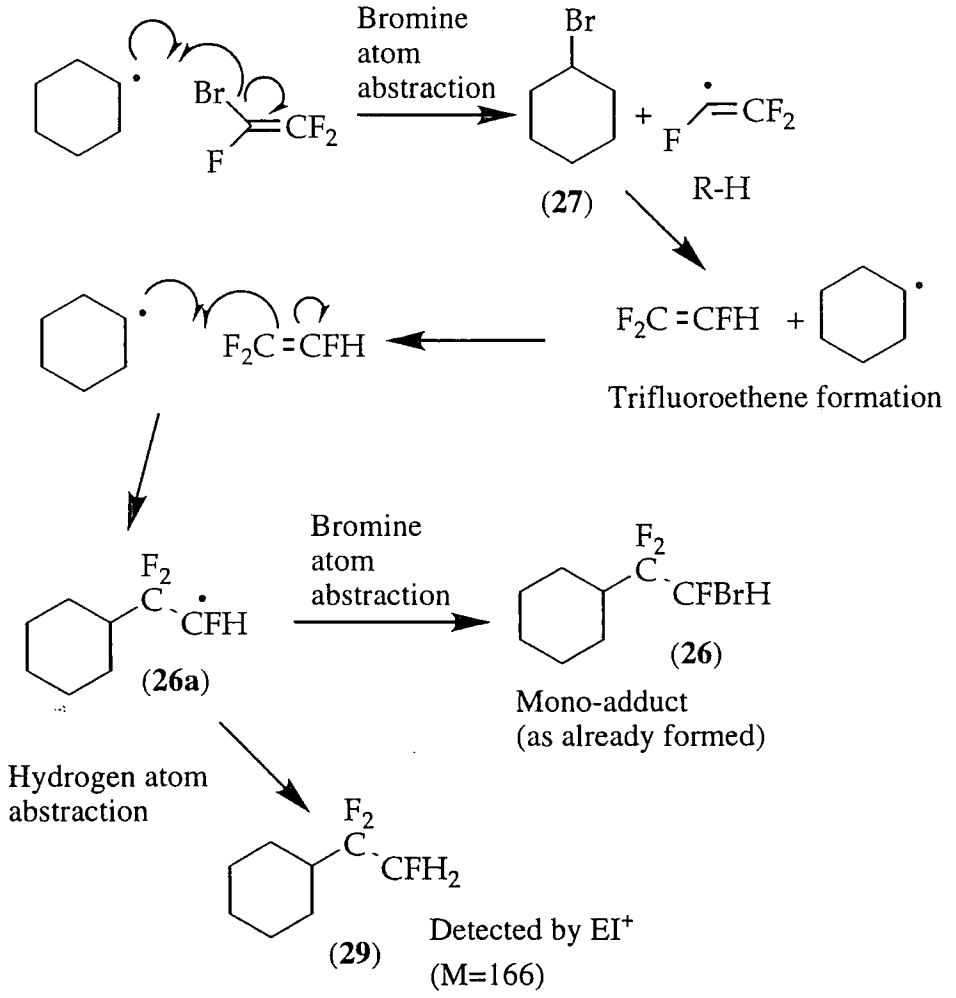
For both of the bromofluoroethenes investigated, no trace of radical attack occurred at the bromine-containing carbon atom because bromine is sterically very bulky. This was in contrast to the chlorofluoroethenes where a trace of reverse-addition product was observed by NMR. Using a larger amount of DTBP initiator would have increased the conversion and the yields, although both reactions produced bromocyclohexane (**27**) as a by-product.

In the case of bromotrifluoroethene, the bromocyclohexane (**27**) can be formed by a cyclohexyl radical abstracting a bromine atom from either a molecule of adduct (**26**) or from a molecule of bromotrifluoroethene. In the former, the new radical (**26a**)

can abstract a hydrogen atom from another molecule of cyclohexane to give 1-cyclohexyl-1,1,2-trifluoroethane (**29**):-



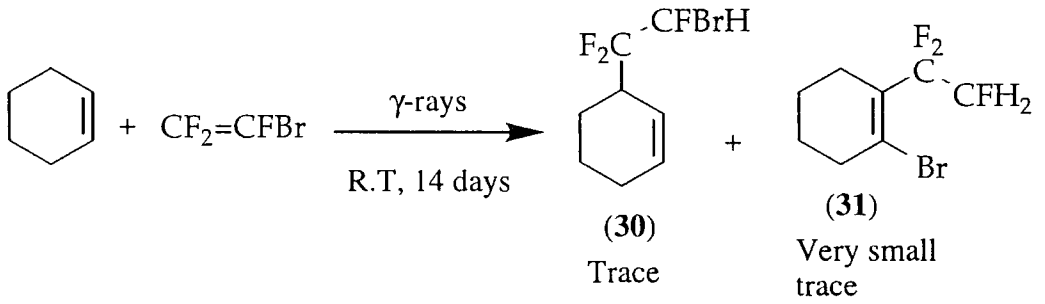
In the latter, bromine abstraction from bromotrifluoroethene results in a new radical which abstracts a hydrogen atom to give trifluoroethene. This can react with a cyclohexyl radical to give the same product:-



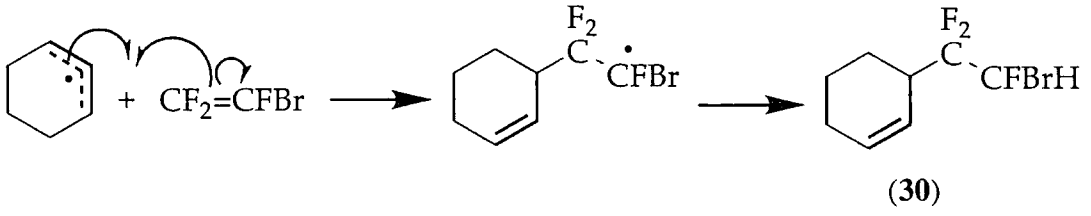
The mechanism was investigated by reacting cyclohexene with bromotrifluoroethene as described below.

3.4.4. Reaction of Cyclohexene with Bromotrifluoroethene

The mechanism of bromocyclohexane formation was investigated by reacting cyclohexene with bromotrifluoroethene to see if addition across the double bond occurred.

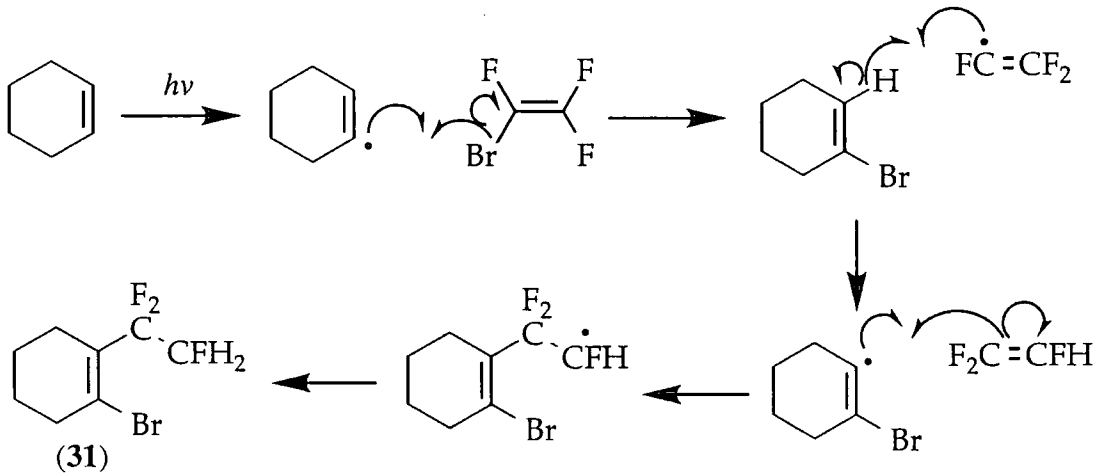


The crude reaction mixture was shown by GLC/MS to consist mainly of unreacted cyclohexene with only trace amounts of product. The major product (**30**) was identified by EI^+ data (M=242/244) and the fragmentation pattern. A major fragment at 131 amu was attributed to loss of CFBrH, and another at 81 amu resulted from loss of CF_2 to leave the cyclohexenyl ring. This resulted from the formation of an allyl radical which reacted with a bromotrifluoroethene molecule:-



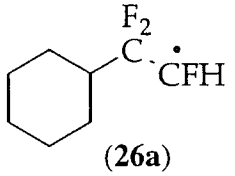
(**30**)

The compound resulting from direct addition of bromotrifluoroethene across the double bond (**31**) was identified by EI^+ data (M=242/244) and the fragmentation was consistent with the structure. The mechanism for its formation is as follows:-

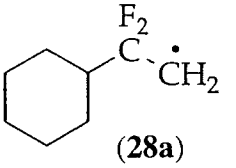


Only a minute trace of (**31**) formed which suggested that this process was not important in the radical reaction of cyclohexane with bromotrifluoroethene, even though the formation of CF_2=CFH was quite plausible. Therefore the cyclohexyl radical abstracted a bromine atom from a molecule of the adduct (**26**) rather than from a molecule of bromotrifluoroethene to form bromocyclohexane by-product.

Radical stabilities accounted for the fact that a larger proportion of bromocyclohexane formed in the reaction using bromotrifluoroethene, than with 1-bromo-2,2-difluoroethene.



(**26a**)
from CF_2=CFBr



(**28a**)
from CF_2=CHBr

As was discussed in chapter 1, fluorine stabilises a radical centre if it is in the α-position.[16] Therefore radical (**26a**) is more stable and easier to form than (**28a**), which accounted for the fact that the quantity of bromocyclohexane produced was much greater than that when 1-bromo-2,2-difluoroethene was used.

3.5. Conclusions

- Carbon-hydrogen bonds in saturated hydrocarbons can be functionalised by producing a free radical and reacting the radical with a range of fluorinated ethenes. This produced fluoroalkylated mono-adducts with the potential for further functionalisation.

- If a telomerisable ethene was used for analogous free radical addition, chain transfer was forced to compete over telomerisation by using a deficiency of alkene.

- For certain reactions involving bromofluoroethenes, bromine is sterically bulky and radical attack did not occur at a bromine-containing carbon atom.

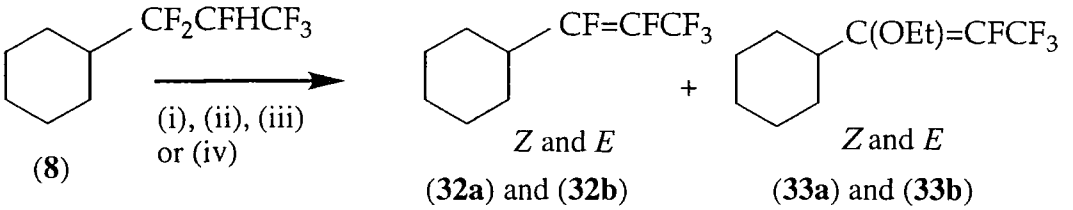
- Similarly, chlorine is also sterically bulky, and the partial attack at =CHCl compared to =CFCl showed that the fluorine lone pairs of electrons repel the incoming nucleophilic radical.

- Bromine abstraction occurred from adducts which contained bromine to give R-Br.

4. Dehydrofluorination of Polyfluorinated Hydrocarbons

4.1. Introduction

The polyfluoroalkyl derivatives prepared in chapters 2 and 3 can easily be functionalised, and one obvious approach is the elimination of hydrogen fluoride. The dehydrofluorination of ether-HFP adducts[42, 100-102] has been achieved by the use of alkoxide bases with or without solvent. This gave moderate to good conversions and in all cases the products consisted of a mixture of *Z* and *E* isomers which could not be separated. Russian workers[92, 103, 104] used alcoholic solutions of sodium hydroxide to dehydrofluorinate 1-cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**) to give (1*Z*) and (1*E*) isomers of 1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32**). However, when an alcoholic solvent was used nucleophilic attack occurred at the newly-formed double bond.[9, 101] Earlier work in this laboratory[7] illustrated in the table below showed that under favourable reaction conditions only one isomer resulted.



(**8**) — *Z* and *E* (**32a**) and (**32b**) — *Z* and *E* (**33a**) and (**33b**)

		Yields (%)			
	Conditions	*Z* (**32a**)	*E* (**32b**)	*Z* (**33a**)	*E* (**33b**)
(i)	KOH (2 eq), EtOH, 50 °C, 20 hrs	71	28	0.7	0.3
(ii)	KO^{t}Bu (2 eq), ^{t}BuOH, 25 °C, 15 min	58	2	-	-
(iii)	KO^{t}Bu (1.5 eq), ^{i}Pr$_2$O, 0 °C, 10 min	92	trace	-	-
(iv)	KO^{t}Bu (1.5 eq), C_6H_{14}, 0 °C, 15 min	85	trace	-	-

By using a non-nucleophilic solvent or a sterically hindered base the formation of ethers was avoided.

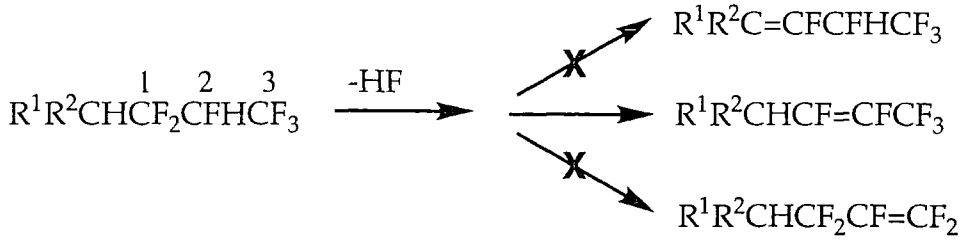
Z and *E* fluoroalkenes can easily be distinguished from each other by the use of fluorine NMR[105, 106] as F-F *trans* coupling constants are greater than for *cis*.

trans $^3J_{F\text{-}F}$ 133

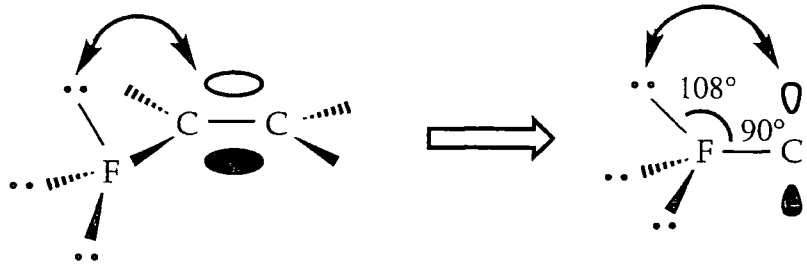
cis $^3J_{F\text{-}F}$ 19

The lone pairs of electrons on the fluorine atoms conjugate with the π electrons of the double bond, and this conjugation is greater when the fluorine atoms are *trans* to one another.[105]

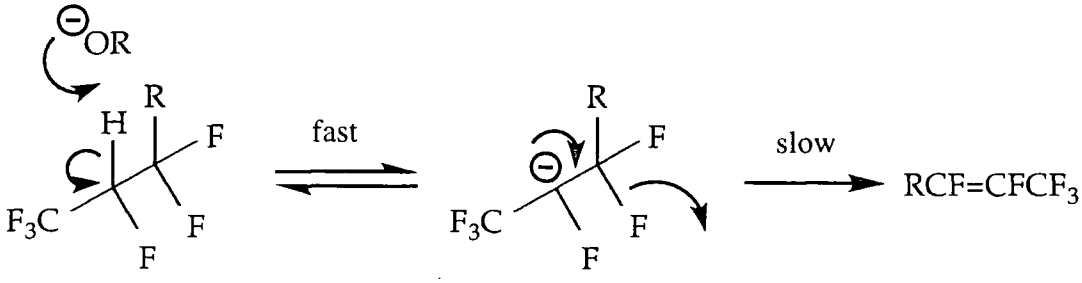
In all cases the double bond is formed at the 2-position, although theoretically three isomers could be produced:-



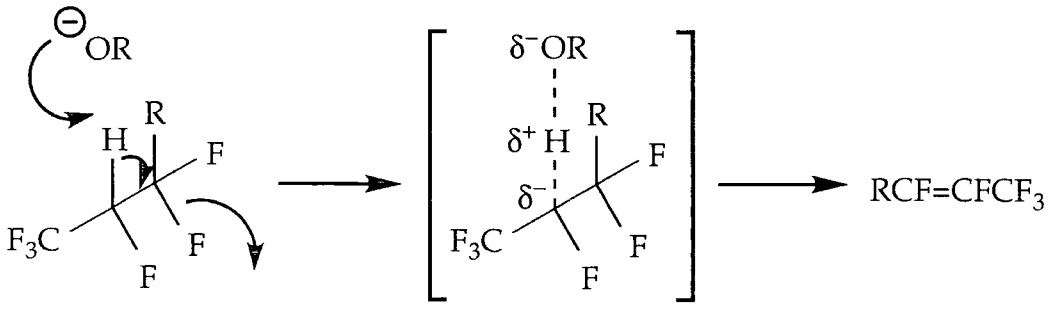
The regiochemistry of the double bond is governed by the acidity of the proton removed and the strength of the C-F bond being broken. The hydrogen atom at the 2-position is most acidic because the neighbouring electron-withdrawing CF_2 and CF_3 groups stabilise the developing carbanion. The fluoride ion which is eliminated comes from the CF_2 rather than the CF_3 group as this leads to a smaller number of vinylic fluorine atoms, whose lone pairs have unfavourable interactions with the π electrons of the double bond:-



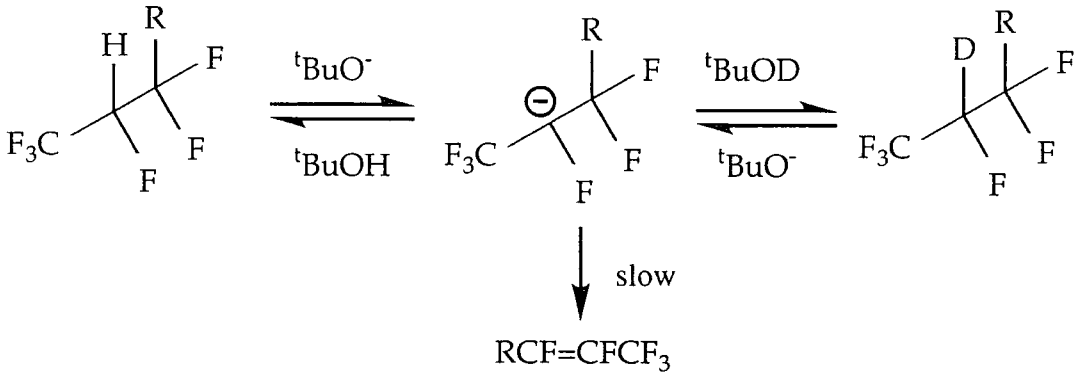
As the fluoride ion is a poor leaving group owing to the high carbon-fluorine bond dissociation energy and the proton which is removed is very acidic, it is most likely that the mechanism is E1cB, or E2 (concerted) with an 'E1cB-like' transition state, where C-H bond stretching occurs before C-F bond stretching. The E1cB mechanism is shown below:-



The E2 mechanism with the E1cB-like transition state:-



Deuterium exchange reactions have been carried out in this laboratory[9] on the elimination from the cyclohexane-HFP and adamantane-HFP mono-adducts, and deuterium was found to be incorporated into the starting material. This showed that the mechanism is E1cB, and not E2 with an E1cB-like transition state. Solvent deuterium exchange in an E1cB process is shown below:-

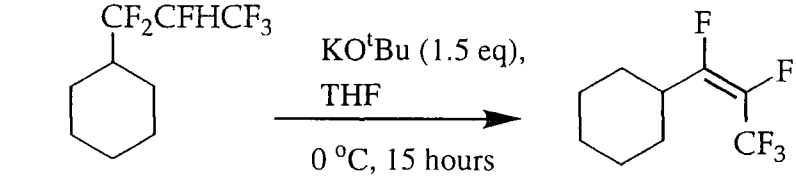


This chapter describes the dehydrofluorination of some of the polyfluoroalkyl derivatives prepared in the current work to produce new fluoroalkenes.

4.2. Dehydrofluorination of Polyfluorinated Hydrocarbons

4.2.1. 1-Cyclohexyl-1,1,2,3,3,3-hexafluoropropane

Dehydrofluorination of 1-cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**) gave (1*Z*)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) in agreement with earlier work in this laboratory.[9]

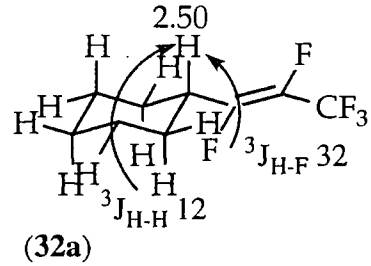


(**8**) Complete conversion

(**32a**) 68%

The stereochemistry of (**32a**) was determined from the fluorine NMR spectrum. The vinylic fluorine atoms were identified by their coupling to one another ($^3J_{F\text{-}F\,cis}$ 30) and the fluorine atom adjacent to the CF_3 group was identified as a quartet ($^3J_{F\text{-}F}$ 12) at -161.2 ppm. The other fluorine atom resonance occurred at -130.9 ppm. Therefore on account of the coupling constant the alkene was assigned to the *Z* isomer.[9] The stereochemistry of the product was surprising, as on steric grounds it might have been expected that the cyclohexyl and trifluoromethyl groups would be *trans* to one another.

The CH ring hydrogen atom resonance occurred at 2.50 ppm as a doublet ($^3J_{H\text{-}F}$ 32) from geminal coupling to the vinylic fluorine, of triplets ($^3J_{H\text{-}H}$ 12) from coupling to two neighbouring hydrogen atoms. The magnitude of the three-bond coupling constant from coupling to hydrogen is characteristic of an antiperiplanar relationship between the hydrogen atoms.[95] Therefore the fluoroalkenyl group occupies an equatorial site on the cyclohexyl ring:-

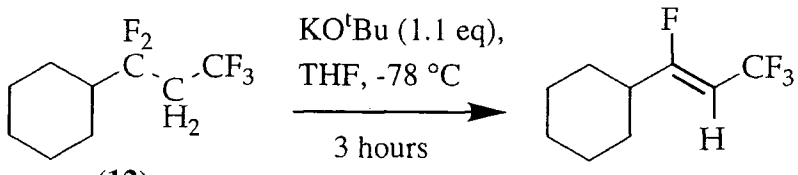


(**32a**)

This avoids destabilising 1,3 diaxial interactions with the hydrogen atoms. Removal of hydrogen fluoride from 1-cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**) has simplified the NMR spectra, allowing the stereochemistry to be observed.

4.2.2. 1-Cyclohexyl-1,1,3,3,3-pentafluoropropane

Dehydrofluorination of 1-cyclohexyl-1,1,3,3,3-pentafluoropropane (**12**) gave (1Z)-1-cyclohexyl-1,3,3,3-tetrafluoroprop-1-ene (**34**).

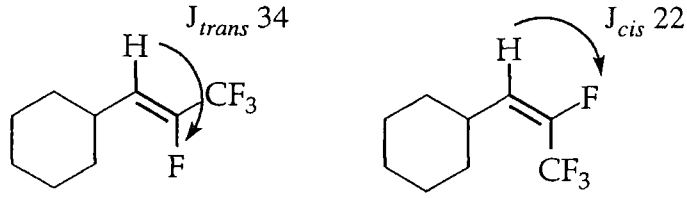


(**12**) Complete conversion

(**34**) 73%

Reaction using a 2.5-fold excess of potassium *tert*-butoxide gave unidentifiable by-products. Reaction at 0 °C was also effective although less baseline material resulted at -78 °C.

The stereochemistry of (**34**) was deduced from the hydrogen NMR spectrum, which gave a doublet ($^3J_{H\text{-}F}$ 34) of quartets ($^3J_{H\text{-}F}$ 7.6) at 4.94 ppm assigned to the vinylic hydrogen atom. The magnitude of the coupling constant for coupling to the vinylic fluorine atom (34 Hz) was the same as that for the H-F *trans* coupling for (1Z)-1-cyclohexyl-2,3,3,3-tetrafluoroprop-1-ene (**45a**), both isomers of which were prepared and fully characterised as described in chapter 5.

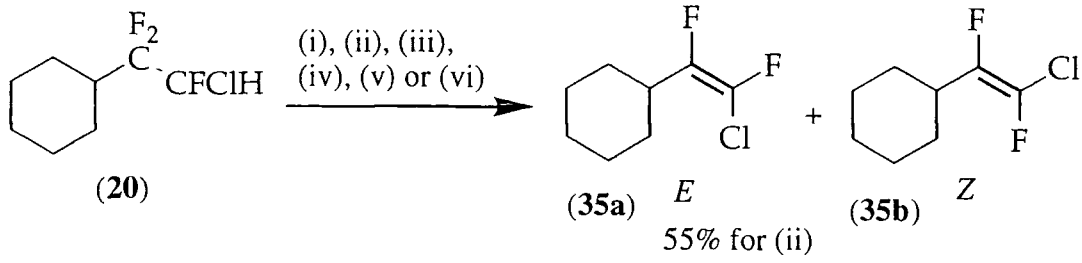


(**45a**) *Z* (**45b**) *E*

The *cis* coupling constant was sufficiently different from the *trans* coupling constant, showing that the vinylic hydrogen and fluorine atoms were on opposite sides of the double bond.[105]

4.2.3. 2-Chloro-1-cyclohexyl-1,1,2-trifluoroethane

Dehydrofluorination of 2-chloro-1-cyclohexyl-1,1,2-trifluoroethane (**20**) gave a mixture of (1*E*) and (1*Z*)-2-chloro-1-cyclohexyl-1,2-difluoroethene (**35a**) and (**35b**).



(**20**) (**35a**) *E* (**35b**) *Z*

55% for (ii)

	Conditions	Conversion (%)	Product Ratio *E*:*Z*
(i)	KO^{t}Bu (2.5 eq), THF, -78 °C, 15 hrs	100	15:1
(ii)	KO^{t}Bu (2.5 eq), THF, 20 °C, 15 hrs	100	4:1
(iii)	KO^{t}Bu (2.5 eq), THF, 80 °C, 15 hrs	100	3:1
(iv)	NaOH (2.5 eq), THF, 20 °C, 15 hrs	0	-
(v)	NaOH (2.5 eq), THF, 80 °C, 15 hrs	0	-
(vi)	NaOH (2.5 eq), Tetraglyme, 200 °C, 96 hrs	100	2:1

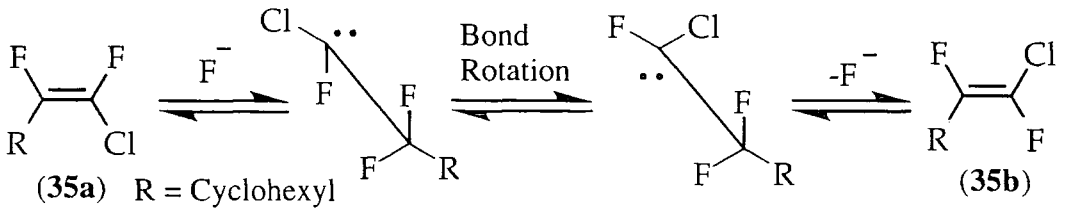
Fluorine NMR of (**35a**) and (**35b**) gave four resonances of two different intensities by relative integration because the *E* isomer predominated. A doublet ($^3J_{F\text{-}Ftrans}$ 126) of doublets ($^3J_{F\text{-}H}$ 29) at -153 ppm and a doublet ($^3J_{F\text{-}Ftrans}$ 126) at -128.7 ppm were assigned to the *Z* isomer (**35b**) on account of the coupling constant. A multiplet at -144.1 ppm and a singlet at -112.1 ppm were assigned to the *E* isomer (**35a**) whose resonances were larger by relative integration than the other two. Although for the *E* isomer the two fluorine atoms couple to each other, the size of the coupling constant for *cis* is much smaller than for *trans* and was not observed.[105]

The proton-decoupled carbon NMR spectrum also showed both isomers, and the relative peak heights enabled a full assignment to be made for each isomer. The four alkenic carbon atom resonances all appeared as a doublet of doublets from coupling to the vinylic fluorine atoms, confirming that dehydrofluorination had occurred.

Kinetic vs Thermodynamic Control

Dehydrofluorination of 2-chloro-1-cyclohexyl-1,1,2-trifluoroethane (**20**) occurred in a directly analogous way to that for 1-cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**). On steric grounds, it would be expected that the *Z* isomer would predominate, but the results obtained show that the *E* isomer formed preferentially. In an attempt to ascertain whether the *Z* isomer was more thermodynamically stable, a mixture of isomers of 2-chloro-1-cyclohexyl-1,2-

difluoroethene (**35a**) and (**35b**) were heated with caesium fluoride as a source of fluoride ion. The mechanism of a possible fluoride ion isomerisation was postulated to be as follows:-

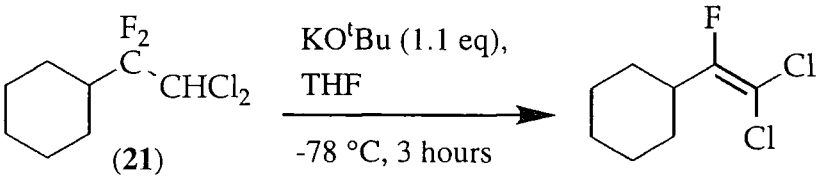


(**35a**) R = Cyclohexyl (**35b**)

Earlier work in this laboratory[9] described the isomerisation of alkenes formed from hexafluoropropene adducts with various alkyl groups. It was shown that for the adamantyl system, the *E* isomer was more stable and for the cyclohexyl system the two isomers were of similar thermodynamic stabilities. When a mixture of (1*E*) and (1*Z*)-2-chloro-1-cyclohexyl-1,2-difluoroethene (**35a**) and (**35b**) (5:1) were heated at 200 °C for 48 hours with caesium fluoride, no isomerisation was observed by fluorine NMR.

4.2.4. 2,2-Dichloro-1-cyclohexyl-1,1-difluoroethane

Dehydrofluorination of 2,2-dichloro-1-cyclohexyl-1,1-difluoroethane (**21**) gave (1*E*)-2,2-dichloro-1-cyclohexyl-1-fluoroethene (**36**).



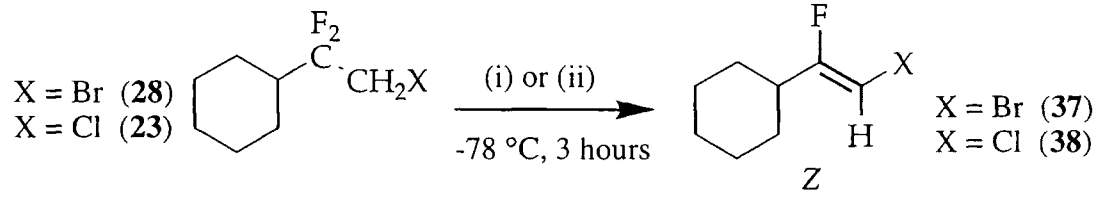
(**21**) Complete conversion (**36**) 81%

The hydrogen NMR spectrum of (**36**) gave a resonance at 2.7 ppm which consisted of a doublet ($^3J_{H\text{-}F}$ 28) of triplets ($^3J_{H\text{-}Faxial}$ 12) of triplets ($^3J_{H\text{-}Fequatorial}$ 3.6) and was assigned to the CH ring hydrogen atom. There were no further signals in the spectrum other than the CH_2 ring hydrogen atoms, showing that dehydrofluorination had occurred.

The magnitude of the larger triplet ($^3J_{H\text{-}H}$ 12) is characteristic of an antiperiplanar relationship between the hydrogen atoms,[95] showing that the fluoroalkenyl side-chain occupies an equatorial position on the cyclohexyl ring. This was also observed in the system derived from hexafluoropropene (**32a**) discussed in section 4.2.1.

4.2.5. and 4.2.6. 2-Bromo-1-cyclohexyl-1,1-difluoroethane and 2-Chloro-1-cyclohexyl-1,1-difluoroethane

Dehydrofluorination of 2-bromo-1-cyclohexyl-1,1-difluoroethane (**28**) and 2-chloro-1-cyclohexyl-1,1-difluoroethane (**23**) gave (1*Z*)-2-bromo-1-cyclohexyl-1-fluoroethene (**37**) and (1*Z*)-2-chloro-1-cyclohexyl-1-fluoroethene (**38**) respectively.



	X	Conditions	Conversion (%)	Yield (%)
(i)	Br	KO^{t}Bu (1.3 eq)	85	(**37**) - [a]
(ii)	Cl	KO^{t}Bu (1.5 eq)	100	(**38**) 62

[a] not worked up

4.2.5. 2-Bromo-1-cyclohexyl-1,1-difluoroethane

The hydrogen NMR spectrum of (**37**) gave a doublet of relative integration 1 at 5.30 ppm ($^3J_{H\text{-}F}$ 29) assigned to the vinylic hydrogen atom. The coupling constant was of the magnitude expected for *trans* H-F coupling,[95] so the alkene (**37**) was assigned to the *Z* isomer.

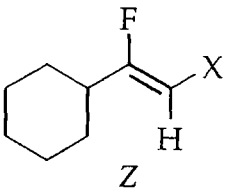
Conversion of starting material (**28**) was incomplete, as decomposition occurred when a larger excess of base was used. Purification using column chromatography was unsuccessful, and the quantity too small for distillation. Therefore a full characterisation was not achieved, although NMR data still enabled the stereochemistry to be determined.

4.2.6. 2-Chloro-1-cyclohexyl-1,1-difluoroethane

The NMR data of (**38**) was analogous to that of (**37**), with the cyclohexyl ring and chlorine atoms *trans* to one another.

4.3. Discussion of Results

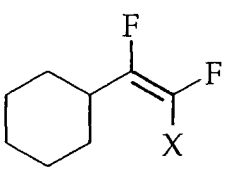
For the formation of alkenes from polyfluoroalkyl derivatives of the general formula RCF_2CH_2X where X is Br, Cl or CF_3, HF was eliminated at -78 °C to give one isomer with the cyclohexyl and X substituents *trans* to one another.



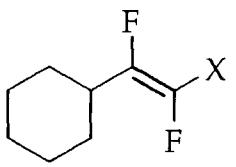
X = Br, Cl or CF_3

The *Z* isomer is expected to be more thermodynamically stable than the *E* isomer, as the sterically bulky cyclohexyl and X groups are on opposite sides of the double bond.

For the formation of alkenes of the general formula R-CF=CFX where X is CF_3 or Cl, the isomer which was observed to form preferentially at -78 °C had the cyclohexyl and X groups *cis* to each other. This result was surprising, as again on steric grounds they would be expected to be *trans*. Earlier work in this laboratory[9] has shown that when X is CF_3 the isomers are of similar thermodynamic stabilities. In the present work it was shown that when X is Cl, the *trans* isomer is more thermodynamically stable and this can be rationalised on the basis of steric factors.



(cis)
kinetic
control



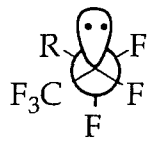
(trans)
thermodynamic
control

X = CF_3 or Cl

Clearly for the less thermodynamically stable isomer to form preferentially, there must be some energy-lowering interaction in the transition state.

One possibility is the *cis* effect,[107] which is a hyperconjugation effect such that a double bond with one fluorine atom on each of the alkenic carbon atoms is more thermodynamically stable if the fluorine atoms are *cis* to each other. This is because in the *trans* isomer conjugation of the fluorine lone pairs with the π electrons of the carbon-carbon double bond causes destabilisation. However, in the present work the *cis* effect appeared to be unimportant otherwise this would have been the more thermodynamically stable isomer.

In the case of the dehydrofluorination of 1-cyclohexyl-1,1,2,3,3-hexafluoropropane (**8**), formation of the *Z* isomer proceeds via *anti* elimination such that the intermediate anion preferentially adopts the *gauche* conformation.



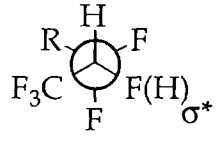
R = Cyclohexyl

Gauche conformer

This is surprising in view of the steric interaction between the cyclohexyl and trifluoromethyl groups. However this is analogous to 1,2-difluoroethane whereby the *gauche* conformation is lowest in energy and may be a result of fluorine-fluorine lone pair attractions.[108]

Another possibility could be an energy-lowering interaction between the cyclohexyl and trifluoromethyl groups such as hydrogen bonding in the carbanion-like transition state. This has been claimed[9] to be a possibility for the observed stereochemistry of R-CF=CF-CF_3 (**32a**). However, this cannot explain the observed stereochemistry for the alkene R-CF=CH-CF_3 (**34**) as no trace of the *cis* (*E*) isomer was observed.

In the transition state, electronic charge could be donated from the cyclohexyl group to the unoccupied σ* orbitals of the fluorine atom, so they would have to be antiperiplanar for such an interaction to occur:-



R = Cyclohexyl

In the alkene R-CF=CH-CF_3 (**34**) this interaction cannot occur, which might explain why the *E* isomer formed. These results are being probed by calculations by other workers,[109] and a full discussion of the theory is beyond the scope of the current project.

4.4. Conclusions

- Polyfluoroalkyl derivatives have been functionalised which opens up new synthetic possibilities.

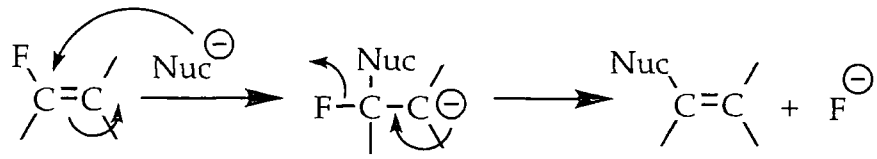
- The dehydrofluorination reactions of polyfluoroalkyl derivatives were regioselective, although this depended on the conditions.

- Loss of HF from these polyfluoroalkyl derivatives simplified the NMR spectra, and in some systems it was shown that the fluoroalkyl group occupied an equatorial position on the cyclohexyl ring.

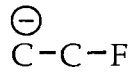
5. Reactions of Fluoroalkenes with Nucleophiles

5.1. Introduction

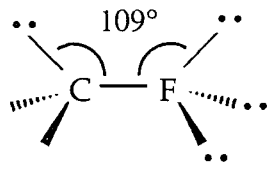
Fluorinated alkenes are electron deficient and are thus susceptible to attack by a range of nucleophiles. The reaction mechanism[1] is addition/elimination via a carbanion intermediate, which expels a fluoride ion to give the neutral product.



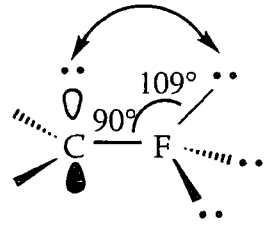
The orientation and rate of nucleophilic attack at a fluorinated alkene is determined by the stability of the carbanion. Fluorine attached to a carbon atom adjacent to a carbanion centre is strongly stabilising owing to the electron inductive effect and hence strongly activating:-



However, fluorine attached directly to a carbanion centre can stabilise or destabilise depending on the geometry of the carbon atom. Although fluorine would be expected to stabilise owing to the inductive effect (electron withdrawal), the lone pair of electrons must also be considered. If the shape of the carbon atom is tetrahedral there is some stabilisation relative to hydrogen, but if it is planar the repulsion between the non-bonding electrons is maximised and destabilisation results.



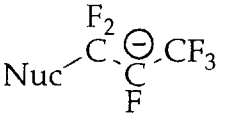
Tetrahedral
$^{-}$C-F slightly stabilised
with respect to C-H



Planar
e^{-} pair repulsions greater
$^{-}$C-F destabilised with
respect to C-H

It follows that when an asymmetric fluoroalkene is reacted with a nucleophile, attack occurs at the carbon atom which forms a carbanion intermediate with the minimum number of fluorine atoms attached directly to the carbanion centre.

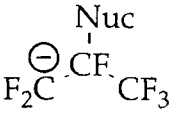
With hexafluoropropene for example, although two possible carbanion intermediates could result, (a) is favoured over (b):-



(a)

1 C-F interaction

5 C-C-F interactions

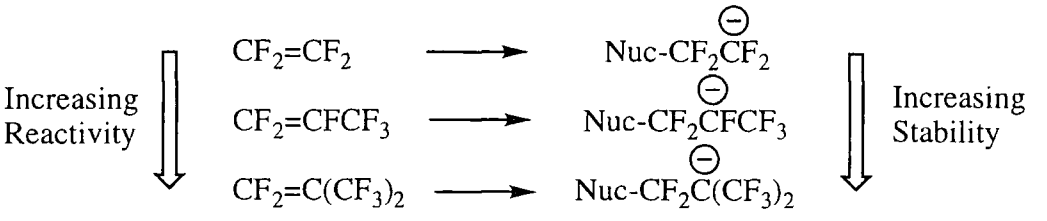


(b)

2 C-F interactions

1 C-C-F interaction

A reactivity order for fluoroalkenes can be predicted, based on increasing perfluoroalkyl substitution at one of the sp^2 carbon atoms which leads to a greater stabilisation of negative charge of the anion intermediate.[110]

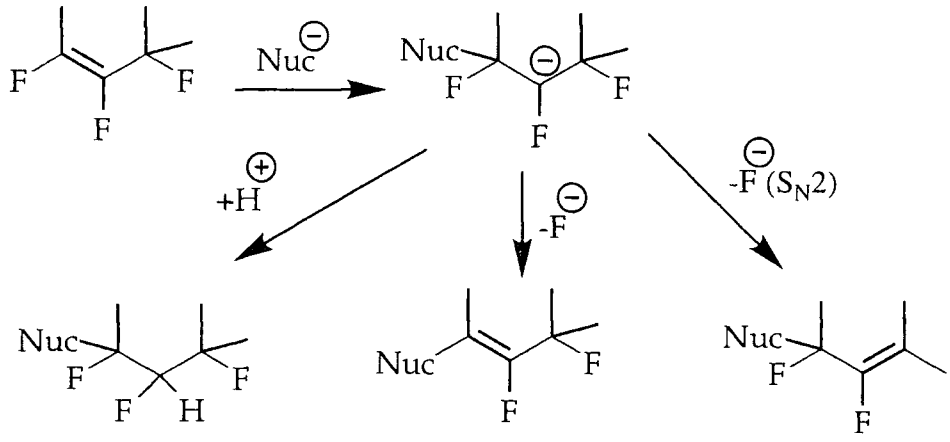


This has been confirmed experimentally by reaction with methanol. Tetrafluoroethene[110] requires a strong base and/or high pressure, hexafluoropropene[111] requires only a weak base whereas perfluoroisobutene[112] reacts quickly with neutral methanol.

The Carbanion Intermediate

Following attack by a nucleophile, the carbanion intermediate can react by one of three possible routes:-

- Direct addition across the double bond
- Vinylic substitution of fluoride ion
- Allylic displacement of fluoride ion (S_N2)



The route followed depends largely on the stability of the carbanion intermediate. A very unstable carbanion usually abstracts a proton from the environment rather than eliminating a fluoride ion. For example, when tetrafluoroethene reacts with an oxygen nucleophile the carbanion intermediate is very unstable because of the two α-fluorine atoms. Therefore an addition product results[13] as proton abstraction occurs in preference to fluoride ion elimination.

$$n\text{-}C_4H_9OH + CF_2{=}CF_2 \xrightarrow[<38\ ^\circ C]{n\text{-}C_4H_9ONa} n\text{-}C_4H_9OCF_2CF_2H \quad (81\%)$$

Carbon, nitrogen, oxygen, sulfur and other nucleophiles all react with polyfluorinated alkenes and there are many examples documented in the literature.[1]

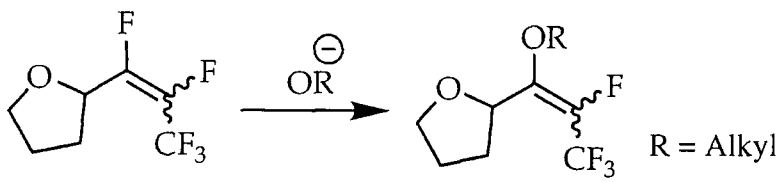
$$CF_2{=}CF_2 + 2\ PhLi \xrightarrow{-80\ ^\circ C} PhCF{=}CFPh \ (50\%) \xrightarrow{2\ PhLi} CPh_2{=}CPh_2 \ (72\%)$$

$$CF_2{=}CF_2 + CH_3O\,Na \xrightarrow[145\ hours]{20 - 40\ ^\circ C} CH_3O\text{-}CF{=}CF_2\ (28\%) + CH_3O\text{-}CF_2\text{-}CHF_2\ (7\%)$$

5.2. Reaction of (1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene with Nucleophiles

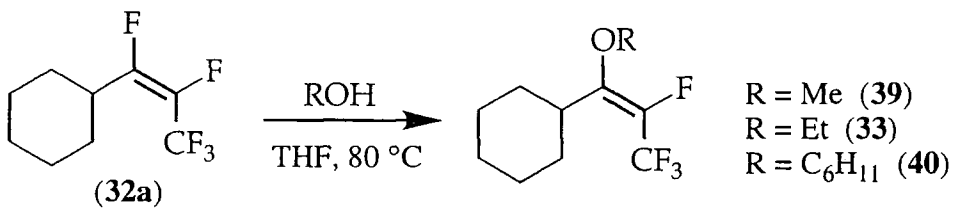
5.2.1. Oxygen Nucleophiles

Dmowski[101] showed that a mixture of *Z* and *E* isomers of the pentafluoropropenyl derivative of tetrahydrofuran readily underwent nucleophilic attack at the double bond via the most stable carbanion intermediate:-



A similar experiment carried out earlier in this laboratory[7] with the pentafluoropropenyl derivative of cyclohexane (**32a**) used ethoxide ions to generate the substitution product. In the present research, a range of alkoxide ions were reacted with (1*Z*)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) to determine the stereochemistry of the products.

The gradual disappearance of the resonance due to the vinylic fluorine atom at -131 ppm in the starting material (**32a**) was used to monitor the course of the reaction. Reaction occurred relatively slowly because the cyclohexyl ring releases electron density, making the reaction site less electrophilic. Therefore this was less susceptible to nucleophilic attack than perfluorinated systems.



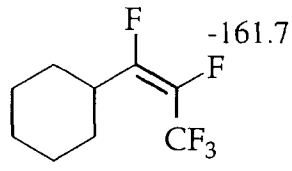
(**32a**)
Complete conversion

R	Conditions	Yield (%)	Stereochemistry
Me	MeOH (4 eq), Na (2 eq), 24 hrs	(**39**) 72	*Z*:*E* = 30:1
Et	EtOH (1.5 eq), Na (1.5 eq), 5 days	(**33**) 58	*Z*
C_6H_{11}	$C_6H_{11}OH$ (1 eq), NaH (1 eq), 24 hrs	(**40**) 67	*Z*

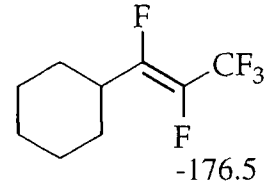
The regiochemistry was determined from the proton-decoupled carbon NMR spectrum for the ethoxy-substituted compound (**33**). A quartet ($^1J_{C\text{-}F}$ 268) of doublets ($^2J_{C\text{-}F}$ 37) at 121.3 ppm was assigned to the trifluoromethyl carbon atom which was adjacent to the CF carbon atom. Therefore the fluorine atom adjacent to the cyclohexyl ring underwent substitution. The fluorine NMR spectrum of (**33**) gave a doublet ($^3J_{F\text{-}F}$

8.6) at -63.1 ppm assigned to the trifluoromethyl fluorine atoms and a quartet ($^3J_{F-F}$ 8.6) at -160.9 ppm assigned to the vinylic fluorine atom. As these coupling constants were of the expected magnitude for three-bond coupling, this also confirmed the regiochemistry.[95]

The stereochemistry was not so apparent. The vinylic fluorine atom resonance of the products gave a chemical shift of about -161 ppm in each case, and this was compared to the chemical shift of this fluorine atom in both isomers of the starting fluoroalkene (**32**), prepared earlier[7] in this laboratory:-



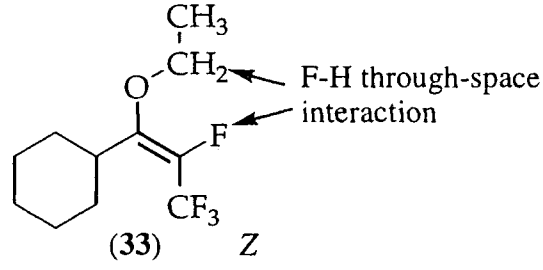
(**32a**) *Z*



(**32b**) *E*

On the basis of this comparison it would be expected that the alkoxy-substituted compounds prepared could also be assigned to the *Z* isomer. An X-ray crystal structure of (**33**) was unobtainable which would have given conclusive proof, because (**33**) did not form a crystal at low temperatures. This was probably due to the low symmetry and high hydrocarbon content of the molecule.

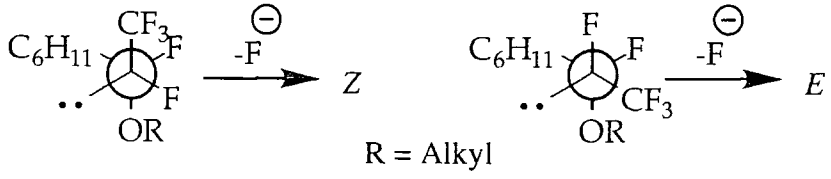
The stereochemistry of (**33**) was determined by obtaining a heteronuclear hydrogen-fluorine NOE spectrum. When (**33**) was irradiated at the frequency of the vinylic fluorine atom, the resonance on the hydrogen NMR spectrum due to the CH_2 hydrogen atoms adjacent to the ether linkage gave a large enhancement. This indicated that the vinylic fluorine atom and the ethoxy hydrogen atoms were interacting through space and therefore sterically close to each other. To confirm this, when the molecule was irradiated at the frequency of the trifluoromethyl fluorine atoms, the CH_2 hydrogen atoms adjacent to the ether linkage gave no enhancement, whereas there was a large enhancement observed for the tertiary hydrogen atom. This gave conclusive proof that the trifluoromethyl and ethoxy groups were *trans* relative to one another, and (**33**) was therefore assigned to the *Z* isomer.



(**33**) *Z*

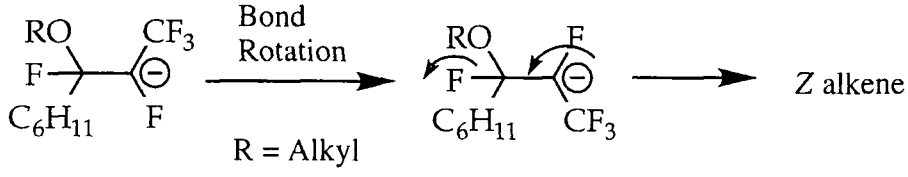
By the similarity of fluorine NMR chemical shifts the other two compounds (**39**) and (**40**) were assumed to be of the same stereochemistry.

One isomer of the fluoroalkene starting material (**32a**) gave one isomer of the substitution product. However, it might have been expected that two isomers of product would result from rotation of the carbon-carbon bond of the carbanion intermediate. The two possible carbanion intermediates can be viewed as Newman projections:-



Dmowski[101] suggested that a combination of steric and electronic repulsions between the alkoxy and trifluoromethyl groups would favour formation of the *Z* isomer by *trans* elimination of the fluoride ion as shown above. This hypothesis was supported by the fact that a mixture of *Z* and *E* isomers of starting fluoroalkene gave predominantly the *Z* isomer of the products.

The carbanion intermediate is relatively long-lived because of the stabilising effect of the fluorine atoms, and the loss of fluoride ion is slow owing to the high strength of the carbon-fluorine bond.[114] Therefore rotation of the carbon-carbon bond can occur to give the more thermodynamically stable isomer:-

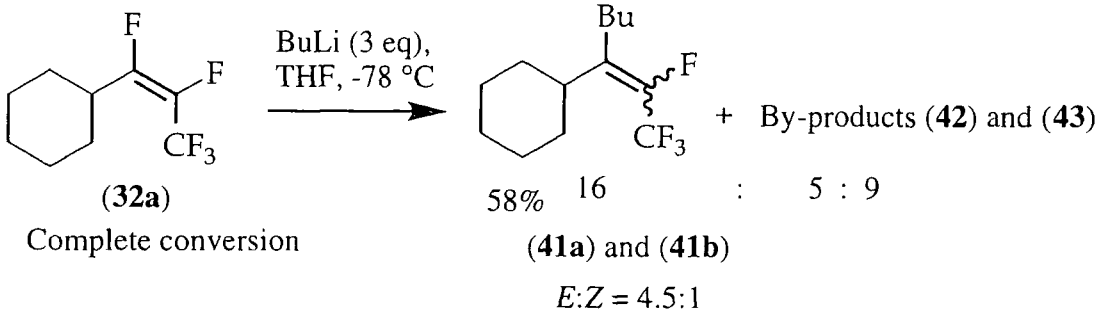


These factors explain why the *Z* isomer was formed in the present work.

5.2.2. Carbon Nucleophiles

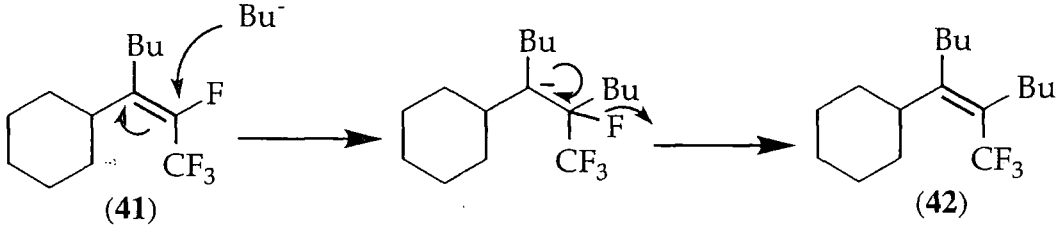
5.2.2.1. Butyl Lithium

Reaction of butyl lithium with (1*Z*)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) gave (1*E*) and (1*Z*)-3-cyclohexyl-1,1,1,2-tetrafluorohept-2-ene (**41**) in the ratio of 4.5:1.

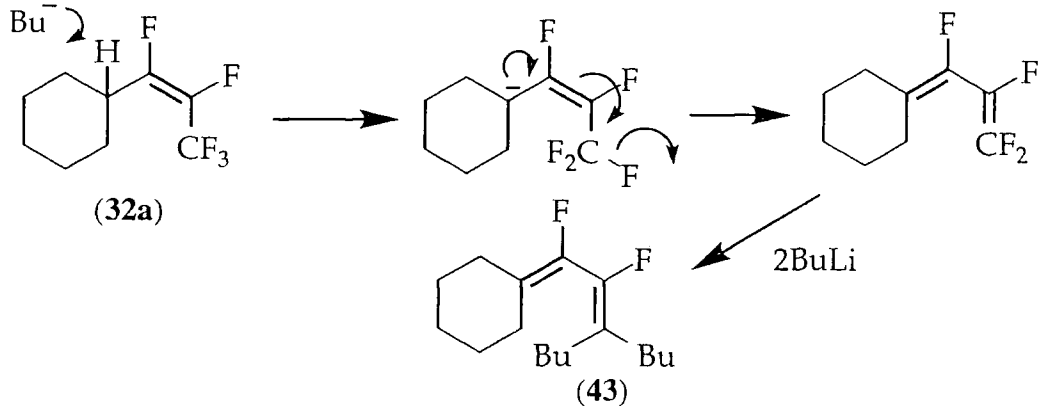


This reaction also gave two by-products with longer retention times by GLC than (**41**). Fluorine NMR of this higher-boiling material gave two sharp resonances at -56 ppm and at -148 ppm, in the ratio of 47:53 by relative integration. The resonance at -148 ppm consisted of two doublets superimposed and the resonance at -56 ppm was assigned as a CF_3 group.

Compound (**42**) was identified from EI^+ data and accounted for the CF_3 fluorine atom resonance at -56 ppm in the fluorine NMR spectrum. This could have resulted from attack of butyl lithium on a molecule of 3-cyclohexyl-1,1,1,2-tetrafluorohept-2-ene (**41**):-

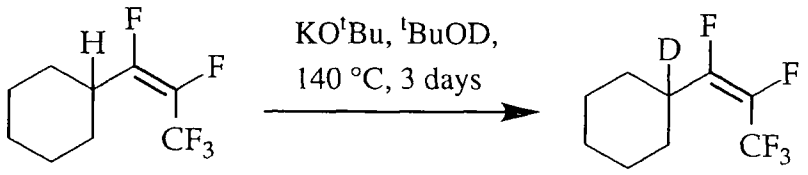


Compound (**43**) was also identified from EI^+ and fluorine NMR data. As the two fluorine atoms are part of a conjugated system, their chemical shifts would be close to each other to account for the two superimposed doublets at -148 ppm. The formation of (**43**) commences with abstraction of an acidic hydrogen atom as illustrated below:-



(32a) (43)

The acidity of the tertiary hydrogen atom on (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) was investigated by heating (**32a**) at 140 °C in a sealed NMR tube with potassium *tert*-butoxide and *t*-butanol(OD).



(32a) (44)

Deuterium incorporation

A hydrogen NMR spectrum showed that the tertiary hydrogen resonance at 2.3 ppm had completely disappeared, indicating that the hydrogen atom had been replaced by deuterium.

Reaction with a six-fold excess of butyl lithium was attempted to increase the proportion of higher molecular weight products, but decomposition occurred. Therefore isolation and full characterisation of (**42**) and (**43**) was not achieved.

5.2.2.2. Grignard Reagents

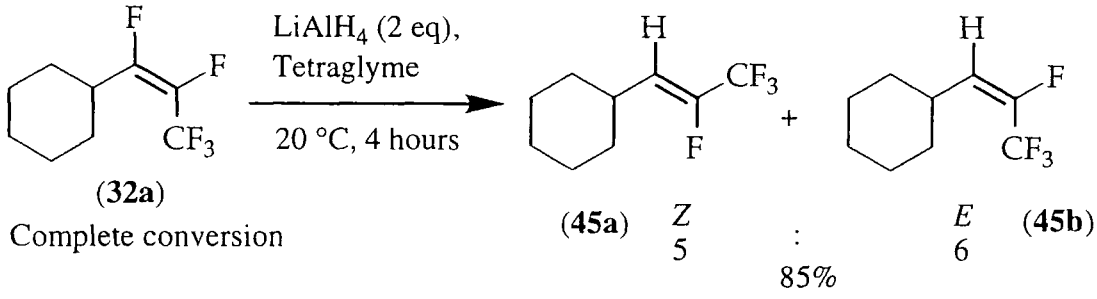
Attempted reactions of (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) with 3-butenyl magnesium bromide and methyl magnesium bromide were unsuccessful, even after heating at reflux for six days.

5.2.3. Reaction with Nitrogen Nucleophiles

Attempted reactions of (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) with aniline, butylamine and sodium amide were unsuccessful, even after heating at reflux for three days. No further investigation of nitrogen nucleophiles was undertaken.

5.2.4. Lithium Aluminium Hydride

Reaction of lithium aluminium hydride with (1*Z*)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) gave (1*Z*) and (1*E*)-1-cyclohexyl-2,3,3,3-tetrafluoroprop-1-ene (**45a**) and (**45b**) in the ratio of 5:6. An earlier attempt using sodium hydride gave no reaction.



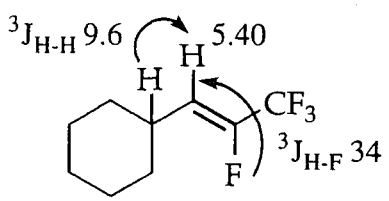
(**32a**)
Complete conversion

(**45a**) *Z* 5 : *E* 6 (**45b**)
85%

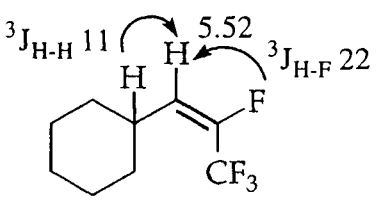
The fluorine NMR spectrum of (**45a**) and (**45b**) showed two resonances due to CF_3 fluorine atoms at -68 ppm and at -73 ppm in the ratio of 5:6 by relative integration. Two resonances due to the vinylic fluorine atoms appeared at -131 ppm and at -138 ppm also in the ratio of 5:6.

These fluorine chemical shifts suggested that the fluorine atom adjacent to the CF_3 group was substituted as the resonance at -161 ppm disappeared. However, the coupling constant for the CF_3 fluorine atoms coupling to the vinylic fluorine atom in (1*Z*) and (1*E*)-1-cyclohexyl-2,3,3,3-tetrafluoroprop-1-ene (**45a**) and (**45b**) was 11 Hz. This was the same as that for (**32a**), which confirmed the regiochemistry as shown above.

The hydrogen NMR spectrum of (**45a**) and (**45b**) gave two doublets of doublets at 5.40 ppm and at 5.52 ppm. This corresponded to the vinylic hydrogen atom of each isomer coupling to the vinylic fluorine atom and the tertiary hydrogen atom. Coupling constants from fluorine coupling to hydrogen[95] are greater if the atoms are *trans* than for *cis*, and this enabled their assignment to each isomer as illustrated below:-



(**45a**) *Z*



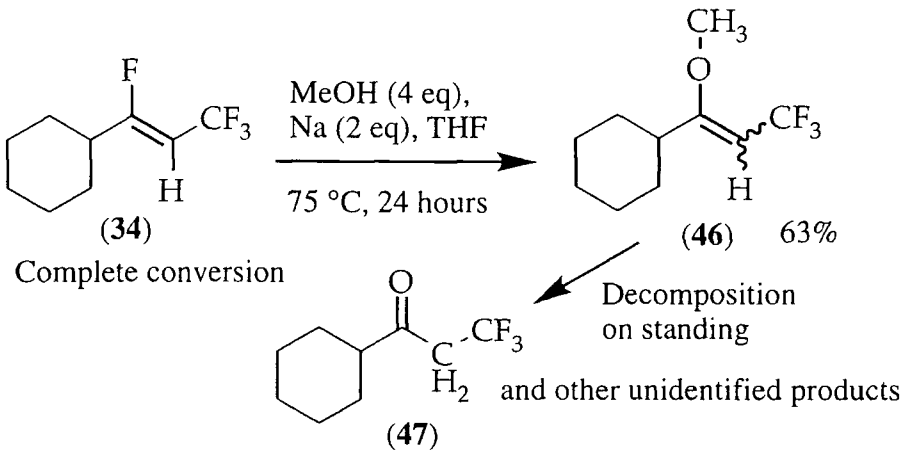
(**45b**) *E*

As the resonance at 5.52 ppm was larger by relative integration than that at 5.40 ppm, the *E* isomer predominated which enabled the resonances on the fluorine NMR spectrum to be assigned.

5.3. Reaction of (1Z)-1-Cyclohexyl-1,3,3,3-tetrafluoroprop-1-ene with Nucleophiles

5.3.1. Methanol

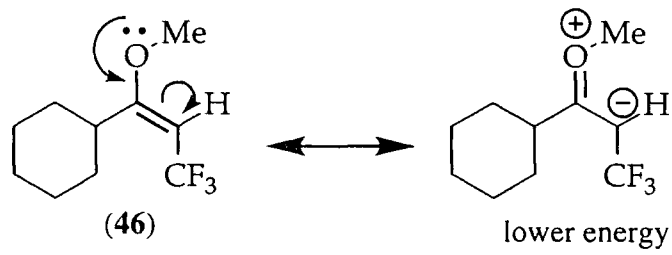
Reaction of methoxide ions with (1Z)-1-cyclohexyl-1,3,3,3-tetrafluoroprop-1-ene (**34**) gave isomers of 1-cyclohexyl-1-methoxy-3,3,3-trifluoroprop-1-ene (**46**) in a ratio of 27:1 by fluorine NMR. This decomposed on standing and one decomposition product was identified as the ketone (**47**). Therefore a heteronuclear NOE spectrum to determine the stereochemistry of (**46**) could not be obtained.



Reaction using methanol as solvent took 5 days to complete. Tetrahydrofuran desolvates the methoxide ions, resulting in a faster reaction. The substitution product (**46**) was characterised by analogy to (**39**) described earlier in this chapter.

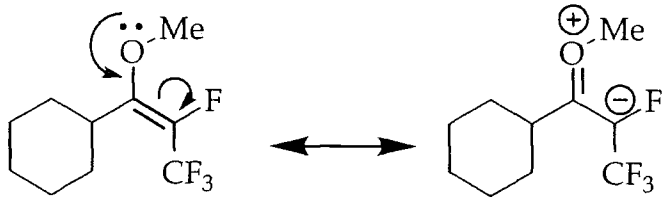
The ketone (**47**) was observed by GLC/MS with a molecular ion at M=194 with fragments corresponding to loss of $C_6H_{11}CO$ and CH_2CF_3. A small resonance in the carbon NMR spectrum at 203.4 ppm was assigned to the carbonyl carbon atom, and the hydrogen NMR spectrum gave a quartet at 2.9 ppm ($^3J_{H\text{-}F}$ 10.4).

The unstable nature of (**46**) could be due to the lone pair of electrons on the oxygen atom being able to delocalise:-



The trifluoromethyl fluorine atoms stabilise the carbanion from (**46**), allowing it to form and undergo further reaction leading to decomposition. In contrast, delocalisation

of (**39**) derived from hexafluoropropene is unlikely to occur as the vinylic fluorine atom would cause considerable destabilisation:-

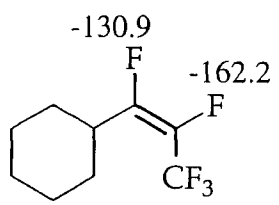


(**39**) higher energy, less stable

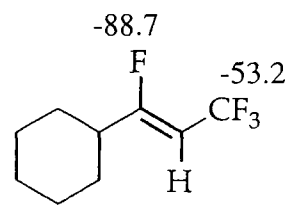
5.3.2. Competition Reaction between (1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene and (1Z)-1-Cyclohexyl-1,3,3,3-tetrafluoroprop-1-ene

The reactivity of (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) and (1Z)-1-cyclohexyl-1,3,3,3-tetrafluoroprop-1-ene (**34**) with oxygen nucleophiles was compared by means of a competition experiment. A near equimolar quantity of the two alkenes (**32a**) and (**34**) was added to a solution of methoxide ions in THF.

A fluorine NMR spectrum of the mixture of the two alkenes was run before and after being added to the solution of methoxide ions, and the relative integration values shown in the table below. The resonances in the fluorine NMR spectrum in ppm of the two alkenes are summarised below:-



(**32a**) -65.7



(**34**)

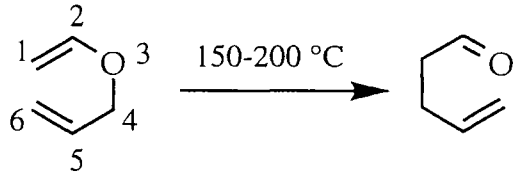
Alkene	Vinylic F shift (ppm)	Rel. Int. before reaction (R_1)	Rel. Int. after reaction (R_2)	(R_1-R_2)
(**32a**)	-130.9	10.81	8.81	2.00
(**34**)	-88.7	9.59	4.27	5.32

The resonance at -88.7 ppm disappeared preferentially, thus indicating that the alkene derived from pentafluoropropene (**34**) reacted faster. As was discussed in section 5.1, reaction with nucleophiles proceeds via a carbanion intermediate. Since the alkene with a hydrogen in place of a fluorine atom reacted faster, this showed that the shape of the transition state was planar because a fluorine atom is destabilising relative to hydrogen.

5.4. Claisen Rearrangements of Fluorinated Systems

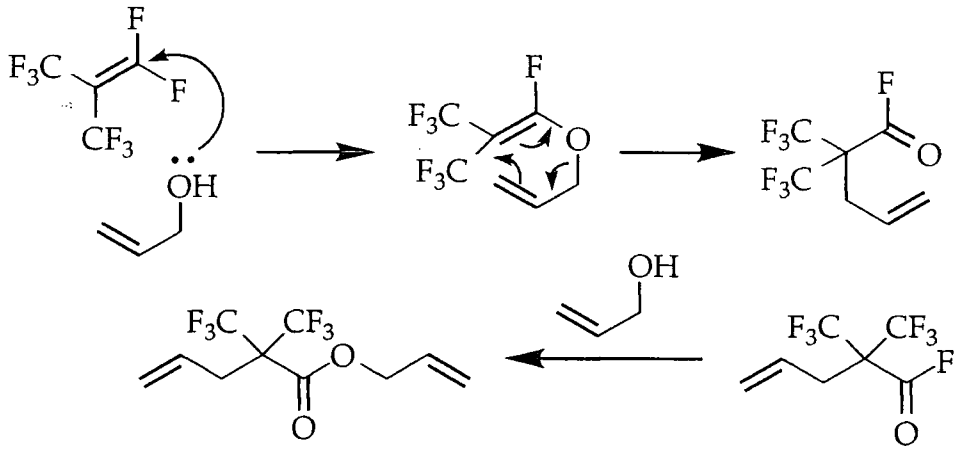
5.4.1. Introduction

The Claisen rearrangement[115, 116] is a sigmatropic rearrangement at elevated temperatures (150 - 200 °C) of an allyl vinyl ether to an isomeric χ,δ-unsaturated carbonyl system. The process is generally considered to be a concerted, intramolecular S_N2 addition of a carbonyl enol to an allylic alcohol to form a carbon-carbon σ-bond ([3,3]-sigmatropic rearrangement) with concomitant double-bond migration.



The transition state is assumed to be chair-like as it minimises 1,3-diaxial interactions. The Claisen rearrangement is a useful synthetic tool as it introduces functionality stereo- and regio-specifically, generates two useful functional groups which allows further functionalisation, and fixes the geometry of the newly-formed carbon-carbon double bond.

There are a number of examples in the literature[117-121] of Claisen rearrangements occurring with fluorine atoms present, and many of them were observed to occur much faster than their non-fluorinated counterparts. One early example[122] is the reaction of allyl alcohol and octafluoroisobutene which resulted in a 4-pentenyl ester. The intermediate allyl vinyl ether rearranged below 50 °C and reacted with another molecule of allyl alcohol as illustrated below:-



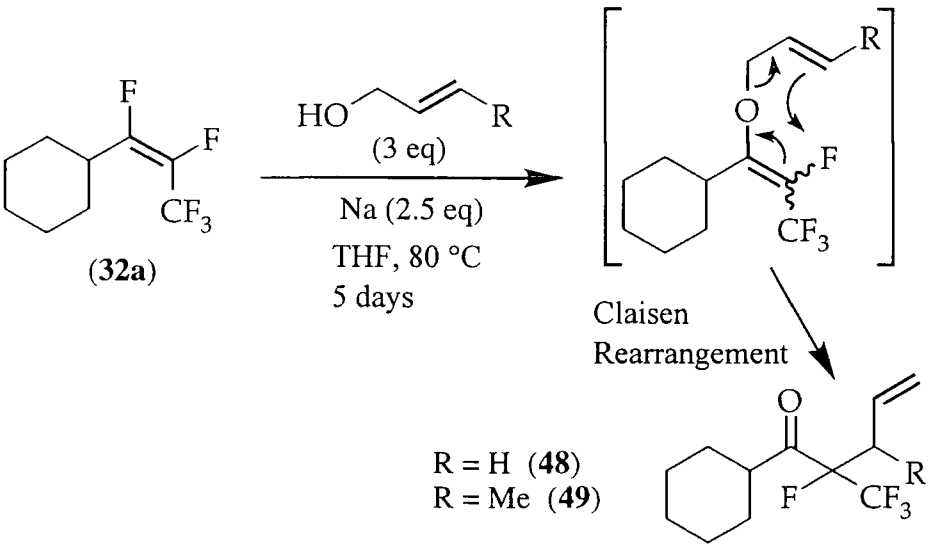
Dramatic accelerations have been observed when there are more halogens directly bound to the vinyl system. With increasing the fluorine substitution, lower temperatures could be used.[123] For example, Cl_2C=CFOallyl rearranges at -20 °C, ClF=CFOallyl rearranges at 35 °C and F_2C=CFOallyl rearranges at -50 °C. When

fluorine is substituted only at C-1, the rearrangement rate appears to be dependant on other substituents in the molecule rather that the presence of fluorine itself.

In the present research the Claisen rearrangement was investigated as a potential route to molecules containing a trifluoromethyl group in the middle of an aliphatic carbon chain.

5.4.2. Claisen Rearrangement reactions with (1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene

Allyl and crotyl alkoxide ions were reacted with (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) to give a substitution intermediate which subsequently underwent a Claisen rearrangement to give a fluoroketone.



R	Duration	Intermediate	Conv (%)	Yield (%)
H	5 days	Not observed	58	(**48**) 52
Me	2 days	Observed by NMR	100	(**49**) 37

5.4.2.1. Reaction with Allyl Alcohol

Reaction with allyl alcohol gave the ketone 1-cyclohexyl-2-fluoro-2-(trifluoromethyl)pent-4-en-1-one (**48**).

The proton-decoupled carbon NMR spectrum of (**48**) gave a resonance at 207 ppm characteristic for a carbonyl carbon atom. The CF fluorine atom resonance occurred at -182 ppm rather than at -161 ppm which is characteristic of a tertiary fluorine atom.[105] The IR spectrum showed a C=O stretch at 1729 cm^{-1} in addition to the expected alkene C=C stretch at 1645 cm^{-1}, confirming the occurrence of rearrangement. No trace of the intermediate substitution product was detected when the reaction was worked up or observed by NMR during the course of the reaction. The

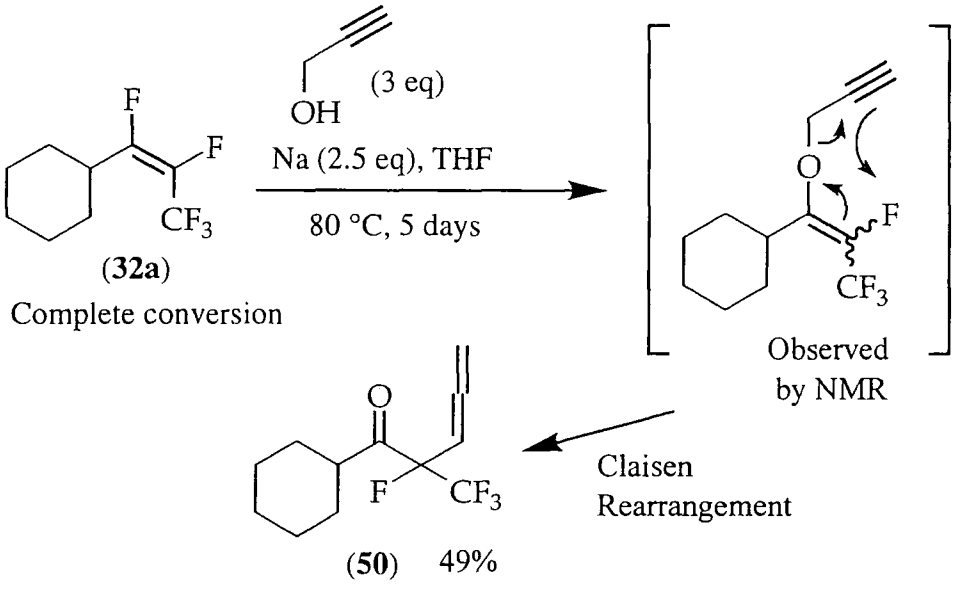
low yield was probably due to difficulties in extraction because fluorinated ketones exist in equilibrium with the geminal diol in water.

5.4.2.2. Reaction with Crotyl Alcohol

Reaction with crotyl alcohol gave a pair of diastereoisomers of the ketone 1-cyclohexyl-2-fluoro-3-methyl-2-(trifluoromethyl)pent-4-en-1-one (**49**) in the ratio of 4:1 by GLC/MS and fluorine NMR. In contrast to the reaction using allyl alcohol, the intermediate was observed by fluorine NMR during the course of the reaction. The vinylic fluorine atom resonance appeared at -162 ppm, compared to -161 ppm in the starting fluoroalkene (**32a**), and subsequently moved to -185 ppm on rearrangement.

5.4.2.3. Reaction with Propargyl Alcohol

Reaction with propargyl alcohol gave the allene 1-cyclohexyl-2-fluoro-2-(trifluoromethyl)penta-3,4-dien-1-one (**50**).



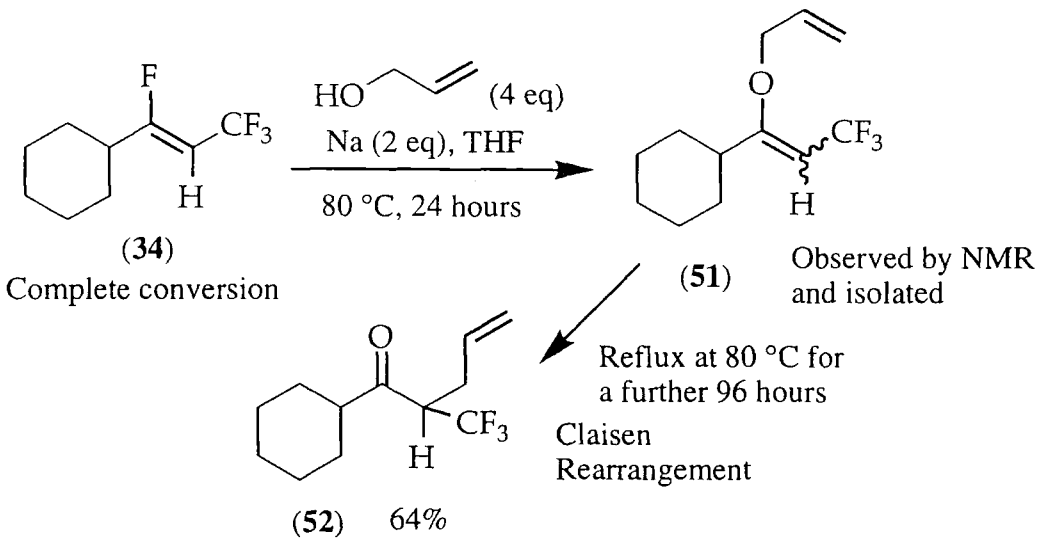
An IR spectrum of (**50**) showed characteristic peaks[124] for an allene at 1955 and at 1982 cm^{-1} and hydrogen NMR showed that no alkyne hydrogen atom was present. Therefore the allene (**50**) had not undergone a 1,3-hydride shift to form a terminal alkyne. There are examples in the literature[124] of non-fluorinated systems where an alkyne undergoes a Claisen rearrangement to form a stable allene, and therefore this methodology can be applied to fluorinated systems.

The proton-decoupled carbon NMR spectrum of (**50**) showed a characteristic allene resonance at 209 ppm,[124] in addition to a carbonyl carbon resonance at 204 ppm.

The yield was low despite complete conversion of starting material and this was again attributed to difficulties in purification.

5.4.3. Reaction of (1Z)-1-Cyclohexyl-1,3,3,3-tetrafluoroprop-1-ene with Allyl Alcohol

Reaction of (1Z)-1-cyclohexyl-1,3,3,3-tetrafluoroprop-1-ene (**34**) with allyl alcohol gave the ketone 1-cyclohexyl-2-(trifluoromethyl)pent-4-en-1-one (**52**).



GLC/MS of the crude reaction mixture showed the presence of two products (M=234) in the ratio of 4.5:1 which were separated by column chromatography.

The major product gave a resonance at 207.0 ppm in the proton-decoupled carbon NMR spectrum assigned to the carbonyl carbon atom, confirming the occurrence of rearrangement. This compound was therefore 1-cyclohexyl-2-(trifluoromethyl)pent-4-en-1-one (**52**).

The NMR data for the minor product gave chemical shifts in close agreement with the methoxy-substituted compound (**46**) prepared in section 5.3.1. The carbon atom at the double bond adjacent to the ether linkage gave a chemical shift of 170.0 ppm, and by comparison to (**46**) confirmed the structure as (1*Z*) or (1*E*)-1-cyclohexyl-1,3,3,3-trifluoro-1-prop-2-enyloxyprop-1-ene (**51**).

The initially-formed substitution product 1-cyclohexyl-1,3,3,3-trifluoro-1-prop-2-enyloxyprop-1-ene (**51**) underwent the Claisen rearrangement to form the ketone (**52**) on standing at room temperature. An IR spectrum of (**51**) taken two months after initial characterisation showed a strong carbonyl stretch at 1725 cm^{-1}. Carbon NMR gave a carbonyl carbon resonance at 207 ppm and the resonance at 170 ppm had disappeared.

The reaction between (1Z)-1-cyclohexyl-1,3,3,3-tetrafluoroprop-1-ene (**34**) with allyl alcohol gave an interesting comparison to that with methanol described in section 5.3.1. The methoxy-substituted compound (**46**) decomposed readily at room temperature, but the allyloxy-substituted compound (**51**) underwent the Claisen rearrangement to (**52**) instead. Presumably the Claisen rearrangement is a much lower energy process, and all of the carbon atoms are already set up for a 6-membered

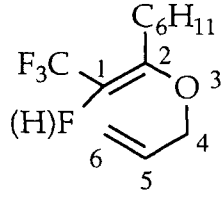
transition state. This also indicated the ease with which the Claisen rearrangement occurred.

5.4.4. Discussion on the Claisen Rearrangements

The Claisen rearrangement has been shown to provide a straightforward approach to the introduction of a trifluoromethyl group in the middle of an aliphatic carbon chain. The rearrangements took place at 80 °C which was surprising, as the Claisen rearrangement normally requires temperatures in the range of 150 - 200 °C.[115]

Although the Claisen rearrangement is known to tolerate a wide variety of functional groups, the substituents do have an effect on the rate. Various studies[125] have been undertaken to assess the effect of substituents, and it is found that donor or acceptor groups at various sites on the six-atom backbone can accelerate or retard the rate of reaction. A complete discussion of the effects of substituents is beyond the scope of this thesis, and the reader is directed to papers and reviews on the subject.[126, 127]

The system studied in the present work can be represented as follows:-



The vinylic fluorine atom did not appear to have a significant effect on the rate of rearrangement, as the formation of compounds (**48**) and (**52**) occurred under similar conditions.

It has been claimed[128, 129] that a trifluoromethyl group at the 1-position has virtually no effect on the rate of rearrangement. However, an electron donor at the 2-position is known to accelerate the rearrangement process.[125] In the systems studied in the present work, the cyclohexyl ring is a weak electron donor and this is the most likely cause behind the ease of rearrangement.

5.5. Conclusions

- Fluoroalkenes can be functionalised regiospecifically by reaction with nucleophiles.

- The trifluoromethyl moiety can be introduced at a central position on an aliphatic carbon chain via a Claisen rearrangement, after reaction of a fluoroalkene with an allyl alcohol.

- New fluorinated building blocks have been produced which have the potential for further functionalisation.

6. Reactions of Fluoroalkenes with Electrophiles

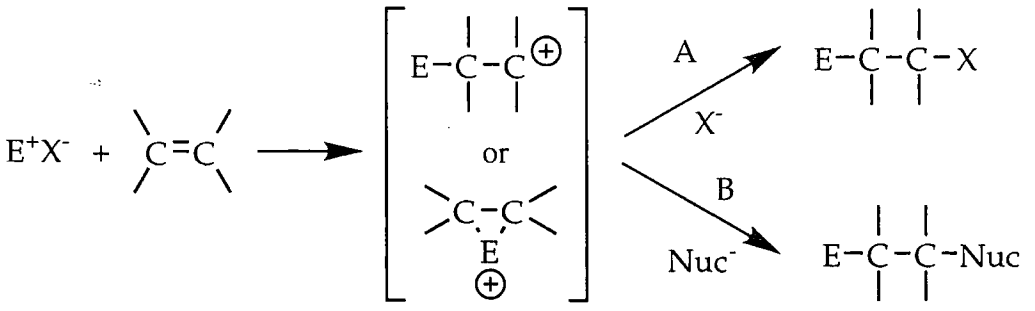
6.1. Introduction

6.1.1. Mechanism

As has been discussed in chapter 5, fluoroalkenes react readily with nucleophiles. This can be accounted for by the electron-acceptor influence of fluorine atoms and perfluoroalkyl groups, which is due to inductive and conjugative effects.[1] However, electrophilic addition reactions, typical of non-fluorinated alkenes, do occur with fluoroalkenes.[130]

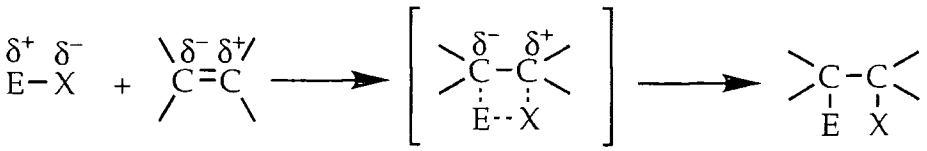
Reaction of an electrophile with an unsaturated system may consist of several steps.[131] The first step is attack of the electrophile at the double bond, and consequently the reactivity of both the alkene and electrophile are important. Polyfluorinated alkenes with one or two fluoroalkyl groups are often resistant to electrophilic attack, as a result of steric and electronic factors. Sterically, perfluoroalkyl groups are very bulky owing to the lone pairs of electrons on the fluorine atoms. Electronically, the electron density at the double bond is reduced considerably compared to a hydrocarbon alkene. They are less reactive than hydrocarbon alkenes towards electrophiles, but this can be overcome by the use of a more powerful electrophile. Carbon-carbon double bonds are generally more stable in fluorinated systems which gives cleaner reactions, because the carbocation intermediate is resistant to secondary processes such as alkyl group migration.

Electrophiles can be divided into two groups according to their mechanism of addition. Firstly, a stepwise mechanism as shown below is applicable to charged electrophiles which proceed via a linear or bridged carbocation intermediate.



The intermediate either reacts with the counter anion (usually F^-) so that E^+X^- is added across the double bond as in path A. Alternatively, it may react with another nucleophile present in the reaction mixture as path B shows.[132]

The second mechanism is a concerted process, involving a cyclic transition state, and is applicable to neutral electrophiles in accordance with the polarisation of the reagents.[133]

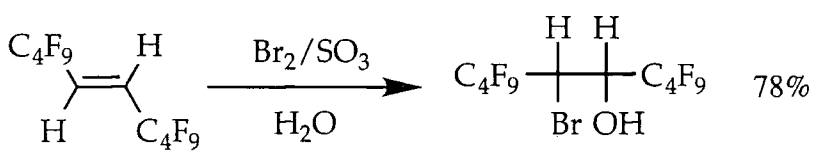


6.1.2. Relative Reactivity of Fluoroalkenes towards Electrophiles

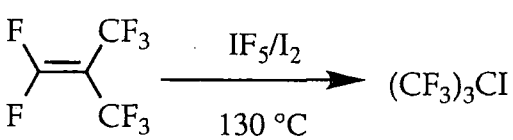
The reactivity of an alkene towards electropilic attack decreases with increasing fluorine content, as the electron density on the double bond is reduced.[131] Highly fluorinated alkenes are often quite resistant to electrophilic attack, especially if several fluoroalkyl groups are present.[134] Therefore, reactivity towards electrophiles[131] decreases going from $CH_2=CF_2$ to tetrakis(trifluoromethyl)ethene, as shown below:-

$CH_2=CF_2 > CFH=CF_2 > CFCl=CF_2 > CF_2=CF_2 > CF_2=CHCF_3 > CF_2=CFCF_3 > R_FCH=CHR_F > CF_2=C(CF_3)_2 > CF_3CF=CFCF_3 \sim CF_3CF=CFC_2F_5 > R_FCF=CFR_F > c\text{-}C_4F_6 > c\text{-}C_5F_8 > (CF_3)_2C=CFCF_3; (CF_3)_2C=CFC_2F_5 > (CF_3)_2C=C(CF_3)_2$

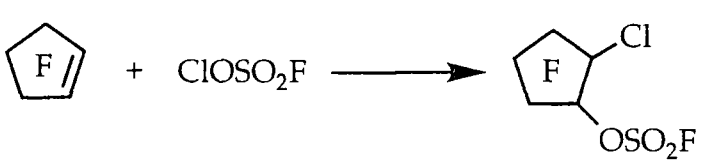
For example, $CH_2=CF_2$ reacts readily with fluorosulfonic acid without a catalyst,[131] and is nitrofluorinated by HNO_3/HF six times faster than $CFH=CF_2$. 1,2-Difluoroalkylethenes are very unreactive to electrophiles, although one reported example[135] is given below:-



The double bond in perfluoroisobutene is less reactive, and a temperature in the region of 100 - 200 °C is usually required for addition to occur.[136]



Cyclic and internal fluoroalkenes are very unreactive towards electrophiles because of the large steric requirement and electron-withdrawing effect of the fluoroalkyl groups. However, they can still interact with very strong electrophiles[137] such as chlorine fluorosulfate:-

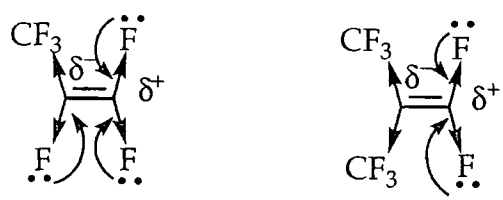


Fluoroalkenes with three or four fluoroalkyl groups have an extremely electron-deficient carbon-carbon double bond and consequently few, if any reactions have been reported.[131]

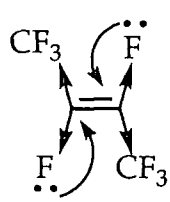
6.1.3. Orientation of Electrophilic Addition

The orientation of addition of an electrophile across the carbon-carbon double bond of a fluoroalkene often proceeds according to the polarisation of the double bond[131] as explained in section 6.1.1. This is dependant on two factors. Firstly, fluoroalkyl groups have an electron-withdrawing effect through the σ-bonded system. Secondly, a fluorine atom directly attached to a π system can interact via resonance. Interaction between the unshared p electrons on the fluorine atoms and the π electrons of the double bond result in a shift of the π electrons from p-π repulsion, and consequently polarisation of the double bond occurs. Although a fluorine atom also has a σ inductive effect, the π resonance effect dominates when it is directly attached to a carbon-carbon double bond, a carbocation or a carbanion.

These factors are illustrated with hexafluoropropene and perfluoroisobutene, where the central carbon atom has a much higher negative charge than that of the terminal carbon atom. Therefore attack of an electrophile E^+ is directed to the central carbon atom, in contrast to a nucleophile which attacks the terminal carbon atom.

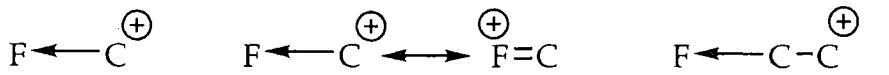


For the internal alkene perfluorobut-2-ene, the CF_3 and F effects cancel each other out by the symmetry of the molecule. The lower polarisation of the carbon-carbon double bond together with the steric shielding from two trifluoromethyl groups reduces its reactivity towards electrophiles.



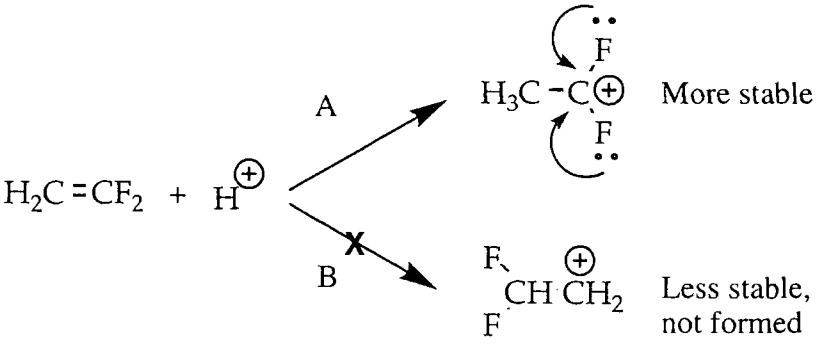
Electrophilic addition may proceed via a carbocation intermediate as illustrated in section 6.1.1 and consequently carbocation stabilities can rationalise and predict the orientation of addition. A fluorine atom directly attached to a carbocation stabilises by back-donation of the unshared p electrons, which dominates over the σ inductive effect.

However, a fluorine atom one carbon atom away from a carbocation strongly destabilises as a result of the strong σ inductive effect.



$-\sigma$ (destabilising) vs $+\pi$ (stabilising) $-\sigma$ (destabilising)

Therefore when an electrophile attacks a fluoroalkene, the carbocation with the minimum number of F-C-C$^+$ fluorine atoms is formed, as exemplified by 1,1-difluoroethene[138] which proceeds via path A:-

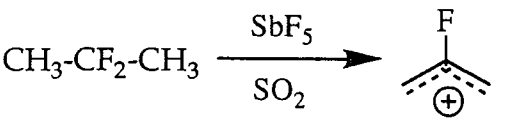


Therefore attack of an electrophile is usually regiospecific, but this is not always the case,[139] especially when a neutral electrophile is used:-

$$CF_3CF{=}CF_2 + CF_3OCl \xrightarrow[-196 - +22\ ^\circ C]{CFCl_3} \underset{71.5}{CF_3CFCl\text{-}CF_2OCF_3} + \underset{28.5}{CF_3CF(OCF_3)\text{-}CF_2Cl}$$

Sometimes a competing radical pathway has been invoked to account for the lack of regiospecificity. Steric factors have also been claimed to be responsible for this.[130]

Olah[140] discovered the ability of a fluorine atom to stabilise a carbocation centre in allylic systems:-



This field has been extensively developed and the reader is directed to material in the literature.[131, 141-144]

For systems of the type $RCX_2^+$and R_2CX^+, stability increases in the series F > Cl > Br > I.[145] Fluorine is so stabilising because of the back-donation. Stability of substituted fluoromethyl cations in the gas phase[134] are as follows:-

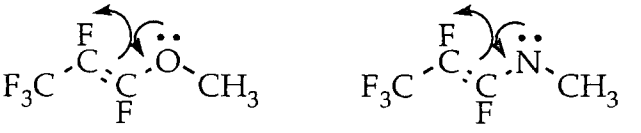
$$CH_3^+ < HCF_2^+ < CFH_2^+ \sim CH_3CH_2^+ << CH_3CF_2^+ < CH_3CFH^+$$

As can be seen, an alkyl group stabilises better than a fluorine atom, which stabilises better than a hydrogen atom. This helps to explain why fluoroalkenes can react with electrophiles.

6.1.4. Electrophilic Reactions of Fluoroalkenes

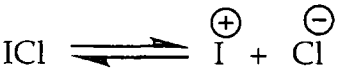
Addition of halogens to fluoroalkenes usually proceeds via a radical mechanism, either initiated photochemically (light) or thermally.[131, 146] There are some examples of halogen addition which proceed via an ionic mechanism and these are often characterised by a low reaction temperature and/or a Lewis acid catalyst. For example, bromine adds to 1,2-difluorochloroethene in the dark at -25 °C.[146] However, an ionic mechanism generally only occurs in hydrogen-containing fluoroalkenes that still retain some similarity to hydrocarbon alkenes.[130]

If the electron density at the double bond is high as with perfluorovinyl ethers and amines, the mechanism of halogen addition is electrophilic. This arises from conjugation of the unshared electron pair on oxygen[112, 147] or nitrogen.[147, 148]

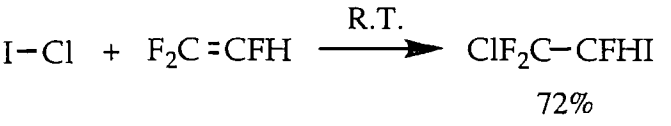


One more recent example[149] is the ionic addition of bromine to $RC_6H_4CF{=}CFX$, presumably owing to the presence of the phenyl group.

The addition of mixed halogen species such as ICl, IBr and IF is ionic.[130, 131, 150, 151] These compounds are polar, owing to the varying affinity of the halogens for electrons, which favours their heterolytic cleavage:-



A large difference in the electronegativity of the halogens results in a faster rate of reaction with a fluoroalkene. For example, iodine monochloride adds readily to fluoroalkenes[152] at room temperature:-



An unstable interhalogen compound such as iodine monofluoride (IF) can be prepared *in situ* in the reaction vessel. IF disproportionates to I_2 and IF_3 and has not

been isolated in a pure form.[153] A mixture of IF_5/I_2 is commonly used to prepare IF *in situ*,[154, 155] although many examples documented in the literature[156] require a catalyst:-

$$I{-}F \;+\; F_2C{=}CF_2 \xrightarrow[R.T.]{Al/AlI_3} F_3C{-}CF_2I \quad (78\%)$$

IF can also be prepared directly from elemental fluorine and iodine.[157]

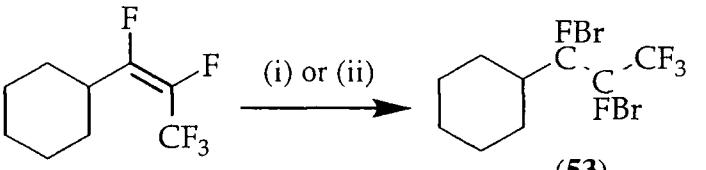
A range of other electrophiles can also be added to fluoroalkenes. A complete discussion of electrophilic reactions is beyond the scope of the current work, and the reader is directed to some reviews in the literature.[130, 131]

This chapter describes the addition of some halogens and interhalogens to (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**).

6.2. Reaction of (1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene with Electrophiles

6.2.1. Bromine

Reaction with bromine occurred rapidly to give a pair of diastereoisomers of 1,2-dibromo-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (**53**) in the ratio of 1.4:1 by GLC and fluorine NMR.



(**32a**)
Complete conversion

(**53**)

(i) Br_2, no solvent, 20 °C, 24 hours, 62%
(ii) Br_2, no solvent, 20 °C, γ-rays, 14 days, 58%

The proton-decoupled carbon NMR spectrum of (**53**) gave two resonances for each carbon atom as a result of the pair of diastereoisomers. The resonances for the carbon atom adjacent to the cyclohexyl ring both occurred as a doublet of doublets at 111.0 and at 113.0 ppm and the other CF carbon atom resonances occurred at a doublet of quintets at 102.2 and at 104.2 ppm. These chemical shifts were characteristic for a saturated system,[95] and EI^+ data confirmed the product as 1,2-dibromo-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (**53**) with peaks at M=372/374/376.

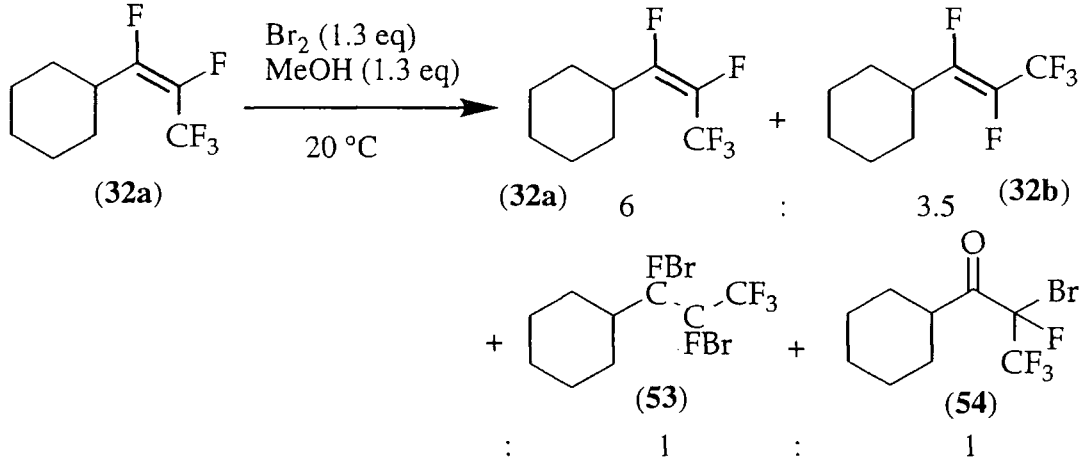
As was discussed in section 2.2, when a cyclohexyl ring has a chiral substituent each ring carbon atom has a different chemical shift on the proton-decoupled carbon NMR spectrum as they are magnetically inequivalent. Therefore each CH_2 ring carbon atom for each pair of diastereoisomers of (**53**) gave a resonance so there were twelve resonances in the low frequency region of the spectrum.

A bromination reaction of (**32a**) was performed whilst irradiated with γ-rays and also gave (**53**). It was likely that reaction occurred as soon as the Carius tube was charged immediately before it was taken to the γ-source. When bromination of (**32a**) was attempted at 120 °C partial decomposition occurred.

As this reaction proceeded so readily, the mechanism was investigated to see if it was an electrophilic rather than a radical process.

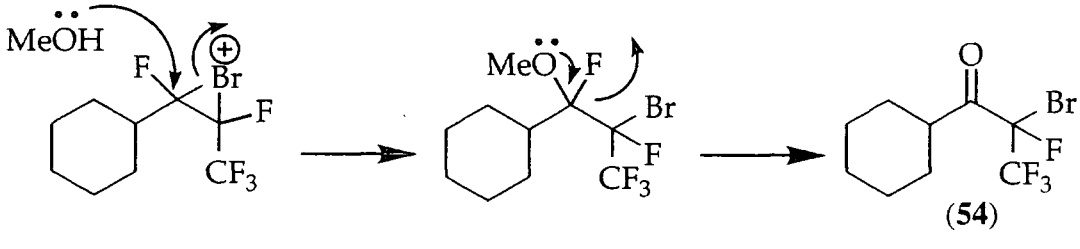
Ionic or Radical Mechanism?

Reaction of (1*Z*)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) with bromine was performed in the presence of a stoichiometric quantity of methanol to trap the bromonium ion (if formed). The products were shown by GLC/MS and fluorine NMR to be (1*Z*) and (1*E*)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) and (**32b**), 1,2-dibromo-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (**53**) and the ketone 2-bromo-1-cyclohexyl-2,3,3,3-tetrafluoropropan-1-one (**54**):-



The formation of (**53**) was rationalised by the fact that reaction proceeded rapidly at room temperature. EI^+ data of the ketone (**54**) gave a mass of 290 amu, with a fragment at 111 amu corresponding to loss of $C_6H_{11}CO$. Fluorine NMR of the crude reaction mixture gave a quartet at -137 pm ($^3J_{C\text{-}F}$ 8.1) and a doublet at -74.6 ppm ($^3J_{C\text{-}F}$ 9.2), with all of the other peaks in the spectrum assigned to (**32a**), (**32b**) and (**53**).

The ketone (**54**) was considered to arise from nucleophilic attack of neutral methanol at a bromonium ion intermediate:-

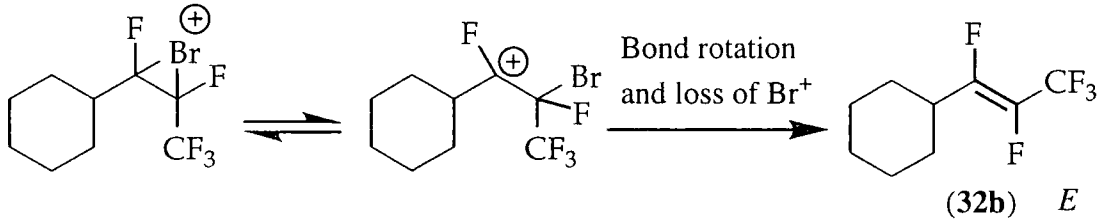


To check that the formation of the ketone (**54**) occurred by attack of methanol at an intermediate, 1,2-dibromo-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (**53**) was heated at 60 °C with methanol. Fluorine NMR showed that no reaction occurred, adding weight to the proposed reaction mechanism above.

Therefore the process was electrophilic and not radical. This could be due to the electron-donating properties of the cyclohexyl ring, so that the alkene was not as electron deficient as might have been expected.

The partial isomerisation of (**32a**) to (**32b**) was unexpected. Earlier work in this laboratory showed the *E* isomer (**32b**) to be of similar thermodynamic stability as the *Z* isomer (**32a**).[9] Although attack by methanol followed by bond rotation and subsequent loss of methanol could have occurred to give (**32b**), this was discounted by a separate experiment as neutral methanol did not react with (**32a**).

It was postulated that the carbocation underwent bond rotation followed by loss of bromide ion:-



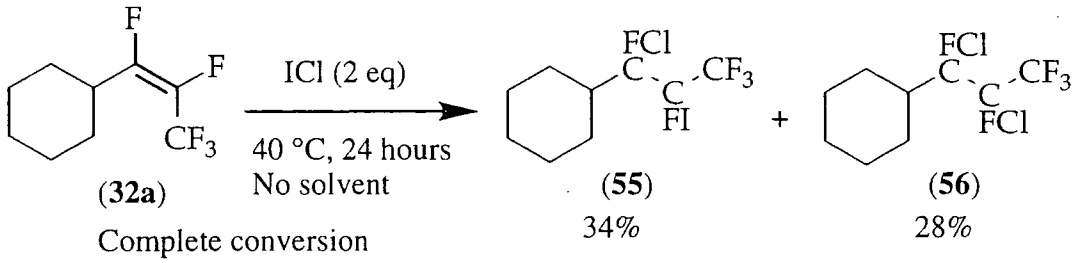
(**32b**) *E*

Cis/trans isomerisation can also be explained by a radical mechanism,[158] but this appeared unlikely given the evidence presented above. Bromination also proceeded rapidly in the dark at 20 °C, such that light could not have initiated a possible radical process.

In an attempt to increase the conversion of (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) into the ketone (**54**), a similar reaction was performed using a large excess of methanol with bromine being added dropwise. Fluorine NMR showed that *cis/trans* isomerisation occurred, but there was no evidence for direct addition of bromine (**53**) or for the ketone (**54**). Addition of more bromine followed by heating at 50 °C for several hours did not result in any further reaction. This was attributed to the bromine reacting with the methanol, forming the hypobromite CH_3OBr. Therefore the ketone (**54**) was not isolated or fully characterised.

6.2.2. Iodine Monochloride

Reaction with iodine monochloride gave 1-chloro-1-cyclohexyl-1,2,3,3,3-pentafluoro-2-iodopropane (**55**) and 1,2-dichloro-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (**56**) in the ratio of 1.5:1 by GLC/MS which were separated by column chromatography.



(**32a**) Complete conversion

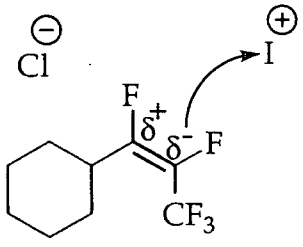
(**55**) 34%

(**56**) 28%

The reaction was carried out at 40 °C to melt the iodine monochloride to achieve better mixing. When carbon tetrachloride as a non-polar solvent solvent was used no reaction occurred, which confirmed an electrophilic process.

Compound (**55**) consisted of a pair of diastereoisomers in the ratio of 30:1 by GLC/MS and only one major resonance was observed for each atom in the NMR spectra. The proton-decoupled carbon NMR spectrum of (**55**) gave a doublet ($^1J_{C\text{-}F}$ 255) of doublets ($^2J_{C\text{-}F}$ 25) at 115.6 ppm assigned to the CF carbon atom adjacent to the cyclohexyl ring. The other CF carbon atom resonance occurred at 89.3 ppm as a doublet ($^1J_{C\text{-}F}$ 268) of quintets ($^2J_{C\text{-}F}$ 34), which was assigned to the CFI carbon atom on account of the lower frequency shift. This confirmed the structure as 1-chloro-1-cyclohexyl-1,2,3,3,3-pentafluoro-2-iodopropane (**55**), and EI^+ data showed a molecular ion (M=376/378) with fragmentation corresponding to loss of IF and ICl.

Addition of iodine monochloride proceeds via a halonium ion intermediate.[131] This was also in accordance with the polarisation of the reagents:-



The cyclohexyl ring is a donor, and the trifluoromethyl group withdraws electron density. Therefore the π electron density on the carbon-carbon double bond shifted, resulting in polarisation. There was no trace of the reverse-addition product.

Compound (**56**) consisted of two pairs of diastereoisomers in the ratio of 3:2 by GLC/MS and so two resonances for each atom in the NMR spectra resulted. The proton-decoupled carbon NMR spectrum of (**56**) gave two doublets of doublets at 114.4

and 114.6 ppm assigned to the CF carbon atom adjacent to the cyclohexyl ring, and two doublets of quintets at 106.6 and 107.8 ppm assigned to the other CF carbon atom. Both of these CF carbon atom chemical shifts were of too high frequency to be CFI carbon atoms, and elemental analysis confirmed the compound as 1,2-dichloro-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (**56**). EI^+ data did not give a molecular ion or any information on fragmentation.

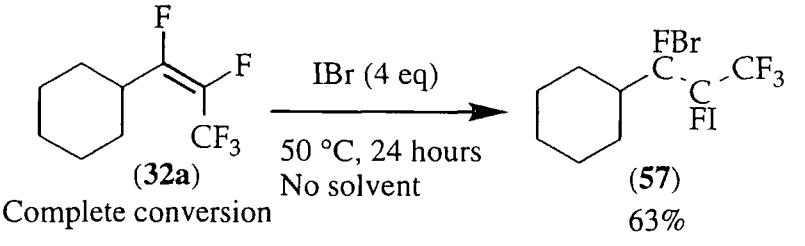
This resulted from decomposition of iodine monochloride, which disproportionated into elemental chlorine and iodine:-

$$2ICl \rightleftharpoons I_2 + Cl_2$$

This enabled chlorine to add across the double bond. A separate experiment found the addition of iodine to 1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) to be unsuccessful. Two iodine atoms bonded to adjacent carbon atoms would be sterically hindered, and carbon-iodine bonds are very weak.

6.2.3. Iodine Monobromide

Reaction with iodine monobromide gave a pair of diastereoisomers of 1-bromo-1-cyclohexyl-1,2,3,3,3-pentafluoro-2-iodopropane (**57**) in the ratio of 6:1 by GLC/MS and fluorine NMR.



(**32a**) Complete conversion

(**57**) 63%

The reaction was carried out at 50 °C to melt the iodine monobromide to achieve better mixing. Although two pairs of diastereoisomers resulted, the resonances in the proton-decoupled carbon NMR spectrum for the carbon atoms bonded directly to fluorine were not observed for the minor pair owing to their low relative intensity.

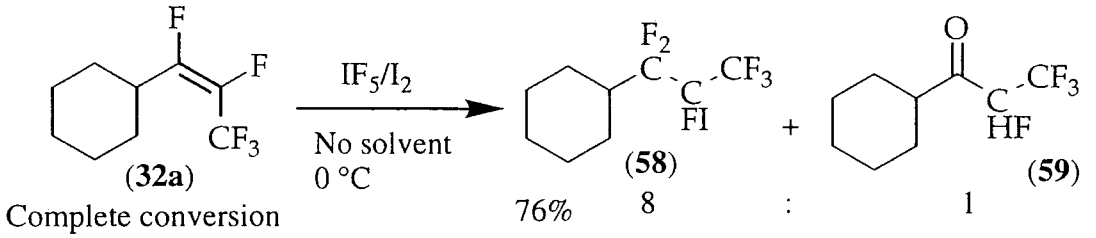
The mode of addition was determined from the proton-decoupled carbon NMR spectrum of (**57**). A doublet ($^1J_{C\text{-}F}$ 272) of a quintet ($^2J_{C\text{-}F}$ 35) at 104.2 ppm was assigned to the carbon atom adjacent to the trifluoromethyl group. The other CF carbon atom resonance occurred at 113.0 ppm as a doublet ($^1J_{C\text{-}F}$ 264) of a doublet ($^2J_{C\text{-}F}$ 27). The carbon atom at 104.2 ppm was therefore assigned to the CFI carbon atom owing to the lower frequency shift, and the bromine atom was bonded to the carbon atom adjacent to the cyclohexyl group.

The mode of addition was analogous to the addition of iodine monochloride, from polarisation of the reactants. However, iodine monobromide did not

disproportionate to its constituent elements as there was no evidence for the formation of the dibromo addition compound (**53**).

6.2.4. Iodine Monofluoride

Reaction with iodine and iodine pentafluoride gave 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**58**) and the ketone (**59**) as a by-product.



(**32a**) Complete conversion

(**58**) 76%

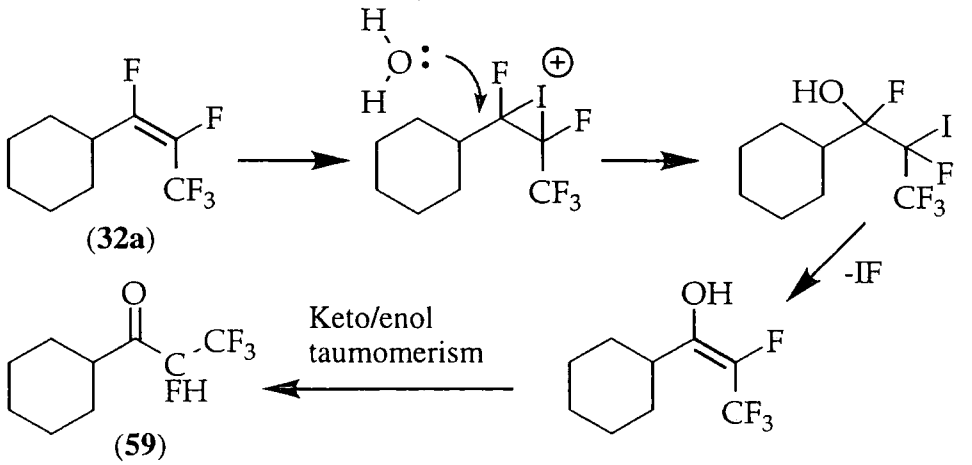
8 : 1

(**59**)

Reaction proceeded rapidly and the major product (**58**) was identified by fluorine NMR. A sextet at -140.1 ppm ($^3J_{F\text{-}F}$ 16) was assigned to the CFI fluorine atom, and the CF_2 fluorine atom resonances appeared as an AB system at -106.95 and at -108.45 ppm (J_{AB} 267). The structure of (**58**) was also confirmed by the proton-decoupled carbon NMR spectrum. The CFI carbon atoms occurred as a doublet of sextets at 83.3 ppm, characteristic for a CFI functionality.[95]

The ketone by-product (**59**) was observed by fluorine NMR. A doublet ($^2J_{F\text{-}H}$ 47) of a quartet ($^3J_{F\text{-}F}$ 18) of a doublet ($^4J_{F\text{-}H}$ 3.4) at -205.9 ppm was assigned to the CFH fluorine atom, and a doublet ($^3J_{F\text{-}H}$ 7.2) of a doublet ($^3J_{F\text{-}F}$ 11) at -75.1 ppm assigned to the CF_3 fluorine atoms. A resonance at 4.9 ppm on the hydrogen NMR spectrum which consisted of a doublet ($^2J_{H\text{-}F}$ 47) of a quartet ($^3J_{H\text{-}F}$ 7.2) was assigned to the CFH hydrogen atom. The EI^+ data showed fragments with masses corresponding to loss of $C_6H_{11}CO$ and $CFHCF_3$.

The formation of (**59**) was considered to arise from hydrolysis of the iodonium ion intermediate, possibly by traces of moisture in the reaction vessel.



No catalyst was required which underscored the fact that the alkene (**32a**) was likely to be relatively electron-rich.[154, 155]

Iodine monofluoride can also be generated *in situ* by reaction of the corresponding elements.[157] Fluorine diluted in nitrogen was bubbled through the alkene (**32a**) and iodine in arklone solvent but only trace quantities of the addition product (**58**) were detected. Decomposition occurred if the quantity of fluorine was increased.

The methodology of removing HF and adding IF enabled the functionalisation of the C-H bond in the fluoroalkyl side chain in 1-cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**). The chemistry of 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**58**) is described in section 6.3.

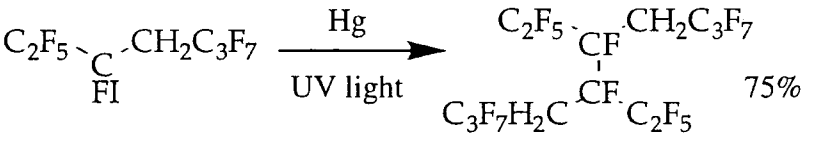
6.2.5. Fluorine

Fluorine diluted in nitrogen was bubbled through the alkene (**32a**) in acetonitrile or arklone solvent at varying temperatures. At low temperatures no reaction took place, and at higher temperatures decomposition occurred. It was surprising that addition of fluorine did not occur, as it has already been shown in this chapter that electrophiles added readily to (**32a**).

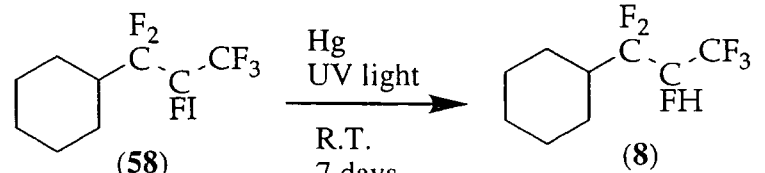
6.3. Reactions of 1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane

6.3.1. Attempted Radical Coupling

There are examples in the literature[159] of free-radical coupling of fluoroalkyl iodides:-



However, in the present work 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**58**) irradiated with ultra-violet light in the presence of mercury gave 1-cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**):-

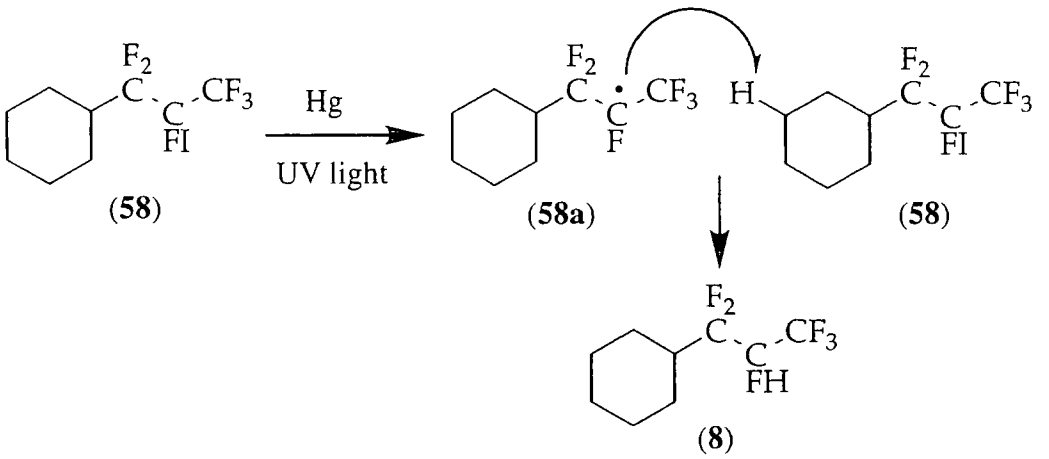


(**58**) Complete conversion

(**8**) 38% recovery

Coupling did not occur and the formation of the product (**8**) was determined from NMR data. Yellow mercury iodide was also observed.

The coupling mechanism proceeds via cleavage of the carbon-iodine bond to form an electrophilic radical (**58a**). This abstracted a hydrogen atom from the cyclohexyl ring of another molecule of fluoroiodide (**58**) as this is a nucleophilic site, in preference to coupling with another electrophilic radical centre. Given the large number of hydrogen atoms, this was not completely unexpected and it also accounted for the poor recovery of (**8**) as the new radical can react further.



(**58**) (**58a**) (**58**) (**8**)

6.3.2. Reaction with alkenes

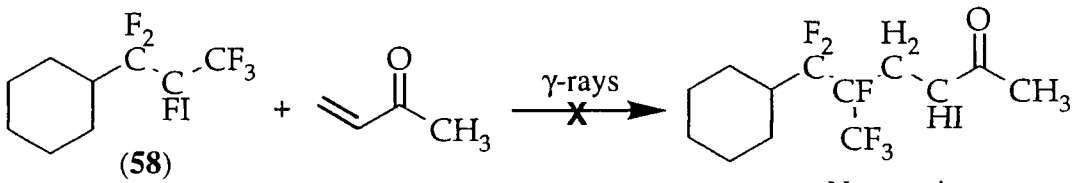
The energy of the carbon-iodine bond in iodoperfluoroalkanes is low and they readily undergo homolytic dissociation to form a fluoroalkyl radical and an iodine atom on thermal or photochemical initiation. The fluoroalkyl radical is highly reactive and can be reacted with a range of molecules including alkenes.

For example,[160] trifluoromethyl iodide can be added to methyl vinyl ketone:-

$$CF_3I + CH_2{=}CHCOCH_3 \xrightarrow{h\nu} CF_3CH_2CHICOCH_3$$

Other iodoperfluoroalkenes have been reacted with a range of substrates.

1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**58**) and methyl vinyl ketone were irradiated with γ-rays in an attempt to produce the addition compound:-



(**58**) No reaction

However, no reaction occurred. Attempted reaction of (**58**) with an excess of 1,1-difluoroethene using γ-ray initiation was also unsuccessful.

The steric hindrance of this system was investigated by reacting radicals with the fluoroalkene (**32a**). Reaction with the nucleophilic acetaldehyde radical gave only

5% conversion using peroxide or γ-ray initiation. This lack of reactivity was attributed to steric factors, which suggested that the radical (**58a**) was also sterically hindered. This would account for the lack of reactivity with alkenes. Attempted reaction with the electrophilic trifluoromethyl radical gave only a trace of conversion.

6.3.3. Attempted Substitution of I by F

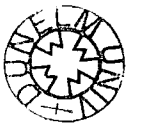
Fluoroiodide (**58**) was reacted with antimony pentafluoride in an attempt to substitute the iodine atom by a fluorine atom. However, no reaction occurred at temperatures ranging from 0 °C to 50 °C using CF_2Cl-$CFCl_2$ or perfluorodecalin solvent. Reaction of fluoroiodide (**58**) with elemental fluorine in acetonitrile or arklone was attempted but again no reaction occurred. If too much fluorine was used or the temperature was too high decomposition occurred.

6.4. Conclusions

- Fluoroalkenes can be functionalised by reaction with electrophiles.

- (1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene reacted surprisingly readily with electrophiles, owing to the electron-donating properties of the cyclohexyl ring.

- Addition of iodine monofluoride to (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene gave a molecule which could be functionalised further by cleavage of the carbon-iodine bond, but this system appeared to be sterically hindered.



7. Experimental

7.1. Instrumentation

Reagents and Solvents

All chemicals were used as received from suppliers unless stated otherwise. Solvents were stored by standard methods and dried over molecular sieves (4Å).

Distillation

Fractional distillations of lower boiling product mixtures (up to 150 °C at atmospheric pressure) were carried out either using either a Fischer Spaltrohr MMS255 small concentric tube apparatus or standard distillation equipment. Higher boiling materials were distilled using a Büchi Kugelrohr GKR-51 apparatus. Boiling points were either recorded during the distillation or by the Siwoloboff method at atmospheric pressure using the Gallenkamp apparatus and are uncorrected.

Gas Liquid Chromatography

Chromatographic analyses were performed on a Hewlett Packard 5890 Series II gas liquid chromatograph equipped with a 25m cross-linked methyl silicone capilliary column with a flame ionization detector. Preparative scale GLC was performed on a Varian Aerograph Model 920 gas chromatograph (catharometer detector), fitted with a 3m 10% SE30 packed column.

Elemental Analysis

Carbon and hydrogen elemental analyses were obtained using a Perkin-Elmer 240 Elemental Analyser or a Carlo Erba Strumentazione 1106 Elemental Analyser.

NMR Spectra

^{1}H spectra were obtained from a Varian VXR400S spectrometer (399.96 MHz). ^{13}C spectra were recorded on the Varian spectrometer (100.58 MHz) and ^{19}F spectra also recorded on the Varian spectrometer (376.29 MHz). All spectra were recorded with TMS and/or $CFCl_3$ as internal references, and J values given in Hertz.

Mass Spectra

Mass spectra were obtained from a VG Trio 1000 Mass Spectrometer (electronic ionisation) coupled to GLC apparatus as above. Accurate mass determinations were performed on a Micromass Autospec Mass Spectrometer.

IR Spectra

Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer using thin films between NaCl plates either as neat liquids or nujol mulls.

7.2. Experimental for Chapter 2

General Procedure for γ-ray Initiation

Liquid reagents were introduced into a Pyrex Carius tube (volume *ca.* 60 ml) which was then degassed three times by freeze-thawing. Gaseous reagents were also degassed, separately and then transferred into the cooled (liquid air) Carius tube using standard vacuum line techniques. The tube was sealed *in vacuo* whilst frozen (liquid air), placed inside a metal sheath and then allowed to reach room temperature within a fumehood. The tube was then taken to the cobalt-60 source and irradiated 10 cm from the source at room temperature for a period of 14 days (*ca.* 15 MRads). On termination of the reaction the tube was cooled (liquid air) and opened. Any remaining gases were recovered as it returned to room temperature and the products were poured out.

General Procedure for Peroxide Initiation

The reactions were carried out in either a 150 ml or a 250 ml stainless steel autoclave fitted with bursting discs (maximum working pressure *ca.* 200 bar). Liquid reagents were added to the autoclave which was then sealed using a copper gasket. The system was degassed three times by freeze-thawing using a vacuum line. Any gases, degassed separately, were transferred into the liquid air cooled autoclave using standard vacuum line techniques. The autoclave valve was closed and then transferred, in a Dewar flask of liquid air, to a purpose built high pressure cell where it was allowed to warm and then heated in a thermostatically-controlled rocking furnace for 24 hours at 140 °C. On completion of the reaction the autoclave was cooled (liquid air), any remaining gases were recovered using a vacuum line as it returned to room temperature and the liquid products were poured out.

Hexafluoropropene Reactions

Cyclohexane with Hexafluoropropene (γ-ray initiation)

Cyclohexane (7.9 g, 93 mmol) and hexafluoropropene (20.9 g, 139 mmol) gave 1-cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**) (14.6 g, 68%) as a colourless oil; bp 154-155 °C (Found: C, 46.3; H, 5.1. $C_9H_{12}F_6$ requires C, 46.15; H, 5.1%); NMR spectrum no. 1; Mass spectrum no. 1; IR spectrum no. 1; and a mixture of isomers of 1,1,2,3,3,3-hexafluoro-1-[x-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl]propane (x=2,3, 4) (**9**) (9.0 g, 25%); bp (10 mmHg) 96 °C; NMR spectrum no. 3; Mass spectrum no. 2; IR spectrum no. 2. A colourless solid crystallised out on standing as 1,1,2,3,3,3-

hexafluoro-1-[*trans*-4-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl]propane (**9a**); (Found: C, 37.2; H, 3.0. $C_{12}H_{12}F_{12}$ requires C, 37.5; H, 3.1%); NMR spectrum no. 4; Mass spectrum no. 3; IR spectrum no. 3.

A trace (~1% by GLC) of the reverse-addition compound 2-cyclohexyl-1,1,1,2,3,3-hexafluoropropane (**8a**) was observed; NMR spectrum no. 2. Hexafluoropropene (2.3 g, 89% conversion) was recovered.

Cyclohexane with Hexafluoropropene (peroxide initiation)

Cyclohexane (22.3 g, 265 mmol), hexafluoropropene (46.2 g, 320 mmol), and DTBP (2.9 g, 20 mmol) gave 1-cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**) (45.4 g, 73%) as described above and a mixture of isomers of 1,1,2,3,3,3-hexafluoro-1-[x-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl]propane (x=2,3,4) (**9**) (22.6 g, 22%) as described above. Crystals of 1,1,2,3,3,3-hexafluoro-1-[*trans*-4-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl]propane (**9a**) and a trace (~1% by GLC) of the reverse-addition compound 2-cyclohexyl-1,1,1,2,3,3-hexafluoropropane (**8a**) were also observed.

Cyclohexane Derivatives with Hexafluoropropene

Nitrocyclohexane with Hexafluoropropene (γ-ray initiation)

Nitrocyclohexane (6.5 g, 50 mmol) and hexafluoropropene (8.3 g, 55 mmol) gave no trace of reaction by GLC/MS and fluorine NMR. The same reaction with acetone (8 ml) had no effect.

Iodocyclohexane with Hexafluoropropene (γ-ray initiation)

Iodocyclohexane (8.4 g, 40 mmol) and hexafluoropropene (7.4 g, 49 mmol) gave no trace of reaction by GLC/MS and fluorine NMR. The same reaction with acetone (8 ml) had no effect.

Methylcyclohexane with Hexafluoropropene (γ-ray initiation)

Methylcyclohexane (4.9 g, 50 mmol) and hexafluoropropene (8.6 g, 57 mmol) gave a mixture of isomers of 1,1,2,3,3,3-hexafluoro-1-(x-methylcyclohexyl)propane (x=2,3,4, 29% conversion) and a mixture of isomers of 1,1,2,3,3,3-hexafluoro-1-(x,y-bis-methylcyclohexyl)propane (x,y=2,3,4, 10% conversion) by GLC/MS. The same reaction with acetone (8 ml) achieved the same conversion also with a mixture of isomers. No further workup of this reaction was performed.

Chlorocyclohexane with Hexafluoropropene (γ-ray initiation)

Chlorocyclohexane (5.9 g, 50 mmol) and hexafluoropropene (8.3 g, 55 mmol) gave a trace of 1-(x-chlorocyclohexyl)-1,1,2,3,3,3-hexafluoropropane (x=2,3,4, 6%

conversion) but no further workup was performed. The same reaction with acetone (8 ml) achieved the same conversion also with a mixture of isomers.

Bromocyclohexane with Hexafluoropropene (γ-ray initiation)

Bromocyclohexane (8.2 g, 50 mmol) and hexafluoropropene (9.3 g, 62 mmol) gave no trace of reaction by GLC/MS and fluorine NMR. The same reaction with acetone (8 ml) had no effect.

Bromomethylcyclohexane with Hexafluoropropene (γ-ray initiation)

Bromomethylcyclohexane (7.1 g, 40 mmol) and hexafluoropropene (7.5 g, 50 mmol) gave a trace of 1-[x-(bromomethyl)cyclohexyl]-1,1,2,3,3,3-hexafluoropropane (x=2,3,4). The same reaction with acetone (8 ml) increased the conversion slightly (3% by GLC) and no further workup was performed.

Bromoethylcyclohexane with Hexafluoropropene (γ-ray initiation)

Bromoethylcyclohexane (7.6 g, 40 mmol) and hexafluoropropene (7.1 g, 47 mmol) gave no trace of reaction by GLC/MS and fluorine NMR. The same reaction with acetone (8 ml) gave some conversion of starting material (10% by GLC) and no further workup was performed.

Bromocyclohexane with Hexafluoropropene (peroxide initiation)

Bromocyclohexane (4.9 g, 30 mmol), hexafluoropropene (6.5 g, 43 mmol) and DTBP (0.9 g, 6 mmol) gave a trace of 1-(x-bromocyclohexyl)-1,1,2,3,3,3-hexafluoropropane (x=2,3,4, 3% conversion) by GLC/MS and fluorine NMR. GLC/MS showed a $(M\text{-}Br)^+$ peak at 233, and evidence for cyclohexene formed by free radical elimination was detected (M^+=82). Volatiles (1.3 g) were recovered and no further workup was performed.

Bromomethylcyclohexane with Hexafluoropropene (peroxide initiation)

Bromomethylcyclohexane (5.3 g, 30 mmol), hexafluoropropene (7.0 g, 47 mmol) and DTBP (0.9 g, 6 mmol) gave a trace of 1-[x-(bromomethyl)cyclohexyl]-1,1,2,3,3,3-hexafluoropropane (x=2,3,4, 7% conversion) by GLC/MS and fluorine NMR. GLC/MS showed a $(M\text{-}Br)^+$ peak at 247 and volatiles (6.5 g) were recovered. No further workup was performed.

Bromoethylcyclohexane with Hexafluoropropene (peroxide initiation)

Bromoethylcyclohexane (5.7 g, 30 mmol), hexafluoropropene (7.0 g, 47 mmol) and DTBP (0.9 g, 6 mmol) gave a trace of 1-[x-(2-bromoethyl)cyclohexyl]-1,1,2,3,3,3-hexafluoropropane (x=2,3,4, 10% conversion) by GLC/MS and fluorine NMR.

GLC/MS showed a M^+ peak at 342, a $(M-Br)^+$ peak at 262 and volatiles (6.2 g) were recovered. No further workup was performed.

Inhibition Investigation Reactions

Cyclohexane and Iodocyclohexane with Hexafluoropropene (γ-ray initiation)

Iodocyclohexane (4.2 g, 20 mmol), cyclohexane (1.7 g, 20 mmol) and hexafluoropropene (6.8 g, 45 mmol) gave a trace of 1-cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**) observed by GLC/MS and fluorine NMR. GLC determined the ratio of unreacted cyclohexane to (**8**) and showed that the radical process was being inhibited.

Cyclohexane and Nitrocyclohexane with Hexafluoropropene (γ-ray initiation)

Nitrocyclohexane (2.6 g, 20 mmol), cyclohexane (1.7 g, 20 mmol) and hexafluoropropene (6.8 g, 45 mmol) gave a trace of 1-cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**) observed by GLC/MS and fluorine NMR. GLC determined the ratio of unreacted cyclohexane to (**8**) and showed that the radical process was being inhibited.

Cyclohexane and Bromocyclohexane with Hexafluoropropene (γ-ray initiation)

Bromocyclohexane (3.3 g, 20 mmol), cyclohexane (1.7 g, 20 mmol) and hexafluoropropene (6.8 g, 45 mmol) gave a trace of 1-cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**) observed by GLC/MS and fluorine NMR. GLC determined the ratio of unreacted cyclohexane to (**8**) and showed that the radical process was being inhibited.

Cyclohexane and Bromomethylcyclohexane with Hexafluoropropene (γ-ray initiation)

Bromomethylcyclohexane (3.5 g, 20 mmol), cyclohexane (1.7 g, 20 mmol) and hexafluoropropene (7.6 g, 51 mmol) gave a trace of 1-cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**) observed by GLC/MS and fluorine NMR. GLC determined the ratio of unreacted cyclohexane to (**8**) and showed that the radical process was being inhibited, although not as much as in the previous reactions.

Cyclohexane and Bromoethylcyclohexane with Hexafluoropropene (γ-ray initiation)

Bromoethylcyclohexane (3.8 g, 20 mmol), cyclohexane (1.7 g, 20 mmol) and hexafluoropropene (7.6 g, 51 mmol) gave a trace of 1-cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**) observed by GLC/MS and fluorine NMR. GLC determined the ratio of unreacted cyclohexane to (**8**) and showed that the radical process was being inhibited, although not as much as in the previous reactions.

Competition Reaction

Competition between Cyclohexane and Methylcyclohexane with Hexafluoropropene (γ-ray initiation)

Methylcyclohexane (3.9 g, 40 mmol), cyclohexane (3.4 g, 40 mmol) and hexafluoropropene (2.2 g, 15 mmol) gave a mixture of adducts of both cyclohexanes and unreacted starting materials. The ratio of methylcyclohexane to cyclohexane was determined by GLC before and after reaction, and reaction occurred preferentially with cyclohexane.

Reactions with 1,1,3,3,3-Pentafluoropropene

Cyclohexane with 1,1,3,3,3-Pentafluoropropene (γ-ray initiation, 14 days)

Cyclohexane (4.0 g, 48 mmol) and 1,1,3,3,3-pentafluoropropene (12.7 g, 96 mmol) irradiated for 14 days gave 1-cyclohexyl-1,1,3,3,3-pentafluoropropane (**12**) with 2-cyclohexyl-1,1,1,3,3-pentafluoropropane (**12a**) impurity in the ratio of 24:1 by GLC/MS. Fractional distillation gave pure (**12**) (1.7 g, 56%) as a colourless liquid; bp 168 °C (Found: C, 49.8; H, 6.1. $C_{12}H_{14}F_4$ requires C, 50.0; H, 6.0%); NMR spectrum no. 5; Mass spectrum no. 4; IR spectrum no. 4; with a trace of 2-cyclohexyl-1,1,1,3,3-pentafluoropropane (**12a**); NMR spectrum no. 6. 1,1,3,3,3-Pentafluoropropene (10.8 g, 15% conversion) was recovered.

Cyclohexane with 1,1,3,3,3-Pentafluoropropene (γ-ray initiation, 28 days)

Cyclohexane (10.0 g, 120 mmol) and 1,1,3,3,3-pentafluoropropene (24.0 g, 180 mmol) irradiated for 28 days gave 1-cyclohexyl-1,1,3,3,3-pentafluoropropane (**12**) with 2-cyclohexyl-1,1,1,3,3-pentafluoropropane (**12a**) impurity in the ratio of 21:1 by GLC/MS. Fractional distillation gave pure (**12**) (21.3 g, 82%) as described above. 1,1,3,3,3-Pentafluoropropene (3.8 g, 84% conversion) was recovered.

Cyclohexane with 1,1,3,3,3-Pentafluoropropene (peroxide initiation)

Cyclohexane (250 g, 2970 mmol), 1,1,3,3,3-pentafluoropropene (54 g, 400 mmol) and DTBP (3.5 g, 24 mmol) gave 1-cyclohexyl-1,1,3,3,3-pentafluoropropane (**12**) with 2-cyclohexyl-1,1,1,3,3-pentafluoropropane (**12a**) impurity in the ratio of 10:1 by GLC/MS. Fractional distillation gave pure (**12**) (58.9 g, 66%) as described above. Further distillation gave 1,1,3,3,3-pentafluoro-1-[x-(1,1,3,3,3-pentafluoropropyl)-cyclohexyl]propane (x=2,3,4) (**13**); NMR spectrum no. 7, Mass spectrum no. 5; IR spectrum no. 5, and one isomer separated out on standing as 1,1,3,3,3-pentafluoro-1-[*trans*-4-(1,1,3,3,3-pentafluoropropyl)cyclohexyl]propane (**13a**) (Found: C, 41.5; H, 4.1. $C_{12}H_{14}F_{10}$ requires C, 41.4; H, 4.0%); NMR spectrum no. 8; Mass spectrum no.

6; IR spectrum no. 6. 1,1,3,3,3-Pentafluoropropene (1.4 g, 97% conversion) was recovered.

Cyclohexane with 1,1,3,3,3-Pentafluoropropene (peroxide initiation)

Cyclohexane (97 g, 1116 mmol), 1,1,3,3,3-pentafluoropropene (102 g, 770 mmol) and DTBP (3.0 g, 20 mmol) gave 1-cyclohexyl-1,1,3,3,3-pentafluoropropane (**12**) with 2-cyclohexyl-1,1,1,3,3-pentafluoropropane (**12a**) impurity in the ratio of 10:1 by GLC/MS. Fractional distillation gave pure (**12**) (88.0 g, 53%) and 1,1,3,3,3-pentafluoro-1-[x-(1,1,3,3,3-pentafluoropropyl)cyclohexyl]propane (x=2,3,4) (**13**) as described above. 1,1,3,3,3-Pentafluoropropene (1.0 g, 99% conversion) was recovered.

Reactions with 3,3,3-Trifluoropropene

Cyclohexane with 3,3,3-Trifluoropropene (excess) (peroxide initiation)

Cyclohexane (4.2 g, 50 mmol), 3,3,3-trifluoropropene (9.6 g, 100 mmol) and DTBP (0.9 g, 6 mmol) gave a complex mixture of liquid (3.2 g) and solid products (7.1 g) which was not worked up any further. The lower adducts were volatile which accounted for the discrepancies in mass. Fluorine NMR confirmed that incorporation of trifluoropropene had occurred and no volatiles were recovered.

Cyclohexane (2-fold excess) with 3,3,3-Trifluoropropene (peroxide initiation)

Cyclohexane (22 g, 260 mmol), 3,3,3-trifluoropropene (12.5 g, 130 mmol) and DTBP (2.9 g, 20 mmol) gave a complex mixture of liquid (2.8 g) and solid products (5.8 g) which was not worked up any further. Fluorine NMR confirmed that incorporation of trifluoropropene had occurred, and 3,3,3-trifluoropropene (0.6 g, 96% conversion) was recovered.

Cyclohexane (10-fold excess) with 3,3,3-Trifluoropropene

Cyclohexane (43.4 g, 520 mmol), 3,3,3-trifluoropropene (5.0 g, 52 mmol) and DTBP (2.9 g, 20 mmol) gave a complex mixture of liquid and solid products. The ratio of adducts to polymeric material was determined by GLC and fluorine NMR confirmed that incorporation of trifluoropropene had occurred. 3,3,3-Trifluoropropene was recovered (2.0 g, 60% conversion) and no further workup was performed.

Cyclohexanol with 3,3,3-Trifluoropropene

Cyclohexanol (12.1 g, 120 mmol), 3,3,3-trifluoropropene (5.9 g, 60 mmol) and DTBP (1.5 g, 10 mmol) gave liquid (8.0 g) and solid products (3.3 g). Fluorine NMR confirmed that incorporation of trifluoropropene had occurred. 3,3,3-Trifluoropropene (0.6 g, 90% conversion) was recovered and no further workup was performed.

Propene with DTBP

Propene (6.7 g, 160 mmol) and DTBP (1.9 g, 13 mmol) gave a clear/pale yellow liquid from the decomposition of DTBP. Propene (6.7 g) was recovered, and no further workup was performed.

3,3,3-Trifluoropropene with DTBP

3,3,3-Trifluoropropene (13.6 g, 140 mmol) and DTBP (1.8 g, 12 mmol) gave a viscous yellow liquid, and distillation of the crude reaction mixture (13.0 g) at 150 °C (9 mbar) isolated polymeric material (3.7 g). 3,3,3-Trifluoropropene (3.0 g, 78% conversion) was recovered and no further workup was performed.

3,3,3-Trifluoropropene with DTBP (equimolar ratio)

3,3,3-Trifluoropropene (12.3 g, 130 mmol) and DTBP (9.2 g, 63 mmol) gave a viscous yellow liquid (16.4 g), and distillation at 150 °C (9 mbar) isolated polymeric material (5.75 g). 3,3,3-Trifluoropropene (0.7 g, 94% conversion) was recovered and no further workup was performed.

3,3,3-Trifluoropropene with DTBP and ^{t}BuOH

3,3,3-Trifluoropropene (14.2 g, 150 mmol), DTBP (1.8 g, 12 mmol) and *tert*-butanol (7.1 g, 96 mmol) gave a viscous yellow liquid (19.6 g), and distillation at 150 °C (9 mbar) isolated polymeric material (8.4 g). 3,3,3-Trifluoropropene (1.3 g, 91% conversion) was recovered and no further workup was performed.

7.3. Experimental for Chapter 3

Cyclohexane with 1,1-Difluoroethene (peroxide initiation)

Cyclohexane (44.3 g, 530 mmol), 1,1-difluoroethene (4.2 g, 65 mmol) and DTBP (0.6 g, 4 mmol) followed by fractional distillation and preparative scale GLC gave a mixture of 2-cyclohexyl-1,1-difluoroethane (**18**) and 1-cyclohexyl-1,1-difluoroethane (**19**) (0.6 g, 8%) as a colourless liquid in the ratio of 3:1 by GLC; bp 149 °C (Found: C, 65.1; H, 9.6. $C_8H_{14}F_2$ requires C, 64.9; H, 9.5%); NMR spectra nos. 9, 10 and 11; Mass spectra nos. 7 and 8; IR spectrum no. 7. 1,1-Difluoroethene (1.0 g, 71% conversion) was recovered and the remaining material was attributed to telomer formation.

Reactions with Chlorofluoroethenes

Cyclohexane with Chlorotrifluoroethene (peroxide initiation)

Cyclohexane (44.7 g, 530 mmol), chlorotrifluoroethene (6.4 g, 55 mmol) and DTBP (0.6 g, 4 mmol) gave 2-chloro-1-cyclohexyl-1,1,2-trifluoroethane (**20**) (3.5 g, 33%) as a colourless liquid; bp 212 °C (Found: C, 47.9; H, 6.1. $C_8H_{12}ClF_3$ requires C, 47.9; H, 6.0%); NMR spectrum no. 12; Mass spectrum no. 9; IR spectrum no. 8. Traces of the reverse-addition compound 1-chloro-1-cyclohexyl-1,2,2-trifluoroethane (**20a**) were observed; NMR spectrum no. 13. Chlorotrifluoroethene (0.3 g, 95% conversion) was recovered, and higher adducts were detected by GLC/MS.

Cyclohexane with 1,1-Dichlorodifluoroethene (γ-ray initiation)

Cyclohexane (10.0 g, 119 mmol) and 1,1-dichlorodifluoroethene (12.7 g, 105 mmol) gave a mixture of 2,2-dichloro-1-cyclohexyl-1,1-difluoroethane (**21**) and one isomer of di-adduct (**22**) in the ratio of 1:1 by GLC/MS. Fractional distillation gave pure (**21**) (5.1 g, 24%) as a colourless liquid; bp 206 °C (Found: C, 44.0; H, 5.5. $C_8H_{12}Cl_2F_2$ requires C, 44.2; H, 5.5%); NMR spectrum no. 14; Mass spectrum no. 10; IR spectrum no. 9. No volatiles were recovered and there was no evidence for the formation of the reverse-addition product. Fluorine NMR showed the recovered cyclohexane contained fluoroalkene.

Cyclohexane with 1,1-Dichlorodifluoroethene (peroxide initiation)

Cyclohexane (52 g, 620 mmol), 1,1-dichlorodifluoroethene (30 g, 225 mmol) and DTBP (1.0 g, 7 mmol) gave a mixture of 2,2-dichloro-1-cyclohexyl-1,1-difluoroethane (**21**) and one isomer of di-adduct (**22**) in the ratio of 6:1 by GLC/MS. Fractional distillation gave pure (**21**) (19.5 g, 40%) as described above. No volatiles were recovered and fluorine NMR showed the recovered cyclohexane contained fluoroalkene.

Cyclohexane with 1-Chloro-2,2-difluoroethene (γ-ray initiation)

Cyclohexane (10.0 g, 120 mmol) and 1-chloro-2,2-difluoroethene (19.7 g, 200 mmol) gave a mixture of 2-chloro-1-cyclohexyl-1,1-difluoroethane (**23**), the reverse-addition product (**23a**), chlorocyclohexane (**24**) and isomers of di-adduct (**25**) in the ratio of 30:1.5:1:34 by GLC/MS. 1-Chloro-2,2-difluoroethene (1.8 g, 91% conversion) was recovered and the product decomposed on distillation.

Cyclohexane with 1-Chloro-2,2-difluoroethene (peroxide initiation)

Cyclohexane (85 g, 1020 mmol), 1-chloro-2,2-difluoroethene (24.2 g, 246 mmol) and DTBP (1.0 g, 7 mmol) gave a mixture of 2-chloro-1-cyclohexyl-1,1-difluoroethane (**23**), the reverse-addition product (**23a**), chlorocyclohexane (**24**) and isomers of di-adduct (**25**) in the ratio of 45:3:1:5 by GLC/MS. Fractional distillation gave pure (**23**) (11.9 g, 49%) as a colourless liquid; bp 184 °C (Found: C, 52.3; H, 7.2. $C_8H_{12}BrF_3$ requires C, 52.6; H, 7.1%); NMR spectrum no. 15; Mass spectrum no. 11; IR spectrum no. 10. 1-Chloro-2,2-difluoroethene (1.6 g, 93% conversion) was recovered.

Reactions with Bromofluoroethenes

Cyclohexane with Bromotrifluoroethene (γ-ray initiation)

Cyclohexane (8.0 g, 95 mmol) and bromotrifluoroethene (7.7 g, 48 mmol) gave 2-bromo-1-cyclohexyl-1,1,2-trifluoroethane (**26**) and bromocyclohexane (**27**) in the ratio of 1:2 by GLC/MS. Fractional distillation gave pure (**26**) (2.6 g, 22%) as a colourless liquid; bp 218 °C (Found: C, 39.2; H, 4.9. $C_8H_{12}BrF_3$ requires C, 39.2; H, 4.9%); NMR spectrum no. 16; Mass spectrum no. 12; IR spectrum no. 11. Bromotrifluoroethene (1.1 g, 86% conversion) was recovered and two unidentified by-products with higher retention times by GLC were also detected (9% and 15% of the total products). Fluorine NMR showed the recovered cyclohexane contained fluoroalkene.

Cyclohexane with Bromotrifluoroethene (peroxide initiation)

Cyclohexane (50 g, 585 mmol), bromotrifluoroethene (23.0 g, 140 mmol) and DTBP (1.0 g, 7 mmol) gave 2-bromo-1-cyclohexyl-1,1,2-trifluoroethane (**26**) and bromocyclohexane (**27**) in the ratio of 3:2 by GLC/MS. Fractional distillation gave pure (**26**) (12.0 g, 35%) as described above. Bromotrifluoroethene (1.3 g, 94% conversion) was recovered, and fluorine NMR showed the recovered cyclohexane contained fluoroalkene.

Cyclohexane with 1-Bromo-2,2-difluoroethene (γ-ray initiation)

Cyclohexane (11.5 g, 137 mmol) and 1-bromo-2,2-difluoroethene (4.5 g, 31.5 mmol) gave 2-bromo-1-cyclohexyl-1,1-difluoroethane (**28**) and bromocyclohexane (**27**) in the ratio of 4:1 by GLC/MS. Fractional distillation gave pure (**28**) (2.6 g, 36%) as a colourless liquid; bp 205 °C (Found: C, 42.2; H, 5.8. $C_8H_{13}BrF_2$ requires C, 42.3; H, 5.7%); NMR spectrum no. 17; Mass spectrum no. 13; IR spectrum no. 12. No volatiles were collected, and the recovered cyclohexane contained fluoroalkene.

Cyclohexane with 1-Bromo-2,2-difluoroethene (peroxide initiation, 1)

Cyclohexane (147 g, 1750 mmol), 1-bromo-2,2-difluoroethene (55 g, 380 mmol) and DTBP (5.0 g, 34 mmol) gave 2-bromo-1-cyclohexyl-1,1-difluoroethane (**28**) and bromocyclohexane (**27**) in the ratio of 4:1 by GLC/MS. Fractional distillation gave pure (**28**) (19.0 g, 22%) as described above. No volatiles were collected, and the recovered cyclohexane contained fluoroalkene.

Cyclohexane with 1-Bromo-2,2-difluoroethene (peroxide initiation, 2)

Cyclohexane (250 g, 3000 mmol), 1-bromo-2,2-difluoroethene (24 g, 170 mmol) and DTBP (2.5 g, 17 mmol) gave 2-bromo-1-cyclohexyl-1,1-difluoroethane (**28**) and bromocyclohexane (**27**) in the ratio of 5.6:1 by GLC/MS. Fractional distillation gave pure (**28**) (7.1 g, 19%) as described above. Fluorine NMR showed the recovered cyclohexane contained fluoroalkene.

Cyclohexene with Bromotrifluoroethene (γ-ray initiation)

Cyclohexene (8.0 g, 98 mmol) and bromotrifluoroethene (7.9 g, 49 mmol) gave a trace of adduct from addition to the allyl radical (**30**) (M=242/244) and a smaller trace of (**31**) (M=242/244) resulting from addition across the cyclohexene double bond. Bromotrifluoroethene (0.7 g) was recovered, and fluorine NMR showed the recovered cyclohexene contained fluoroalkene.

7.4. Experimental for Chapter 4

General Procedure for Dehydrofluorination

A mixture of dry potassium *tert*-butoxide and THF was cooled to the required temperature under nitrogen. The polyfluoroalkyl derivative was added dropwise and stirred for 3 hours before being allowed to warm up slowly to room temperature overnight. On termination the reaction mixture was poured into water and neutralised with 10% hydrochloric acid, extracted into dichloromethane, dried ($MgSO_4$) and distilled to give the desired fluoroalkene.

1-Cyclohexyl-1,1,2,3,3,3-hexafluoropropane

Potassium *tert*-butoxide (18.8 g, 168 mmol) and 1-cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**) (26.2 g, 112 mmol) in THF (50 ml) at 0 °C gave (1*Z*)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (16.4 g, 68%) as a colourless liquid; bp 142-144 °C (Found: C, 50.2; H, 5.15. $C_9H_{11}F_5$ requires C, 50.5; H, 5.1%); NMR spectrum no. 18; Mass spectrum no. 14; IR spectrum no. 13.

1-Cyclohexyl-1,1,3,3,3-pentafluoropropane

Potassium *tert*-butoxide (6.3 g, 56 mmol) and 1-cyclohexyl-1,1,3,3,3-pentafluoropropane (**12**) (11.0 g, 51 mmol) in THF (30 ml) at -78 °C gave (1*Z*)-1-cyclohexyl-1,3,3,3-tetrafluoroprop-1-ene (**34**) (7.3 g, 73%) as a colourless liquid; bp 172 °C (Found: C, 55.1; H, 6.2. $C_9H_{12}F_4$ requires C, 55.1; H, 6.1%); NMR spectrum no. 20; Mass spectrum no. 15; IR spectrum no. 14.

2-Chloro-1-cyclohexyl-1,1,2-trifluoroethane with KO^{t}Bu at -78 °C

Potassium *tert*-butoxide (1.4 g, 12.5 mmol) and 2-chloro-1-cyclohexyl-1,1,2-trifluoroethane (**20**) (2.0 g, 10 mmol) in THF (25 ml) at -78 °C gave (1*E*) and (1*Z*)-2-chloro-1-cyclohexyl-1,2-difluoroethene (**35a**) and (**35b**) in the ratio of 15:1 by fluorine NMR as described below. No further workup was performed.

2-Chloro-1-cyclohexyl-1,1,2-trifluoroethane with KO^{t}Bu at 20 °C

Potassium *tert*-butoxide (2.8 g, 25 mmol) and 2-chloro-1-cyclohexyl-1,1,2-trifluoroethane (**20**) (2.0 g, 10 mmol) in THF (25 ml) at 20 °C gave (1*E*) and (1*Z*)-2-chloro-1-cyclohexyl-1,2-difluoroethene (**35a**) and (**35b**) (1.0 g, 55%) in the ratio of 4:1 by fluorine NMR as a colourless liquid; bp 190 °C; (Found: C, 53.4; H, 6.25. $C_8H_{11}ClF_2$ requires C, 53.2; H, 6.1%); NMR spectra nos. 22 and 23; Mass spectra nos. 16 and 17; IR spectrum no. 15.

2-Chloro-1-cyclohexyl-1,1,2-trifluoroethane with KO^{t}Bu at 80 °C

Potassium *tert*-butoxide (1.4 g, 12.5 mmol) and 2-chloro-1-cyclohexyl-1,1,2-trifluoroethane (**20**) (1.0 g, 5 mmol) in THF (20 ml) at 80 °C for 15 hours gave (1*E*) and (1*Z*)-2-chloro-1-cyclohexyl-1,2-difluoroethene (**35a**) and (**35b**) in the ratio of 3:1 by fluorine NMR. No further workup was performed.

2-Chloro-1-cyclohexyl-1,1,2-trifluoroethane with NaOH at 20 °C

Sodium hydroxide (1.0 g, 25 mmol) and 2-chloro-1-cyclohexyl-1,1,2-trifluoroethane (**20**) (2.0 g, 10 mmol) in THF (15 ml) at 20 °C gave no trace of reaction by fluorine NMR. No further workup was performed.

2-Chloro-1-cyclohexyl-1,1,2-trifluoroethane with NaOH at 80 °C

Sodium hydroxide (1.0 g, 25 mmol) and 2-chloro-1-cyclohexyl-1,1,2-trifluoroethane (**20**) (2.0 g, 10 mmol) in THF (15 ml) at 80 °C for 15 hours gave no trace of reaction by fluorine NMR. No further workup was performed.

2-Chloro-1-cyclohexyl-1,1,2-trifluoroethane with NaOH at 200 °C

Sodium hydroxide (0.5 g, 12.5 mmol) and 2-chloro-1-cyclohexyl-1,1,2-trifluoroethane (**20**) (1.0 g, 5 mmol) in tetraglyme (5 ml) in a sealed Carius Tube in a rotating oil bath at 200 °C gave (1*E*) and (1*Z*)-2-chloro-1-cyclohexyl-1,2-difluoroethene (**35a**) and (**35b**) in the ratio of 2:1 by fluorine NMR. No further workup was performed.

Caesium Fluoride Isomerisation

Caesium fluoride (2.1 g, 13.9 mmol) which had been dried rigorously by heating at 160 °C in a vacuum was reacted with (1*E*) and (1*Z*)-2-chloro-1-cyclohexyl-1,2-difluoroethene (**35a**) and (**35b**) (0.5 g, 2.8 mmol) in tetraglyme (5 ml) under nitrogen in a sealed Carius tube at 200 °C for 48 hours in a rotating oil bath. On termination, fluorine NMR showed that the ratio of *E*:*Z* was unchanged at 5:1.

2,2-Dichloro-1-cyclohexyl-1,1-difluoroethane

Potassium *tert*-butoxide (0.9 g, 7.6 mmol) and 2,2-dichloro-1-cyclohexyl-1,1-difluoroethane (**21**) (1.5 g, 6.9 mmol) in THF (15 ml) at -78 °C gave (1*Z*)-2,2-dichloro-1-cyclohexyl-1-fluoroethene (**36**) (1.1 g, 81%) as a colourless liquid; bp 199 °C (Found: C, 48.8; H, 5.7. $C_8H_{12}ClF$ requires C, 48.7; H, 5.6%); NMR spectrum no. 21; Mass spectrum no. 18; IR spectrum no. 16.

2-Bromo-1-cyclohexyl-1,1-difluoroethane

Potassium *tert*-butoxide (2.6 g, 23 mmol) and 2-bromo-1-cyclohexyl-1,1-difluoroethane (**28**) (4.0 g, 18 mmol) in THF (15 ml) at -78 °C gave a mixture of unreacted starting material (**28**) and (1*Z*)-2-bromo-1-cyclohexyl-1-fluoroethene (**37**) which could not be separated by distillation or by column chromatography; NMR spectrum no. 24; Mass spectrum no. 19.

2-Chloro-1-cyclohexyl-1,1-difluoroethane

Potassium *tert*-butoxide (5.0 g, 44 mmol) and 2-chloro-1-cyclohexyl-1,1-difluoroethane (**23**) (5.4 g, 30 mmol) in THF (25 ml) at -78 °C gave (1*Z*)-2-chloro-1-cyclohexyl-1-fluoroethene (**38**) (3.0 g, 62%) as a colourless liquid; bp 180 °C (Found: C, 59.0; H, 7.5. $C_8H_{12}ClF$ requires C, 59.1; H, 7.5%); NMR spectrum no. 25; Mass spectrum no. 20; IR spectrum no. 17.

7.5. Experimental for Chapter 5

General Procedure for Reaction with Oxygen Nucleophiles

Sodium or sodium hydride (60% dispersion in oil, removed with hexane) was added to the alcohol in THF under nitrogen and the mixture stirred at 50 °C. The fluoroalkene was added dropwise and the reaction mixture heated at reflux at 80 °C until fluorine NMR showed the reaction to be complete. The crude reaction mixture was extracted into dichloromethane, dried ($MgSO_4$) and solvent removed by rotary evaporation. Purification was achieved either by distillation or by column chromatography using 5% diethylether/cyclohexane as eluent.

Reaction of (1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene with Nucleophiles

Methanol

Sodium (0.9 g, 37 mmol), methanol (2.4 g, 75 mmol) and (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (4.0 g, 19 mmol) gave (1Z)-1-cyclohexyl-1-methoxy-2,3,3,3-tetrafluoroprop-1-ene (**39a**) (3.1 g, 72%) as a colourless oil after purification by distillation; bp 168 °C (Found: C, 53.1; H, 6.2. $C_{10}H_{14}F_4O$ requires C, 53.1; H, 6.2%); NMR spectrum no. 26; Mass spectrum no. 21; IR spectrum no. 18. Traces of (1*E*)-1-cyclohexyl-1-methoxy-2,3,3,3-tetrafluoroprop-1-ene (**39b**) were observed by NMR; NMR spectrum no. 27.

Ethanol

Sodium (0.6 g, 24 mmol), ethanol (1.1 g, 24 mmol) and (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (3.4 g, 16 mmol) gave (1Z)-1-cyclohexyl-1-ethoxy-2,3,3,3-tetrafluoroprop-1-ene (**33**) (2.5 g, 58%) as a clear yellow oil after purification by column chromatography; bp 178 °C (Found: C, 55.2; H, 6.9. $C_{11}H_{16}F_4O$ requires C, 55.0; H, 6.7%); R_f 0.3; NMR spectrum no. 28; Mass spectrum no. 22; IR spectrum no. 19.

Cyclohexanol

Sodium hydride (0.4 g, 18 mmol), cyclohexanol (1.8 g, 18 mmol) and (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (3.2 g, 18 mmol) gave (1Z)-1-cyclohexyl-1-cyclohexyloxy-2,3,3,3-tetrafluoroprop-1-ene (**40**) (3.6 g, 67%) as a clear yellow oil after purification by column chromatography; bp 205 °C (Found: C, 61.2; H, 7.5. $C_{15}H_{22}F_4O$ requires C, 61.2; H, 7.5%); R_f 0.25; NMR spectrum no. 29; Mass spectrum no. 23; IR spectrum no. 20.

Butyl Lithium

Butyl lithium (1.6 M in hexanes, 20 ml, 30 mmol) and (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (2.0 g, 10 mmol) in THF (20 ml) was stirred at -78 °C for 3 hours. This was allowed to warm to room temperature whilst stirring for a further 3 hours before being quenched by the addition of water. This gave (2*E*)-3-cyclohexyl-1,1,1,2-tetrafluorohept-2-ene (**41a**) (1.8 g, 58%) as a colourless oil after purification by distillation; bp 228 °C (Found: C, 61.7; H, 8.1. $C_{13}H_{20}F_4$ requires C, 61.9; H, 7.9%); NMR spectrum no. 30; Mass spectrum no. 24; IR spectrum no. 21. The *Z* isomer (**41b**) was observed (4.5:1 by ^{19}F NMR); NMR spectrum no. 31. Higher adducts in trace amounts were detected by GLC/MS with M=290 and M=270.

Mechanistic Test for the Acidic Proton

A sealable quartz NMR tube was charged with (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (0.1 g), potassium *tert*-butoxide (0.07 g), *tert*-butanol(OD) (1 ml), a drop of $CDCl_3$ (to lock the NMR) and heated at 140 °C in a steel sheath for 3 days. A hydrogen NMR spectrum showed that the resonance due to the CH ring hydrogen atom had disappeared, which confirmed the fact that it is acidic.

Grignard Reagents

(1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (2.0 g, 10 mmol) with 3-butenyl magnesium bromide (0.5 M in THF, 40 ml, 20 mmol) or methyl magnesium bromide (3.0 M in Et_2O with THF) at 80 °C for 5 days gave no trace of reaction by fluorine NMR. No further workup was performed.

Nitrogen Nucleophiles

(1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (2.1 g, 10 mmol) with aniline (2.8 g, 30 mmol at 125 °C), butylamine (2.2 g, 30 mmol at 75 °C) or sodium amide (1.2 g, 30 mmol at 80 °C) gave no trace of reaction by fluorine NMR. No further workup was performed.

Lithium Aluminium Hydride

(1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (3.6 g, 17 mmol) and lithium aluminium hydride (1.5 g, 30 mmol) in tetraglyme (10 ml) at room temperature gave a mixture of (1*Z*) and (1*E*)-1-cyclohexyl-2,3,3,3-tetrafluoroprop-1-ene (**45a**) and (**45b**) (*Z*:*E* 6:5) (2.8 g, 85%) as a colourless volatile liquid after purification by vacuum transfer; bp 146 °C (Found: C, 55.1; H, 6.2. $C_9H_{12}F_4$ requires C, 55.1; H, 6.1%); NMR spectra nos. 32, 33 and 34; Mass spectrum no. 25; IR spectrum no. 22.

Reaction of (1Z)-1-Cyclohexyl-1,3,3,3-tetrafluoroprop-1-ene with Nucleophiles

Methanol

Sodium (0.9 g, 37 mmol), methanol (2.6 g, 80 mmol) and (1Z)-1-cyclohexyl-1,3,3,3-tetrafluoroprop-1-ene (**34**) (4.0 g, 20 mmol) gave (1Z) and (1*E*)-1-cyclohexyl-1-methoxy-3,3,3-trifluoroprop-1-ene (**46**) (2.6 g, 63%) as a colourless oil after purification by column chromatography; dec. 170 °C (Found: C, 57.8; H, 7.4. $C_{10}H_{15}F_3O$ requires C, 57.7; H, 7.2%); R_f 0.3; NMR spectrum no. 35; Mass spectrum no. 26; IR spectrum no. 23.

Competition Reaction

Sodium (0.05 g, 25 mmol), methanol (0.1 g, 25 mmol), (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (1.1 g, 5 mmol) and (1Z)-1-cyclohexyl-1,3,3,3-tetrafluoroprop-1-ene (**34**) (1.0 g, 5 mmol) were added to THF (10 ml) under nitrogen and heated. Fluorine NMR after three hours showed that the resonance due to the vinylic fluorine atom of (1Z)-1-cyclohexyl-1,3,3,3-tetrafluoroprop-1-ene (**34**) had decreased to about half of the initial size by relative integration. The resonance due to the vinylic fluorine atom for (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) decreased by about one-fifth of the initial size.

Claisen Rearrangements of Fluorinated Systems

(1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene with Allyl Alcohol

Sodium (1.1 g, 47 mmol), allyl alcohol (3.3 g, 56 mmol) and (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (4.0 g, 19 mmol) gave 1-cyclohexyl-2-fluoro-2-(trifluoromethyl)pent-4-en-1-one (**48**) (2.6 g, 52% yield, 58% conversion) as a colourless oil after purification by column chromatography; bp 216 °C (Found: C, 56.9; H, 6.2. $C_{12}H_{16}F_4O$ requires C, 57.15; H, 6.35%); R_f 0.4; NMR spectrum no. 36; Mass spectrum no. 27; IR spectrum no. 24.

(1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene with Crotyl Alcohol

Sodium (2.7 g, 120 mmol), crotyl alcohol (10.1 g, 140 mmol) and (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (10.0 g, 47 mmol) gave a mixture of diastereoisomers of 1-cyclohexyl-2-fluoro-3-methyl-2-(trifluoromethyl)pent-4-en-1-one (**49**) (4.7 g, 37%) in the ratio of 4.5:1 by GLC/MS as a colourless oil after purification by distillation; bp 222 °C (Found: C, 58.8; H, 6.8. $C_{13}H_{18}F_4O$ requires C, 58.65; H, 6.8%); NMR spectrum no. 37; Mass spectrum no. 28; IR spectrum no. 25.

(1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene with Propargyl Alcohol

Sodium (2.7 g, 120 mmol), propargyl alcohol (7.9 g, 140 mmol) and (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (10.0 g, 47 mmol) gave 1-cyclohexyl-2-fluoro-2-(trifluoromethyl)penta-3,4-dien-1-one (**50**) (5.4 g, 49%) as a colourless oil after purification by distillation; bp 208 °C (Found: C, 57.7; H, 5.6. $C_{12}H_{14}F_4O$ requires C, 57.6; H, 5.6%); NMR spectrum no. 38; Mass spectrum no. 29; IR spectrum no. 26.

(1Z)-1-Cyclohexyl-1,3,3,3-tetrafluoroprop-1-ene with Allyl Alcohol

Sodium (0.9 g, 40 mmol), allyl alcohol (4.6 g, 80 mmol) and (1Z)-1-cyclohexyl-1,3,3,3-tetrafluoroprop-1-ene (**34**) (4.0 g, 20 mmol) gave 1-cyclohexyl-2-(trifluoromethyl)pent-4-en-1-one (**52**) (3.0 g, 64%) as a colourless oil after purification by column chromatography; bp 218 °C (Found; C, 61.3; H, 7.4. $C_{12}H_{17}F_3O$ requires C, 61.5; H, 7.3%); NMR spectrum no. 40; Mass spectrum no. 30; IR spectrum no. 27; and (1Z)-cyclohexyl-3,3,3-trifluoro-1-prop-2-enyloxyprop-1-ene (**51**) (0.9 g, 12%) as a colourless oil; NMR spectrum no. 39; which rearranged to (**52**) on standing at room temperature.

7.6. Experimental for Chapter 6

General Procedure for Reaction with Electrophiles

The fluoroalkene was added to the electrophile without solvent under nitrogen and the mixture stirred at the required temperature. When the reaction was shown by fluorine NMR to be complete, aqueous sodium metabisulfite was added until the crude reaction mixture turned colourless. This was extracted into dichloromethane, dried ($MgSO_4$) and solvent removed by rotary evaporation. Purification was achieved either by distillation or by column chromatography using hexane as eluent.

Reaction of (1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene with Electrophiles

Bromine at 20 °C

(1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (2.0 g, 9.3 mmol) with bromine (3.0 g, 18.7 mmol) at 20 °C followed by purification by distillation gave a pair of diastereoisomers of 1,2-dibromo-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (**53**) (2.2 g, 62%) in the ratio of 1.4:1 by GLC/MS as a colourless liquid; bp 228 °C (Found: C, 29.0; H, 2.9. $C_9H_{11}BrF_5$ requires C, 28.9; H, 2.9%); NMR spectrum no. 41; Mass spectrum no. 31; IR spectrum no. 28.

Bromine (γ-ray initiation)

(1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (1.5 g, 7 mmol) with bromine (1.7 g, 10.5 mmol) irradiated with γ-rays at 20 °C gave a pair of diastereoisomers of 1,2-dibromo-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (**53**) (1.52 g, 58%) in the ratio of 1.4:1 by GLC/MS as described above.

Bromine and Methanol

(1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (1.0 g, 4.7 mmol), bromine (1.0 g, 6 mmol) and methanol (0.2 g, 6 mmol) at 20 °C gave a mixture of (1Z) and (1*E*)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) and (**32b**), 1,2-dibromo-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (**53**) and 2-bromo-1-cyclohexyl-2,3,3,3-tetrafluoropropan-1-one (**54**) in the ratio of 6:3.5:1:1 by GLC/MS and fluorine NMR. No further workup was performed.

1,2-Dibromo-1-cyclohexyl-1,2,3,3,3-pentafluoropropane and Methanol

Methanol (10 ml) was added to 1,2-dibromo-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (**53**) (1.1 g, 3 mmol) and heated at 60 °C overnight. Fluorine NMR showed that no reaction occurred, and therefore the formation of the ketone (**54**) did not occur from reaction of (**53**) with methanol.

Bromine in the dark at 20 °C

(1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (1.0 g, 4.7 mmol) with bromine (1.5 g, 9.35 mmol) in the dark at 20 °C gave a pair of diastereoisomers of 1,2-dibromo-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (**53**) in the ratio of 1.4:1 by GLC/MS and fluorine NMR. No further workup was performed.

Bromine and Methanol (excess)

A mixture of (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (1.0 g, 4.7 mmol) in methanol (5 ml) at 20 °C with bromine (1.5 g, 9.35 mmol) added dropwise over a few hours gave a mixture of (1Z) and (1*E*)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) and (**32b**) observed by GLC/MS and fluorine NMR.

Iodine Monochloride

(1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (2.0 g, 9.3 mmol) and iodine monochloride (3.0 g, 18.5 mmol) at 40 °C gave a mixture of 1-chloro-1-cyclohexyl-1,2,3,3,3-pentafluoro-2-iodopropane (**55**) and 1,2-dichloro-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (**56**) in the ratio of 1.5:1 by GLC/MS and fluorine NMR. Purification by column chromatography gave a pair of diastereoisomers of 1-chloro-1-cyclohexyl-1,2,3,3,3-pentafluoro-2-iodopropane (**55**) (1.2 g, 34%) in the ratio of 30:1 by GLC/MS as a colourless oil; bp 183 °C (Found: C, 28.8; H, 3.0. $C_9H_{11}ClF_5I$ requires C, 28.7; H, 2.9%); NMR spectrum no. 42; Mass spectrum no. 32; IR spectrum no. 29; and a pair of diastereoisomers of 1,2-dichloro-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (**56**) (1.0 g, 28%) in the ratio of 1.2:1 by GLC/MS as a colourless oil; bp 212 °C (Found: C, 37.8; H, 3.9. $C_9H_{11}Cl_2F_5$ requires C, 37.9; H, 3.9%); NMR spectrum no. 44; Mass spectrum no. 33; IR spectrum no. 30.

Iodine Monobromide

(1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (2.0 g, 9.3 mmol) and iodine monobromide (7.7 g, 37 mmol) at 40 °C followed by purification by distillation gave a pair of diastereoisomers of 1-bromo-1-cyclohexyl-1,2,3,3,3-pentafluoro-2-iodopropane (**57**) (2.5 g, 63%) in the ratio of 6:1 by GLC/MS as a colourless oil; bp 230 °C (Found: *m/z*) $[M\text{-}IFH]^+$ 272.9897 and 274.9886. $C_9H_{10}F_4Br$ requires *m/z* $[M\text{-}IFH]^+$, 272.9902 and 274.9882); NMR spectrum no. 45; Mass spectrum no. 34; IR spectrum no. 31.

Iodine Monofluoride

Iodine (3.6 g, 14 mmol) was added to iodine pentafluoride (3.5 g, 15.7 mmol) at 0 °C and stirred for 10 minutes. (1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (1.5 g, 7 mmol) was added dropwise and the mixture stirred for 15 hours to give 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**58**) and the impurity of 1-

cyclohexyl-2,3,3,3-tetrafluoropropan-1-one (**59**) in a ratio of 8:1 by GLC/MS. Column chromatography gave pure (**58**) (1.9 g, 76%) as a colourless oil which turned purple rapidly; bp 227-228 °C (Found: C, 30.1; H, 3.1. $C_9H_{11}F_6I$ requires C, 30.0; H, 3.1); NMR spectrum no. 43; Mass spectrum no. 35; IR spectrum no. 32.

Iodine and Fluorine

Fluorine (3.5 mmol in 10% F_2/N_2) was bubbled through a solution of (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (1.5 g, 7 mmol) and iodine (7.1 g, 28 mmol) in arklone (50 ml) at 0 °C. Fluorine NMR showed that no reaction occurred. With more fluorine (14 mmol) only a trace of addition of IF was observed with some baseline material. On workup unreacted alkene (**32a**) was recovered.

Fluorine

Fluorine (12 mmol in 10% F_2/N_2) was bubbled through a solution of (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (2.1 g, 10 mmol) in acetonitrile (140 ml) at 0 °C. The crude reaction mixture was poured into water (150 ml), neutralised ($NaHCO_3$), extracted into dichloromethane and fluorine NMR showed extensive decomposition. With less fluorine (0.5 equivalents) decomposition also occurred.

Reactions of 1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane

Attempted Radical Coupling

A Carius tube was charged with 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**58**) (2.0 g, 5.6 mmol), mercury (11.1 g, 55 mmol) and irradiated with UV light from a 1 KW Hanovia lamp for 7 days. The tube was opened and 1-cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**) (0.5 g, 38% recovery) removed by vacuum transfer. The low recovery was attributed to side reactions and telomerisation, with no evidence for the desired coupling product. Yellow mercury iodide was observed.

Alkenes

A Carius tube was charged with 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**58**) (2.5 g, 7 mmol), stabilised methyl vinyl ketone (0.5 g, 7 mmol) and irradiated with γ-rays for 28 days, but no reaction occurred. Reaction with 1,1-difluoroethene (1.1 g, 17 mmol) was also unsuccessful.

Radical Reactions with (1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene

(1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (3.0 g, 14 mmol), acetaldehyde (1.2 g, 28 mmol) and DTBP (0.4 g, 2.7 mmol) gave a trace of mono-adducts by GLC/MS (5% conversion) and no further workup was performed. Reaction using γ-rays gave a poorer conversion.

(1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**) (2.0 g, 9.3 mmol), trifluoromethyl iodide (3.4 g, 17 mmol) and DTBP (0.3 g, 2 mmol) gave a trace of reaction by GLC/MS and no further workup was performed. Reaction using γ-rays gave a poorer conversion.

Antimony Pentafluoride

1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**58**) (2.7 g, 7.5 mmol) and antimony pentafluoride (5.0 g, 23 mmol) in arklone (5 ml) at 0 °C gave no reaction. Reaction using perfluorodecalin solvent at 0 °C, 20 °C or 50 °C also gave no reaction.

Fluorine

Fluorine (5 mmol in 10% F_2/N_2) was bubbled through a solution of 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**58**) (1.5 g, 4.2 mmol) in acetonitrile (50 ml) at 0 °C. No reaction occurred, nor did it occur using arklone solvent.

Appendices

A. NMR Spectra

Chapter 2

1. 1-Cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**)
2. 2-Cyclohexyl-1,1,1,2,3,3-hexafluoropropane (**8a**)
3. 1,1,2,3,3,3-Hexafluoro-1-[x-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl]propane (x=2,3,4) (**9**)
4. 1,1,2,3,3,3-Hexafluoro-1-[*trans*-4-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl]propane (**9a**)
5. 1-Cyclohexyl-1,1,3,3,3-pentafluoropropane (**12**)
6. 2-Cyclohexyl-1,1,1,3,3-pentafluoropropane (**12a**)
7. 1,1,3,3,3-Pentafluoro-1-[x-(1,1,3,3,3-pentafluoropropyl)cyclohexyl]propane (x=2,3,4) (**13**)
8. 1,1,3,3,3-Pentafluoro-1-[*trans*-4-(1,1,3,3,3-pentafluoropropyl)cyclohexyl]propane (**13a**)

Chapter 3

9. 2-Cyclohexyl-1,1-difluoroethane (**18**)
10. 1-Cyclohexyl-1,1-difluoroethane (**19**)
11. 2-Cyclohexyl-1,1-difluoroethane (**18**) and 1-Cyclohexyl-1,1-difluoroethane (**19**)
12. 2-Chloro-1-cyclohexyl-1,1,2-trifluoroethane (**20**)
13. 1-Chloro-1-cyclohexyl-1,2,2-trifluoroethane (**20a**)
14. 2,2-Dichloro-1-cyclohexyl-1,1-difluoroethane (**21**)
15. 2-Chloro-1-cyclohexyl-1,1-difluoroethane (**23**)
16. 2-Bromo-1-cyclohexyl-1,1,2-trifluoroethane (**26**)
17. 2-Bromo-1-cyclohexyl-1,1-difluoroethane (**28**)

Chapter 4

18. (1*Z*)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**)
19. (1*E*)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32b**)
20. (1*Z*)-1-Cyclohexyl-1,3,3,3-tetrafluoroprop-1-ene (**34**)
21. (1*Z*)-2,2-Dichloro-1-cyclohexyl-1-fluoroethene (**36**)
22. (1*E*)-2-Chloro-1-cyclohexyl-1,2-difluoroethene (**35a**)
23. (1*Z*)-2-Chloro-1-cyclohexyl-1,2-difluoroethene (**35b**)
24. (1*Z*)-2-Bromo-1-cyclohexyl-1-fluoroethene (**37**)
25. (1*Z*)-2-Chloro-1-cyclohexyl-1-fluoroethene (**38**)

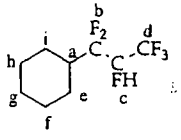
Chapter 5

26. (1*Z*)-1-Cyclohexyl-1-methoxy-2,3,3,3-tetrafluoroprop-1-ene (**39a**)
27. (1*E*)-1-Cyclohexyl-1-methoxy-2,3,3,3-tetrafluoroprop-1-ene (**39b**)
28. (1*Z*)-1-Cyclohexyl-1-ethoxy-2,3,3,3-tetrafluoroprop-1-ene (**33**)
29. (1*Z*)-1-Cyclohexyl-1-cyclohexyloxy-2,3,3,3-tetrafluoroprop-1-ene (**40**)
30. (2*E*)-3-Cyclohexyl-1,1,1,2-tetrafluorohept-2-ene (**41a**)
31. (2*Z*)-3-Cyclohexyl-1,1,1,2-tetrafluorohept-2-ene (**41b**)
32. (1*Z*)-1-Cyclohexyl-2,3,3,3-tetrafluoroprop-1-ene (**45a**)
33. (1*E*)-1-Cyclohexyl-2,3,3,3-tetrafluoroprop-1-ene (**45b**)
34. (1*Z*) and (1*E*)-1-Cyclohexyl-2,3,3,3-tetrafluoroprop-1-ene (**45a**) and (**45b**)
35. (1*Z*) and (1*E*)-1-Cyclohexyl-1-methoxy-3,3,3-trifluoroprop-1-ene (**46**)
36. (1*Z*)-Cyclohexyl-3,3,3-trifluoro-1-prop-2-enyloxyprop-1-ene (**51**)
37. 1-Cyclohexyl-2-fluoro-2-(trifluoromethyl)pent-4-en-1-one (**48**)
38. 1-Cyclohexyl-2-(trifluoromethyl)pent-4-en-1-one (**52**)
39. 1-Cyclohexyl-2-fluoro-3-methyl-2-(trifluoromethyl)pent-4-en-1-one (**49**)
40. 1-Cyclohexyl-2-fluoro-2-(trifluoromethyl)penta-3,4-dien-1-one (**50**)

Chapter 6

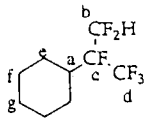
41. 1,2-Dibromo-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (**53**)
42. 1-Chloro-1-cyclohexyl-1,2,3,3,3-pentafluoro-2-iodopropane (**55**)
43. 1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**58**)
44. 1,2-Dichloro-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (**56**)
45. 1-Bromo-1-cyclohexyl-1,2,3,3,3-pentafluoro-2-iodopropane (**57**)

1. 1-Cyclohexyl-1,1,2,3,3,3-hexafluoropropane (8)



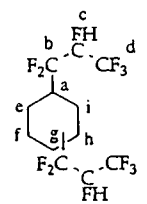
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
23.9	t	$^{3}J_{C-F}$ 4.5		e
25.3	s			f
25.5	s			g
25.5	m			i
25.7	s			h
41.4	t	$^{2}J_{C-F}$ 22		a
84.7	d	$^{1}J_{C-F}$ 195		c
	d	$^{2}J_{C-F}$ 37		
	q	$^{2}J_{C-F}$ 34		
	d	$^{2}J_{C-F}$ 31		
119.7	d	$^{1}J_{C-F}$ 252		b
	d	$^{1}J_{C-F}$ 242		
	d	$^{2}J_{C-F}$ 25		
121.0	q	$^{1}J_{C-F}$ 293		d
	d	$^{2}J_{C-F}$ 26		
^{1}H				
1.24	m		5	e-i_{ax}
1.85	m		6	a, e-i_{eq}
4.82	d	$^{2}J_{H-F}$ 41	1	c
	d	$^{3}J_{H-F}$ 14		
	q	$^{3}J_{H-F}$ 7.0		
	d	$^{3}J_{H-F}$ 6.6		
^{19}F				
-74.3	s		3	d
-118.1	AB	J_{AB} 271	2	b
-118.8	AB			
-211.9	d	$^{2}J_{F-H}$ 45	1	c

2. 2-Cyclohexyl-1,1,1,2,3,3-hexafluoropropane (8a)



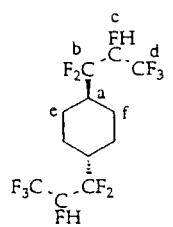
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
112.3	t	$^{1}J_{C-F}$ 250		c
	d	$^{2}J_{C-F}$ 32		
^{1}H				
5.98	t	$^{2}J_{H-F}$ 53	1	c
	d	$^{3}J_{H-F}$ 6.8		
^{19}F				
-130.5 and -133.25	AB	J_{AB} 376	2	b
-183.0	s		1	c

3. 1,1,2,3,3,3-Hexafluoro-1-[x-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl]propane (x=2,3,4) (9)



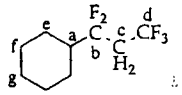
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{1}H				
1.35	m			a,e-i
1.70	m			a,e-i
2.0	m			a,e-i
4.84	dm	$^{2}J_{H-F}$ 44		c
^{19}F				
-74.7	s		3	d
-118.2	m		2	b
-212.0	s		1	c

4. 1,1,2,3,3,3-Hexafluoro-1-[*trans*-4-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl]propane (9a)



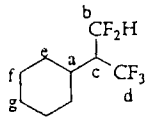
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
22.9	t	$^{3}J_{C-F}$ 15		e
24.3	t	$^{3}J_{C-F}$ 16		f
40.7	t	$^{2}J_{C-F}$ 22		a
85.0	d	$^{1}J_{C-F}$ 192		b
	d	$^{2}J_{C-F}$ 38		
	q	$^{2}J_{C-F}$ 34		
	d	$^{2}J_{C-F}$ 30		
119.5	d	$^{1}J_{C-F}$ 253		c
	d	$^{1}J_{C-F}$ 249		
	d	$^{2}J_{C-F}$ 24		
121.0	q	$^{1}J_{C-F}$ 283		d
	d	$^{2}J_{C-F}$ 26		
^{1}H				
1.4	m		2	e,f_{ax}
2.04	m		3	a,e_{eq},f_{eq}
4.83	dm	$^{2}J_{H-F}$ 44	1	c
^{19}F				
-74.6	s		3	d
-117.6	A or AB	$^{2}J_{F-F}$ 270	2.5	b
-118.8	B or AB	$^{2}J_{F-F}$ 270		b
-211.5	d	$^{2}J_{F-H}$ 44	1	c
	q	$^{3}J_{F-F}$ 8		

5. 1-Cyclohexyl-1,1,3,3,3-pentafluoropropane (12)



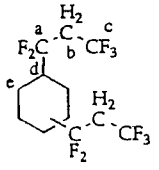
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
25.4	s			g
25.4	d	$^{3}J_{C-F}$ 9.2		e
25.7	s			f
38.2	6 lines	$^{2}J_{C-F}$ 29		c
44.1	t	$^{2}J_{C-F}$ 23		a
121.7	t	$^{1}J_{C-F}$ 245		b
	q	$^{3}J_{C-F}$ 2.7		
124.0	q	$^{1}J_{C-F}$ 277		d
	t	$^{3}J_{C-F}$ 4.2		
^{1}H				
1.0-1.2	m		5	e,f,g_{ax}
1.6-1.8	m		5	e,f,g_{eq}
1.8	m		1	a
2.8	q	$^{3}J_{H-F}$ 10	2	c
	t	$^{3}J_{H-F}$ 10		
^{19}F				
-60.3	m		3	d
-102.7	m		2	b

6. 2-Cyclohexyl-1,1,1,3,3-pentafluoropropane (12a)



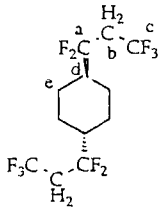
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{1}H				
5.7	t	$^{2}J_{H-F}$ 54	1	b
	d	$^{3}J_{H-F}$ 6		
^{19}F				
-62.1	s		3	d
-118.9	d	$^{2}J_{F-H}$ 93	2	b

7. 1,1,3,3,3-Pentafluoro-1-[x-(1,1,3,3,3-pentafluoropropyl)cyclohexyl]propane (x=2,3,4) (13)



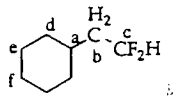
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{1}H				
1.1-1.9	m		4	e
2.7	m		1	d
6.05	m		2	b
^{19}F				
-62.0	m		3	c
-104.0	m		2	a

8. 1,1,3,3,3-Pentafluoro-1-[*trans*-4-(1,1,3,3,3-pentafluoropropyl)cyclohexyl]propane (13a)



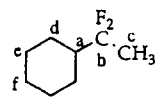
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
24.1	t	$^{3}J_{C-F}$ 4.5		c
38.66	sextet	$^{2}J_{C-F}$ 29		b
38.74	sextet	$^{2}J_{C-F}$ 30		b
43.0	t	$^{2}J_{C-F}$ 30		d
121.4	t	$^{1}J_{C-F}$ 246		a
124.0	q	$^{1}J_{C-F}$ 277		c
	t	$^{3}J_{C-F}$ 5.3		
^{1}H				
1.1-1.3	m		4	e_{ax}
1.8-2.0	m		6	d,e_{eq}
2.7	m		4	b
^{19}F				
-62.0	m		3	c
-103.9	m		2	a

9. 2-Cyclohexyl-1,1-difluoroethane (18)



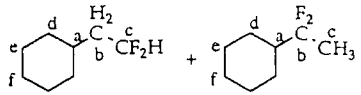
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
32.4	t	$^{3}J_{C\text{-}F}$ 5.3		a
41.4	t	$^{2}J_{C\text{-}F}$ 20		b
116.9	t	$^{1}J_{C\text{-}F}$ 238		c
^{1}H				
5.8	t	$^{2}J_{H\text{-}F}$ 57	1	c
	t	$^{3}J_{H\text{-}H}$ 4.8		
^{19}F				
-113.2	m		2	c

10. 1-Cyclohexyl-1,1-difluoroethane (19)



Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
21.0	t	$^{2}J_{C\text{-}F}$ 28		c
45.4	t	$^{2}J_{C\text{-}F}$ 24		a
125.9	t	$^{1}J_{C\text{-}F}$ 240		b
^{19}F				
-95.0	m		2	b

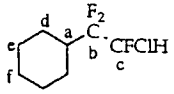
11. 2-Cyclohexyl-1,1-difluoroethane (18) and 1-Cyclohexyl-1,1-difluoroethane (19)



A B

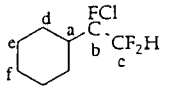
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
25,7	s			f (A and B)
26.2	s			e (A and B)
26.4	s			d (A or B)
33.1	s			d (A or B)
^{1}H				
0.9-1.2	m			

12. 2-Chloro-1-cyclohexyl-1,1,2-trifluoroethane (20)



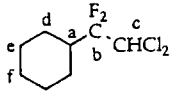
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
24.8	s			f
25.1	s			e
25.6	s			d
40.7	t	$^{2}J_{C-F}$ 22		a
97.4	d	$^{1}J_{C-F}$ 250		c
	t	$^{2}J_{C-F}$ 37		
119.4	t	$^{1}J_{C-F}$ 251		b
	d	$^{2}J_{C-F}$ 24		
^{1}H				
1.1-1.3	m		5	d,e,f_{ax}
1.6-1.8	m		5	d,e,f_{eq}
2.4	m		1	a
6.2	d	$^{2}J_{H-F}$ 48	1	c
	d (AB)	$^{3}J_{H-F}$ 6.4		
	d	$^{3}J_{H-F}$ 6.4		
^{19}F				
-119.7	m			b
-153.7	d	$^{2}J_{F-H}$ 48		c
	t	$^{3}J_{F-F}$ 13		

13. 1-Chloro-1-cyclohexyl-1,2,2-trifluoroethane (20a)



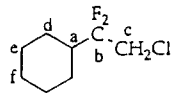
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{1}H				
5.8	t	$^{2}J_{H-F}$ 54		c
	d	$^{3}J_{H-F}$ 6.0		

14. 2,2-Dichloro-1-cyclohexyl-1,1-difluoroethane (21)



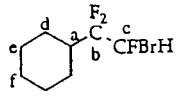
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
24.9	t	$^{3}J_{C\text{-}F}$ 4.1		d
25.3	s			f
26.6	s			e
40.9	t	$^{2}J_{C\text{-}F}$ 23		a
69.4	t	$^{2}J_{C\text{-}F}$ 35		c
120.4	t	$^{1}J_{C\text{-}F}$ 252		b
^{1}H				
1.2-1.3	m		5	d,e,f_{ax}
1.8-1.9	m		5	d,e,f_{eq}
2.2	m		1	a
5.8	t	$^{3}J_{H\text{-}F}$ 9.2	1	c
^{19}F				
-115.9	d	$^{3}J_{F\text{-}H}$ 9.0 $^{3}J_{F\text{-}H}$ 8.3	2	b

15. 2-Chloro-1-cyclohexyl-1,1-difluoroethane (23)



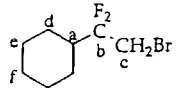
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
25.1	t	$^{3}J_{C\text{-}F}$ 4		d
25.5	s			f
25.8	s			e
41.1	t	$^{2}J_{C\text{-}F}$ 35		a
43.0	t	$^{2}J_{C\text{-}F}$ 23		c
122.5	t	$^{1}J_{C\text{-}F}$ 245		b
^{1}H				
1.1-1.2	m		5	d,e,f_{ax}
1.6-1.8	m		5	d,e,f_{eq}
2.0	m		1	a
3.6	t	$^{3}J_{H\text{-}F}$ 13	1	c
^{19}F				
-109.4	m		2	b

16. 2-Bromo-1-cyclohexyl-1,1,2-trifluoroethane (26)



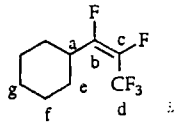
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
24.5	s			f
25.1	s			e
25.6	s			d
40.7	t	$^{2}J_{C-F}$ 22		a
89.8	d	$^{1}J_{C-F}$ 259		c
	t	$^{2}J_{C-F}$ 38		
119.2	t	$^{1}J_{C-F}$ 249		b
	d	$^{2}J_{C-F}$ 24		
^{1}H				
1.1-1.2	m		5	d,e,f_{ax}
1.6-1.8	m		5	d,e,f_{eq}
2.1	m		1	a
6.40	d	$^{2}J_{H-F}$ 47	1	c
	d	$^{3}J_{H-F}$ 11		
	d	$^{3}J_{H-F}$ 11		
^{19}F				
-117.3	m		2	b
-156.4	d	$^{2}J_{F-H}$ 47	1	c
	t	$^{3}J_{F-F}$ 17		

17. 2-Bromo-1-cyclohexyl-1,1-difluoroethane (28)



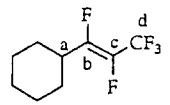
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
25.5	t	$^{3}J_{C-F}$ 4.2		d
25.7	s			f
26.0	s			e
30.8	t	$^{2}J_{C-F}$ 34		a
41.8	t	$^{2}J_{C-F}$ 22		c
121.9	t	$^{1}J_{C-F}$ 245		b
^{1}H				
1.1-1.2	m		5	d_{ax},e_{ax},f_{ax}
1.7-1.8	m		5	d_{eq},e_{eq},f_{eq}
2.0	m		1	a
3.5	t	$^{2}J_{H-F}$ 14	2	c
^{19}F				
-104.1	m		2	b

18. (1*Z*)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**)



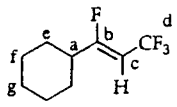
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
25.2	s			g
25.6	s			f
28.6	d	$^{3}J_{C\text{-}F}$ 2.6		e
36.3	d	$^{2}J_{C\text{-}F}$ 21		a
120.4	q	$^{1}J_{C\text{-}F}$ 270		d
	d	$^{2}J_{C\text{-}F}$ 35		
	d	$^{3}J_{C\text{-}F}$ 9.6		
134.9	d	$^{1}J_{C\text{-}F}$ 250		c
	q	$^{2}J_{C\text{-}F}$ 40		
	d	$^{2}J_{C\text{-}F}$ 24		
156.3	d	$^{1}J_{C\text{-}F}$ 264		b
	d	$^{3}J_{C\text{-}F}$ 9.6		
	q	$^{4}J_{C\text{-}F}$ 3.4		
^{1}H				
1.20	q	$^{3}J_{H\text{-}F}$ 12	1	g_{ax}
	t	$^{3}J_{H\text{-}F}$ 3.2		
1.29	q	$^{3}J_{H\text{-}H}$ 13	2	f_{ax}
1.54	q	$^{3}J_{H\text{-}H}$ 12	2	e_{ax}
	d	$^{3}J_{H\text{-}H}$ 3.2		
1.71	d	$^{3}J_{H\text{-}H}$ 12	3	e,g_{eq}
1.84	d	$^{4}J_{H\text{-}F}$ 13	2	f_{eq}
2.50	d	$^{3}J_{H\text{-}F}$ 32	1	a
	t	$^{3}J_{H\text{-}H}$ 12		
^{19}F				
-65.7	s		3	d
-130.9	d	$^{2}J_{F\text{-}H}$ 30	1	b
-161.2	m		1	c

19. (1*E*)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32b**)



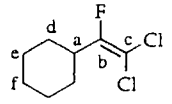
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{19}F				
-68.2	m		3	d
-148.3	d	$^{3}J_{F\text{-}F\,trans}$ 131	1	c
	quintet	$^{4}J_{F\text{-}F,\,F\text{-}H}$ 23		
-176.4	d	$^{3}J_{F\text{-}F\,trans}$ 132	1	b
	m			

20. (1Z)-1-Cyclohexyl-1,3,3,3-tetrafluoroprop-1-ene (34)



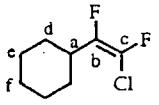
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
25.4	s			g
25.6	s			f
29.0	s			e
40.5	d	$^{3}J_{C\text{-}F}$ 22		a
95.2	q	$^{2}J_{C\text{-}F}$ 26		c
	d	$^{2}J_{C\text{-}F}$ 10		
122.5	q	$^{1}J_{C\text{-}F}$ 270		d
171.9	d	$^{1}J_{C\text{-}F}$ 278		b
	q	$^{3}J_{C\text{-}F}$ 5.5		
^{1}H				
1.1-1.2	m		5H	e,f,g_{ax}
1.7-1.9	m		5H	e,f,g_{eq}
2.1	m		1H	a
4.94	d	$^{3}J_{H\text{-}F trans}$ 34	1H	c
	q	$^{3}J_{H\text{-}F}$ 7.6		
^{19}F				
-53.2	s		3F	d
-88.7	s		1F	b

21. (1Z)-2,2-Dichloro-1-cyclohexyl-1-fluoroethene (36)



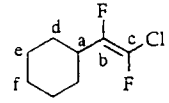
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
25.4	s			f
25.7	s			e
28.2	s			d
38.5	d	$^{2}J_{C\text{-}F}$ 22		a
105.7	d	$^{2}J_{C\text{-}F}$ 46		c
160.6	d	$^{1}J_{C\text{-}F}$ 264		b
^{1}H				
1.2-1.4	m		5	d,e,f_{ax}
1.6-1.8	m		5	de,f_{eq}
2.7	d	$^{3}J_{H\text{-}F}$ 28	1	a
	t	$^{3}J_{H\text{-}Hax}$ 12		
	t	$^{3}J_{H\text{-}Heq}$ 3.6		
^{19}F				
-111.6	d	$^{3}J_{F\text{-}H}$ 28	1	b

22.(1*E*)-2-Chloro-1-cyclohexyl-1,2-difluoroethene (35a)



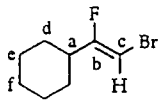
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
25.4	s			f
25.9	s			e
28.3	d	$^{3}J_{C\text{-}F}$ 2.7		d
36.8	d	$^{2}J_{C\text{-}F}$ 21		a
	d	$^{3}J_{C\text{-}F}$ 2.4		
134.8	d	$^{1}J_{C\text{-}F}$ 296		b
	d	$^{2}J_{C\text{-}F}$ 39		
146.8	d	$^{1}J_{C\text{-}F}$ 255		c
	d	$^{2}J_{C\text{-}F}$ 12		
^{1}H				
1.0-1.4	m		5	d,e,f_{ax}
1.5-1.8	m		5	d.e.f_{eq}
2.3	d	$^{3}J_{H\text{-}F}$ 30	1	a
	t	$^{3}J_{H\text{-}H}$ 12		
	m			
^{19}F				
-112.1	s		1	c
-144.4	m		1	b

23. (1*Z*)-2-Chloro-1-cyclohexyl-1,2-difluoroethene (35b)



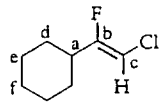
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
25.5	s			f
26.0	s			e
28.8	d	$^{3}J_{C\text{-}F}$ 2.3		d
36.8	d	$^{2}J_{C\text{-}F}$ 21		a
	d	$^{3}J_{C\text{-}F}$ 2.4		
135.6	d	$^{1}J_{C\text{-}F}$ 282		b
	d	$^{2}J_{C\text{-}F}$ 57		
151.4	d	$^{1}J_{C\text{-}F}$ 248		c
	d	$^{2}J_{C\text{-}F}$ 50		
^{1}H				
1.0-1.4	m		5	d,e,f_{ax}
1.5-1.8	m		5	d.e.f_{eq}
2.5	d	$^{3}J_{H\text{-}F}$ 28	1	a
	t	$^{3}J_{H\text{-}H}$ 12		
	m			
^{19}F				
-128.7	d	$^{3}J_{F\text{-}F}$ 126	1	c
-153.8	d	$^{3}J_{F\text{-}F}$ 126	1	b
	d	$^{3}J_{F\text{-}H}$ 29		

24. (1Z)-2-Bromo-1-cyclohexyl-1-fluoroethene (37)



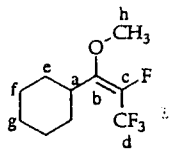
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
29.4	d	$^{3}J_{C\text{-}F}$ 1.9		d
41.0	d	$^{2}J_{C\text{-}F}$ 24		a
81.4	d	$^{2}J_{C\text{-}F}$ 23		c
166.3	d	$^{1}J_{C\text{-}F}$ 263		b
^{1}H				
1.1-1.2	m		5	d,e,f_{ax}
1.6-1.8	m		5	d,e,f_{eq}
2.1	m		1	a
5.3	d	$^{3}J_{H\text{-}F}$*trans* 29	1	c
^{19}F				
-99.1	d	$^{3}J_{F\text{-}H}$ 29	1	b
	d	$^{3}J_{F\text{-}H}$ 29		

25. (1Z)-2-Chloro-1-cyclohexyl-1-fluoroethene (38)



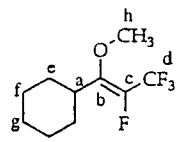
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
25.6	s			f
25.7	s			e
29.3	d	$^{3}J_{C\text{-}F}$ 1.5		d
40.1	d	$^{2}J_{C\text{-}F}$ 23		a
94.9	d	$^{2}J_{C\text{-}F}$ 19		c
164.8	d	$^{1}J_{C\text{-}F}$ 263		b
^{1}H				
1.1-1.2	m		5	d,e,f_{ax}
1.7-1.8	m		5	d,e,f_{eq}
2.1	m		1	a
5.23	dm	$^{3}J_{H\text{-}F}$ 26	1	c
^{19}F				
-108.5	2d	$^{3}J_{F\text{-}H}$*trans* 26 $^{3}J_{F\text{-}H}$ 24	1	c

26. (1Z)-1-Cyclohexyl-1-methoxy-2,3,3,3-tetrafluoroprop-1-ene (39a)



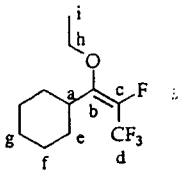
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
25.6	s			g
25.8	s			f
29.3	s			e
38.4	s			a
60.8	d	$^{4}J_{C\text{-}F}$ 12		h
121.2	q	$^{1}J_{C\text{-}F}$ 120		d
	d	$^{2}J_{C\text{-}F}$ 37		
133.7	d	$^{1}J_{C\text{-}F}$ 243		c
	q	$^{2}J_{C\text{-}F}$ 39		
151.5	m			b
^{1}H				
1.1-1.2	m		5	e,f,g_{ax}
1.4-1.7	m		5	e,f,g_{eq}
2.2	m		1	a
3.8	d	$^{5}J_{H\text{-}F}$ 5.2	3	h
^{19}F				
-63.3	d	$^{3}J_{F\text{-}F}$ 9.0	3	d
-161.5	d	$^{5}J_{F\text{-}H}$ 4.1	1	c

27. (1*E*)-1-Cyclohexyl-1-methoxy-2,3,3,3-tetrafluoroprop-1-ene (39b)



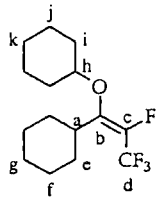
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{1}H				
3.6	s		3	h
^{19}F				
-67.2	d	$^{3}J_{F\text{-}F}$ 9.0	3	d
-162.3	d	$^{5}J_{F\text{-}H}$ 7.1	1	c

28. (1Z)-1-Cyclohexyl-1-ethoxy-2,3,3,3-tetrafluoroprop-1-ene (33)



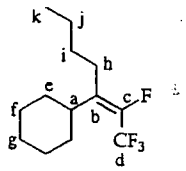
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
15.6	s			i
25.6	s			g
25.9	s			f
29.5	s			e
38.2	s			a
68.9	d	$^{4}J_{C\text{-}F}$ 11.7		h
121.3	q	$^{1}J_{C\text{-}F}$ 268		d
	d	$^{2}J_{C\text{-}F}$ 37		
133.4	d	$^{1}J_{C\text{-}F}$ 240		c
	q	$^{2}J_{C\text{-}F}$ 39		
150.5	s			b
^{1}H				
1.1-1.75	m		10	e,f,g
1.29	t	$^{3}J_{H\text{-}H}$ 7.2	3	i
2.3	m		1	a
4.13	q	$^{3}J_{H\text{-}H}$ 7.2	2	h
	d	$^{5}J_{H\text{-}F}$ 5.6		
^{19}F				
-63.1	d	$^{3}J_{F\text{-}F}$ 8.6	3	d
-160.9	q	$^{3}J_{F\text{-}F}$ 8.6	1	c

29. (1Z)-1-Cyclohexyl-1-cyclohexyloxy-2,3,3,3-tetrafluoroprop-1-ene (40)



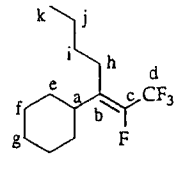
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
23.7	s			g
25.5	s			k
25.7	s			j
25.9	s			f
29.9	s			e
32.5	s			i
38.3	s			a
79.2	d	$^{4}J_{C\text{-}F}$ 11		h
121.4	q	$^{1}J_{C\text{-}F}$ 270		d
	d	$^{2}J_{C\text{-}F}$ 37		
132.1	d	$^{1}J_{C\text{-}F}$ 241		c
	q	$^{2}J_{C\text{-}F}$ 39		
151.0	s			b
^{1}H				
1.1-1.9	m		20	e,f,g,i,j,k
2.29	s		1	a
4.33	s		1	b
^{19}F				
-62.0	d	$^{3}J_{F\text{-}F}$ 9.4	3	d
-160.7	s		1	c

30. (2*E*)-3-Cyclohexyl-1,1,1,2-tetrafluorohept-2-ene (**41a**)



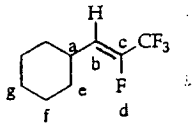
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
13.8	s			k
23.1	s			j
25.5	s			i
25.7	s			g
25.8	s			f
26.0	s			e
30.8	s			h
37.9	s			a
120.1	q	$^{1}J_{C\text{-}F}$ 273		d
	d	$^{2}J_{C\text{-}F}$ 44		
133.4	m			b
142.1	d	$^{1}J_{C\text{-}F}$ 248		c
	q	$^{2}J_{C\text{-}F}$ 38		
^{1}H				
0.85	t	$^{3}J_{H\text{-}H}$ 7.6	3	k
1.2-1.4	m		11	e,f,g_{ax}, h,i,j
1.7-2.2	m		5	e,f,g_{eq}
2.45	m		1	a
^{19}F				
-62.2	m		3	d
-131.0	m		1	c

31. (2*Z*)-3-Cyclohexyl-1,1,1,2-tetrafluorohept-2-ene (**41b**)



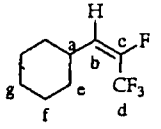
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{19}F				
-56.0	s		3	d
-104.0	s		1	c

32. (1*Z*)-1-Cyclohexyl-2,3,3,3-tetrafluoroprop-1-ene (45a)



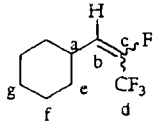
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{1}H				
5.40	d	$^{3}J_{H-F}$ 34	1	b
	d	$^{3}J_{H-H}$ 9.6		
^{19}F				
-73.3	d	$^{3}J_{F-F}$ 5.6	3	d
-138.3	q	$^{3}J_{F-F}$ 11	1	c

33. (1*E*)-1-Cyclohexyl-2,3,3,3-tetrafluoroprop-1-ene (45b)



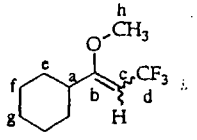
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{1}H				
5.52	d	$^{3}J_{H-F}$ 22	1	b
	d	$^{3}J_{H-H}$ 11		
^{19}F				
-68.1	d	$^{3}J_{F-F}$ 9	3	d
-131.2	q	$^{3}J_{F-F}$ 9.8	1	c

34. (1*E*) and (1*Z*)-1-Cyclohexyl-2,3,3,3-tetrafluoroprop-1-ene (45a) and (45b)



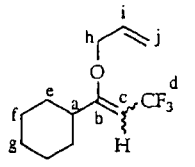
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
25.4	s			g
25.5	s			g
25.6	s			f
25.7	s			f
32.2	s			e
33.1	m			a
33.2	s			e
33.5	m			a
118.2	d	$^{2}J_{C-F}$ 8.8		b
	q	$^{3}J_{C-F}$ 3.0		
118.9	q	$^{1}J_{C-F}$ 269		d
	d	$^{2}J_{C-F}$ 63		
119.1	q	$^{1}J_{C-F}$ 269		d
	d	$^{2}J_{C-F}$ 59		
121.1	d	$^{2}J_{C-F}$ 13		b
	q	$^{3}J_{C-F}$ 2.6		
144.3	d	$^{1}J_{C-F}$ 248		c
	q	$^{2}J_{C-F}$ 39		
144.8	d	$^{1}J_{C-F}$ 253		c
	q	$^{2}J_{C-F}$ 38		
^{1}H				
1.2	m		5	e,f,g_{ax}
1.7	m		5	e,f,g_{eq}
2.4	m		1	a

35. 1-Cyclohexyl-1-methoxy-3,3,3-trifluoroprop-1-ene (46)



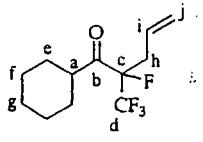
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
25.6	s			g
26.0	s			f
26.4	s			e
39.4	s			a
56.7	d	$^{5}J_{C\text{-}F}$ 1.2		h
95.2	q	$^{2}J_{C\text{-}F}$ 36		c
124.3	q	$^{1}J_{C\text{-}F}$ 269		d
171.0	q	$^{3}J_{C\text{-}F}$ 5.7		b
^{1}H				
1.1-1.2	m		5	e,f,g_{ax}
1.6-1.8	m		5	e,f,g_{eq}
2.1	m		1	a
3.1	s		1	c
3.6	s		3	h
^{19}F				
-55.8	d	$^{3}J_{F\text{-}H}$ 7.1	3	d

36. (1Z)-1-Cyclohexyl-3,3,3-trifluoro-1-prop-2-enyloxyprop-1-ene (51)



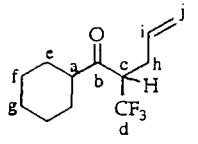
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
26.0	s			g
26.1	s			f
30.4	s			e
39.6	s			a
69.6	s			h
96.4	q	$^{2}J_{C\text{-}F}$ 34		c
117.5	s			j
124.2	q	$^{1}J_{C\text{-}F}$ 269		d
133.1	s			i
170.0	s			b
^{1}H				
1.1-1.2	m		5	e,f,g_{ax}
1.6-1.8	m		5	e,f,g_{eq}
2.1	m		1	a
4.3	m		2	h
4.74	q	$^{3}J_{H\text{-}F}$ 8.0	1	c
5.2	m		2	j
5.9	m		1	i
^{19}F				
-56.2	d	$^{2}J_{F\text{-}H}$ 7.1	3	d

37. 1-Cyclohexyl-2-fluoro-2-(trifluoromethyl)pent-4-en-1-one (48)



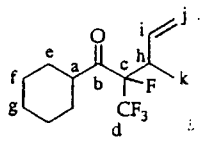
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
25.6	s			g
25.8	s			f
27.8	d	$^{4}J_{C-F}$ 7.8		e
35.8	d	$^{3}J_{C-F}$ 20		a
46.4				h
98.1	d	$^{1}J_{C-F}$ 202		c
	q	$^{2}J_{C-F}$ 29		
121.8	q	$^{1}J_{C-F}$ 286		d
	d	$^{2}J_{C-F}$ 29		
122.2	s			j
127.7	s			i
207.0	d	$^{2}J_{C-F}$ 27		b
^{1}H				
1.2-1.3	m		5	e,f,g_{ax}
1.6-1.8	m		5	e,f,g_{eq}
2.69	t	$^{3}J_{H-H}$ 14	1	a
	d	$^{4}J_{H-F}$ 6.8		
2.84	m		2	h
5.20	dm, AB	$^{3}J_{H-H\,trans}$ 9.6	1	j
5.23	m, AB		1	j
5.64	d	$^{3}J_{H-H\,trans}$ 9.6	1	i
	d	$^{3}J_{H-H\,cis}$ 7.6		
	t	$^{3}J_{H-H}$ 7.2		
^{19}F				
-77.6	d	$^{3}J_{F-F}$ 7.5	3	d
-181.5	dm	$^{3}J_{F-H}$ 35	1	c

38. 1-Cyclohexyl-2-(trifluoromethyl)pent-4-en-1-one (52)



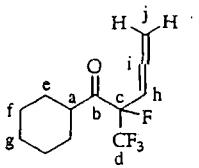
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
25.5	s			g
25.6	s			f
27.6	s			e
30.8	s			a
52.3	s			h
53.3	q	$^{2}J_{C-F}$ 25		c
118.8	s			j
124.8	q	$^{1}J_{C-F}$ 281		d
132.9	s			i
207.0	s			b
^{1}H				
1.1-1.3	m		5	e,f,g_{ax}
1.6-1.9	m		5	e,f,g_{eq}
2.45	m		2	h
2.6	m		1	a
3.5	m		1	c
5.1	m		2	j
5.7	d	$^{3}J_{H-H\,trans}$ 7.6	1	i
	t	$^{3}J_{H-H}$ 7.2		
	d	$^{3}J_{H-H\,cis}$ 6.8		
^{19}F				
-67.1	d	$^{3}J_{F-H}$ 8.6	3	d

39. 1-Cyclohexyl-2-fluoro-3-methyl-2-(trifluoromethyl)pent-4-en-1-one (49)



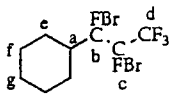
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assognment
^{13}C				
13.9	s			k major
14.8	s			k minor
25.7	s			g
27.2	s			f
28.3	s			e
41.2	d	$^{3}J_{C\text{-}F}$ 20		a minor
41.8	d	$^{3}J_{C\text{-}F}$ 20		a major
46.6	s			h, major
46.7	s			h, minor
99.95	d	$^{1}J_{C\text{-}F}$ 206		c, major
	q	$^{2}J_{C\text{-}F}$ 28		
100.0	d	$^{1}J_{C\text{-}F}$ 205		c, minor
	q	$^{2}J_{C\text{-}F}$ 28		
117.7	s			j minor
119.0	s			j major
121.8	q	$^{1}J_{C\text{-}F}$ 287		d minor
	d	$^{2}J_{C\text{-}F}$ 29		
121.9	q	$^{1}J_{C\text{-}F}$ 287		d major
	d	$^{2}J_{C\text{-}F}$ 30		
134.9	s			i, major
134.9	s			i, minor
208.0	d	$^{2}J_{C\text{-}F}$ 27		b, major
208.1	d	$^{2}J_{C\text{-}F}$ 27		b, minor
^{1}H				
1.0-1.2	m		3	k
1.0-1.4	m		5	e,f,g_{ax}
1.6-1.9	m		5	e,f,g_{eq}
2.75	m		1	h
3.0	d	$^{3}J_{C\text{-}F}$ 30	1	a
	m			
5.1	m		2	j
5.66	m		1	i major
5.78	m		1	i minor
^{19}F				
-68.5	s		3	d major
-68.9	q	$^{3}J_{F\text{-}F}$ 4.5	3	d minor
-185.3	s		1	c minor
-186.5	s		1	c major

40. 1-Cyclohexyl-2-fluoro-2-(trifluoromethyl)penta-3,4-dien-1-one (**50**)



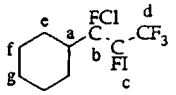
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
25.4	s			g
27.6	s			f
28.8	s			e
46.1	d	$^{3}J_{C\text{-}F}$ 26		a
81.0	s			j
85.1	d	$^{2}J_{C\text{-}F}$ 22		h
93.7	d	$^{1}J_{C\text{-}F}$ 203		c
	q	$^{2}J_{C\text{-}F}$ 30		
121.2	q	$^{1}J_{C\text{-}F}$ 286		d
	d	$^{2}J_{C\text{-}F}$ 30		
204.1	d	$^{2}J_{C\text{-}F}$ 26		b
209.0	d	$^{3}J_{C\text{-}F}$ 8.5		i
^{1}H				
1.1-1.4	m		5	e,f,g_{ax}
1.5-1.8	m		5	e,f,g_{eq}
2.92	m		1	a
5.15	m		2	j
5.41	d	$^{3}J_{H\text{-}F}$ 16	1	h
	t	$^{4}J_{H\text{-}H}$ 6.8		
^{19}F				
-77.8	d	$^{3}J_{F\text{-}F}$ 8.6	3	d
-172.5	m		1	c

41. 1,2-Dibromo-1-cyclohexyl-1,2,3,3,3-trifluoropropane (53)



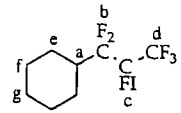
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
25.0	s			g major
25.1	s			g minor
25.2	s			f major
25.5	s			f minor
25.7	s			f major
25.7	s			f minor
27.2	d	$^{3}J_{C\text{-}F}$ 4.2		e major
27.9	t	$^{3}J_{C\text{-}F}$ 4.1		e minor
28.2	t	$^{3}J_{C\text{-}F}$ 4.6		c major
29.2	d	$^{3}J_{C\text{-}F}$ 4.0		e minor
47.2	d	$^{2}J_{C\text{-}F}$ 19		a minor
48.5	d	$^{2}J_{C\text{-}F}$ 18		a major
102.2	d	$^{1}J_{C\text{-}F}$ 275		c major
	quintet	$^{2}J_{C\text{-}F}$ 34		
104.4	d	$^{1}J_{C\text{-}F}$ 272		c minor
	quintet	$^{2}J_{C\text{-}F}$ 35		
111.0	d	$^{1}J_{C\text{-}F}$ 263		b major
	d	$^{2}J_{C\text{-}F}$ 26		
113.0	d	$^{1}J_{C\text{-}F}$ 264		b minor
	d	$^{2}J_{C\text{-}F}$ 27		
120.17	q	$^{1}J_{C\text{-}F}$ 287		d major
	d	$^{2}J_{C\text{-}F}$ 30		
	d	$^{3}J_{C\text{-}F}$ 1.5		
120.23	q	$^{1}J_{C\text{-}F}$ 287		d minor
	d	$^{2}J_{C\text{-}F}$ 30		
	d	$^{3}J_{C\text{-}F}$ 1.5		
^{1}H				
1.1-1.2	m		5	e,f,g_{ax}
1.6-1.8	m		5	e,f,g_{eq}
2.3	m		1	a
^{19}F				
-71.8	m		3	d major
-72.6	m		3	d minor
-104.8	m		1	c minor
-114.6	m		1	c major
-120.0	m		1	b major
-122.2	m		1	b minor

42. 1-Chloro-1-cyclohexyl-1,2,3,3,3-pentafluoro-2-iodopropane (55)



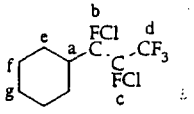
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
25.3	s			g
25.6	s			f
25.7	s			f
27.2	t	$^{3}J_{C\text{-}F}$ 5.0		e
28.2	t	$^{3}J_{C\text{-}F}$ 4.2		e
45.7	d	$^{2}J_{C\text{-}F}$ 21		a
	t	$^{3}J_{C\text{-}F}$ 1.5		
89.3	d	$^{1}J_{C\text{-}F}$ 268		c
	quintet	$^{2}J_{C\text{-}F}$ 34		
115.6	d	$^{1}J_{C\text{-}F}$ 255		b
	d	$^{2}J_{C\text{-}F}$ 25		
121.4	q	$^{1}J_{C\text{-}F}$ 286		d
	d	$^{2}J_{C\text{-}F}$ 28		
	d	$^{3}J_{C\text{-}F}$ 1.9		
^{1}H				
1.1-1.2	m		5	e,f,g_{ax}
1.6-1.8	m		5	e,f,g_{eq}
2.2	t	$^{3}J_{H\text{-}Hax}$ 7.6	1	a
	d	$^{3}J_{H\text{-}F}$ 6.8		
	t	$^{3}J_{H\text{-}Heq}$ 3.2		
^{19}F				
-70.8	d	$^{3}J_{F\text{-}F}$ 12	3	d
	d	$^{4}J_{F\text{-}F}$ 12		
-101.8	d	$^{3}J_{F\text{-}F}$ 32	1	b
	m			
-128.9	d	$^{3}J_{F\text{-}F}$ 36	1	c
	q	$^{3}J_{F\text{-}F}$ 13		
	d	$^{4}J_{F\text{-}H}$ 4.5		

43. 1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (58)



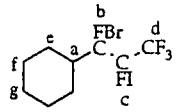
Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
25.4	s			g
25.5	s			f
25.6	s			e
42.7	t	$^{2}J_{C\text{-}F}$ 22		a
83.3	d	$^{1}J_{C\text{-}F}$ 270		c
	sextet	$^{2}J_{C\text{-}F}$ 38		
118.9	t	$^{1}J_{C\text{-}F}$ 256		b
	d	$^{2}J_{C\text{-}F}$ 24		
120.9	q	$^{1}J_{C\text{-}F}$ 285		d
	d	$^{2}J_{C\text{-}F}$ 29		
^{1}H				
1.2-1.4	m		5	e,f,g_{ax}
1.7-2.0	m		5	e,f,g_{eq}
2.4	m		1	a
^{19}F				
-73.2	m		3	d
-107.0 and -108.5	AB	$^{2}J_{A\text{-}B}$ 267	2	b
-140.1	sextet	$^{3}J_{F\text{-}F}$ 16	1	c

44. 1,2-Dichloro-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (56)



Chemical Shift	Multiplcity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
25.2	s			g
25.3	s			g
25.3	s			f
25.5	s			f
25.6	s			f
25.7	s			f
26.9	s			e
26.9	s			e
27.0	s			e
27.1	s			e
46.2	d	$^{2}J_{C-F}$ 20		a major
46.5	d	$^{2}J_{C-F}$ 20		a minor
106.6	d	$^{1}J_{C-F}$ 267		c major
	quint	$^{2}J_{C-F}$ 35		
107.8	d	$^{1}J_{C-F}$ 262		c minor
	quint	$^{2}J_{C-F}$ 37		
114.4	d	$^{1}J_{C-F}$ 255		b minor
	d	$^{2}J_{C-F}$ 11		
114.6	d	$^{1}J_{C-F}$ 257		b major
	d	$^{2}J_{C-F}$ 17		
120.1	q	$^{1}J_{C-F}$ 288		d minor
	d	$^{2}J_{C-F}$ 32		
120.3	q	$^{1}J_{C-F}$ 288		d major
	d	$^{2}J_{C-F}$ 31		
^{1}H				
1.1-1.2	m		5	e,f,g_{ax}
1.6-1.8	m		5	e,f,g_{eq}
2.3	m		1	a major
2.5	t	$^{3}J_{H-Hax}$ 7.6	1	a minor
	d	$^{3}J_{H-F}$ 6.8		
	t	$^{3}J_{H-Heq}$ 3.2		
^{19}F				
-74.8	d	$^{3}J_{F-F}$ 14	3	d minor
	d	$^{4}J_{F-F}$ 15		
-75.3	d	$^{3}J_{F-F}$ 12	3	d major
	d	$^{4}J_{F-F}$ 12		
-112.4	q	$^{3}J_{F-F}$ 12	1	c major
-116.8	m		1	c minor
-123.5	m		1	b major
-125.0	m		1	b minor

45. 1-Bromo-1-cyclohexyl-1,2,3,3,3-pentafluoro-2-iodopropane (57)



Chemical Shift	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
^{13}C				
25.0	s			g minor
25.2	s			g major
25.2	s			f minor
25.6	s			f major
25.7	s			f minor
25.7	s			f major
27.2	d	$^{3}J_{C\text{-}F}$ 4.1		e minor
28.0	t	$^{3}J_{C\text{-}F}$ 4.5		e minor
28.2	t	$^{3}J_{C\text{-}F}$ 4.6		e major
29.2	d	$^{3}J_{C\text{-}F}$ 4.2		e major
47.2	d	$^{2}J_{C\text{-}F}$ 19		a major
48.5	d	$^{2}J_{C\text{-}F}$ 18		a minor
104.2	d	$^{1}J_{C\text{-}F}$ 272		c major
	quint	$^{2}J_{C\text{-}F}$ 35		
113.0	d	$^{1}J_{C\text{-}F}$ 264		b major
	d	$^{2}J_{C\text{-}F}$ 27		
120.2	q	$^{1}J_{C\text{-}F}$ 287		d major
	d	$^{2}J_{C\text{-}F}$ 31		
^{1}H				
1.1-1.2	m		5	e,f,g_{ax}
1.6-1.8	m		6	e,f,g_{eq} and a
2.4	t	$^{3}J_{H\text{-}Hax}$ 11	1	a minor
	d	$^{3}J_{H\text{-}F}$ 7.6		
	t	$^{3}J_{H\text{-}Heq}$ 3.2		
^{19}F				
-71.7	m		3	d minor
-72.5	m		3	d major
-104.8	d	$^{3}J_{F\text{-}F}$ 30	1	b major
	m			
-114.6	m		1	b minor
-120.0	m		1	c minor
-122.2	m		1	c major

B. Mass Spectra

Chapter 2

1. 1-Cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**)
2. 1,1,2,3,3,3-Hexafluoro-1-[x-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl]propane (x=2,3,4) (**9**)
3. 1,1,2,3,3,3-Hexafluoro-1-[*trans*-4-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl]propane (**9a**)
4. 1-Cyclohexyl-1,1,3,3,3-pentafluoropropane (**12**)
5. 1,1,3,3,3-pentafluoro-1-[x-(1,1,3,3,3-pentafluoropropyl)cyclohexyl]propane (x=2,3,4) (**13**)
6. 1,1,3,3,3-Pentafluoro-1-[*trans*-4-(1,1,3,3,3-pentafluoropropyl)cyclohexyl]propane (**13a**)

Chapter 3

7. 2-Cyclohexyl-1,1-difluoroethane (**18**)
8. 1-Cyclohexyl-1,1-difluoroethane (**19**)
9. 2-Chloro-1-cyclohexyl-1,1,2-trifluoroethane (**20**)
10. 2,2-Dichloro-1-cyclohexyl-1,1-difluoroethane (**21**)
11. 2-Chloro-1-cyclohexyl-1,1-difluoroethane (**23**)
12. 2-Bromo-1-cyclohexyl-1,1,2-trifluoroethane (**26**)
13. 2-Bromo-1-cyclohexyl-1,1-difluoroethane (**28**)

Chapter 4

14. (1*Z*)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**)
15. (1*Z*)-1-Cyclohexyl-1,3,3,3-tetrafluoroprop-1-ene (**34**)
16. (1*E*)-2-Chloro-1-cyclohexyl-1,2-difluoroethene (**35a**)
17. (1*Z*)-2-Chloro-1-cyclohexyl-1,2-difluoroethene (**35b**)
18. (1*Z*)-2,2-Dichloro-1-cyclohexyl-1-fluoroethene (**36**)
19. (1*Z*)-2-Bromo-1-cyclohexyl-1-fluoroethene (**37**)
20. (1*Z*)-2-Chloro-1-cyclohexyl-1-fluoroethene (**38**)

Chapter 5

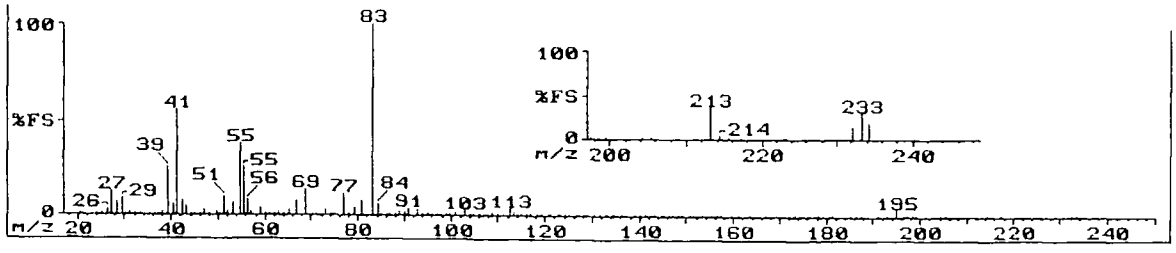
21. (1*Z*)-1-Cyclohexyl-1-methoxy-2,3,3,3-tetrafluoroprop-1-ene (**39a**)
22. (1*Z*)-1-Cyclohexyl-1-ethoxy-2,3,3,3-tetrafluoroprop-1-ene (**33**)
23. (1*Z*)-1-Cyclohexyl-1-cyclohexyloxy-2,3,3,3-tetrafluoroprop-1-ene (**40**)
24. (2*E*)-3-Cyclohexyl-1,1,1,2-tetrafluorohept-2-ene (**41a**)
25. (1*Z*) and (1*E*)-1-Cyclohexyl-2,3,3,3-tetrafluoroprop-1-ene (**45a**) and (**45b**)
26. (1*Z*) and (1*E*)-1-Cyclohexyl-1-methoxy-3,3,3-trifluoroprop-1-ene (**46**)
27. 1-Cyclohexyl-2-fluoro-2-(trifluoromethyl)pent-4-en-1-one (**48**)

28. 1-Cyclohexyl-2-fluoro-3-methyl-2-(trifluoromethyl)pent-4-en-1-one (**49**)
29. 1-Cyclohexyl-2-fluoro-2-(trifluoromethyl)penta-3,4-dien-1-one (**50**)
30. 1-Cyclohexyl-2-(trifluoromethyl)pent-4-en-1-one (**52**)

Chapter 6

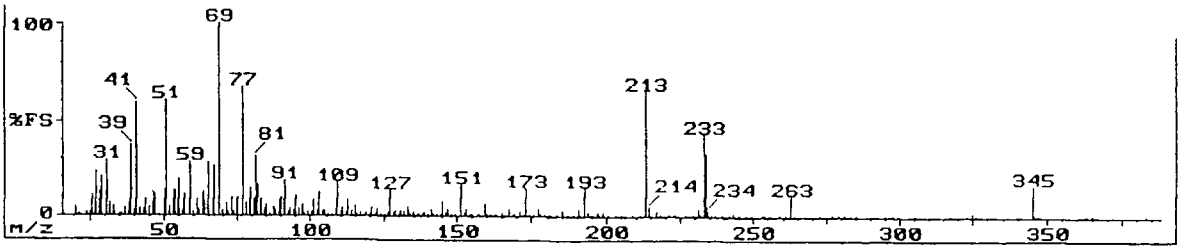
31. 1,2-Dibromo-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (**53**)
32. 1-Chloro-1-cyclohexyl-1,2,3,3,3-pentafluoro-2-iodopropane (**55**)
33. 1,2-Dichloro-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (**56**)
34. 1-Bromo-1-cyclohexyl-1,2,3,3,3-pentafluoro-2-iodopropane (**57**)
35. 1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**58**)

1. 1-Cyclohexyl-1,1,2,3,3,3-hexafluoropropane (8)



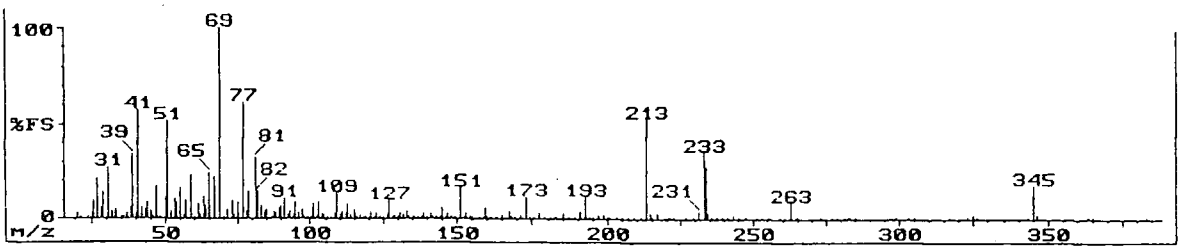
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.45	65	3.30	114	0.56	155	0.25
24	0.23	67	7.70	115	0.92	156	0.03
25	0.62	69	13.50	116	0.13	157	0.05
26	3.23	70	0.34	117	0.20	159	0.10
27	12.30	71	1.18	118	0.18	161	0.02
28	7.00	73	2.78	119	0.11	163	0.03
29	8.80	74	0.38	121	0.46	165	0.05
30	0.35	75	1.34	121	0.19	167	0.25
31	2.00	77	11.40	123	0.23	169	0.01
32	0.37	78	1.14	123	0.12	172	0.30
33	0.64	79	3.68	124	0.04	173	0.42
35	0.04	81	7.60	125	0.06	174	0.06
36	0.08	83	100.00	127	0.98	175	0.10
37	0.94	84	6.20	127	0.48	176	0.02
38	2.33	85	1.33	128	0.13	177	0.03
39	25.50	86	0.19	129	0.21	178	0.01
40	5.70	87	0.43	130	0.30	179	0.02
41	55.20	88	0.50	131	0.34	180	0.01
42	7.80	89	1.48	133	0.69	181	0.01
43	4.70	90	1.88	133	0.37	185	0.05
44	1.06	91	3.45	134	0.06	186	0.01
45	0.63	93	2.75	135	0.16	187	0.01
46	0.63	94	0.66	136	0.03	191	0.06
47	2.75	95	1.75	137	0.05	193	0.19
48	0.16	96	0.61	139	0.26	195	3.40
50	1.63	97	1.16	140	0.07	196	0.22
50	1.35	98	0.21	141	0.09	197	0.02
51	9.50	99	0.15	142	0.02	198	0.01
52	1.90	100	0.34	143	0.02	199	0.02
53	7.00	101	1.73	145	0.42	204	0.02
55	38.00	103	3.13	145	0.27	205	0.01
55	25.60	104	0.71	146	0.05	213	0.70
56	7.80	105	0.48	147	0.19	214	0.10
57	1.63	106	0.10	148	0.03	215	0.02
59	3.83	107	0.26	149	0.12	217	0.02
60	0.25	109	2.25	151	1.13	232	0.28
61	0.76	110	0.23	151	0.57	233	0.56
62	0.37	111	0.41	152	0.06	234	0.35
63	1.59	113	3.43	153	0.08		
64	1.32	113	2.15	155	0.21		

2. 1,1,2,3,3,3-Hexafluoro-1-[x-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl]propane (x=2,3,4) (9)



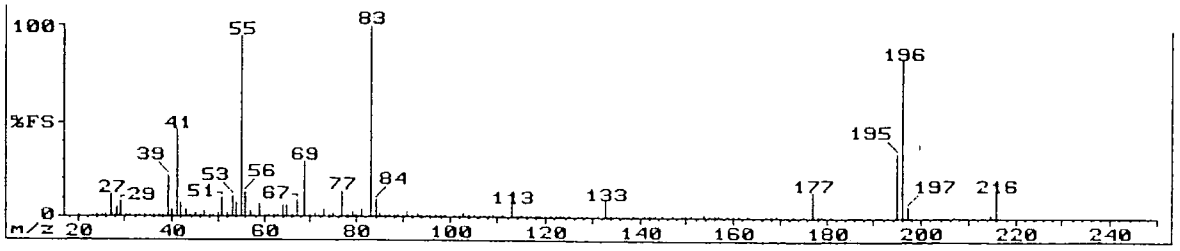
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	4.53	83	8.45	137	0.45	214	5.15
21	0.08	84	3.72	138	0.28	217	3.28
24	1.54	85	5.63	139	2.05	218	0.28
25	1.91	86	0.78	140	1.41	221	0.52
26	10.65	87	4.73	141	3.61	221	0.25
27	22.89	88	3.17	142	0.65	223	1.14
28	12.24	89	7.57	143	0.62	223	1.00
29	20.51	90	9.86	144	1.19	227	0.37
31	28.87	91	18.49	145	8.10	229	0.32
32	6.43	92	2.22	146	1.61	231	4.01
33	4.97	93	4.07	147	4.03	232	0.52
35	0.23	94	2.44	148	0.48	233	42.96
36	0.22	95	10.39	149	1.06	233	33.10
37	3.68	96	3.70	151	16.29	234	3.19
38	6.60	97	5.99	152	1.47	235	0.41
39	37.32	98	1.12	153	3.61	237	0.11
40	2.55	99	1.47	154	0.59	239	0.20
41	59.15	100	2.29	155	0.75	241	0.31
42	3.46	101	8.80	156	0.09	243	2.33
43	3.90	102	3.32	157	0.64	245	0.08
44	8.89	103	12.15	159	6.95	247	0.13
45	4.64	104	2.84	160	0.71	249	0.18
47	12.50	105	2.75	161	0.56	253	0.22
47	11.44	106	0.57	162	0.21	253	0.17
48	0.55	107	1.01	163	1.10	255	0.08
50	13.82	108	3.43	165	1.89	259	0.26
51	60.21	109	17.52	167	4.29	259	0.20
52	4.69	110	2.66	168	0.47	261	0.46
53	13.47	111	4.64	169	1.02	263	11.00
54	13.29	112	2.02	171	2.95	264	0.98
55	19.10	113	8.63	172	1.40	273	0.11
56	2.75	114	2.77	173	14.35	277	0.07
57	11.36	115	5.44	174	1.20	279	0.24
59	28.52	116	1.24	175	0.35	279	0.19
60	1.56	117	2.13	177	3.57	281	0.24
61	8.71	118	0.22	178	0.22	281	0.16
62	2.55	119	1.52	179	1.00	283	0.42
63	12.94	120	1.03	181	0.43	285	0.43
64	8.19	121	5.11	183	0.95	295	0.13
65	28.17	122	1.45	185	3.13	297	0.10
67	26.41	123	3.70	187	0.34	299	0.22
69	100.00	124	0.77	189	0.39	305	0.63
70	3.15	125	1.07	191	4.31	317	0.13
71	6.69	126	2.11	193	14.44	323	0.16
72	1.80	127	13.82	194	1.56	325	1.98
73	10.04	128	1.65	195	0.69	326	0.25
74	2.00	129	2.53	197	2.16	345	16.90
75	9.77	130	0.58	199	2.38	346	0.74
77	66.55	131	3.13	201	0.24	347	0.13
78	6.43	132	2.95	203	1.34	363	0.51
79	14.26	133	5.06	205	1.39	365	0.42
80	8.71	134	0.93	209	0.75	383	0.26
81	30.99	135	1.47	211	0.80		
82	16.29	136	0.22	213	65.14		

3. 1,1,2,3,3,3-Hexafluoro-1-[*trans*-4-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl]propane (**9a**)



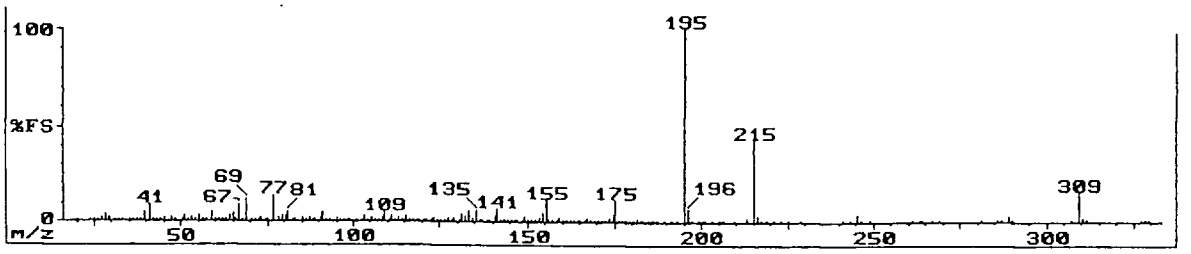
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	3.30	84	3.42	137	0.37	213	52.19
21	0.18	85	4.92	138	0.49	214	2.62
24	1.41	86	0.61	139	2.46	215	0.66
25	2.75	87	3.65	140	0.91	217	2.68
26	9.69	88	2.75	141	3.13	219	0.35
27	21.25	89	5.70	142	0.60	221	0.60
28	5.86	90	7.19	143	0.55	221	0.48
29	15.00	91	11.09	144	1.06	223	0.98
31	27.50	92	1.82	145	6.02	227	0.23
32	3.85	93	3.73	146	1.24	229	0.24
33	4.80	94	2.30	147	3.16	231	4.30
35	0.18	95	9.22	148	0.25	233	35.31
36	0.38	96	3.16	149	0.88	233	27.50
37	3.24	97	5.16	151	16.88	234	2.95
38	5.86	98	0.94	152	1.25	235	0.36
39	34.38	99	1.41	153	3.09	237	0.30
40	2.97	100	1.37	154	0.50	239	0.31
41	57.50	101	7.34	155	0.66	241	0.66
42	5.94	102	1.41	157	0.65	243	2.07
43	4.47	103	9.06	158	1.02	245	0.29
44	8.44	104	2.56	159	5.86	247	0.10
45	3.93	105	1.48	160	0.58	251	0.06
46	1.18	106	0.42	161	0.53	253	0.21
47	17.66	107	0.92	163	1.06	255	0.21
48	0.69	108	2.60	165	1.54	259	0.27
50	12.03	109	13.52	167	3.42	259	0.21
51	51.56	110	2.25	168	0.17	261	0.55
52	4.04	111	4.00	169	0.87	263	9.06
53	10.47	112	2.83	171	2.30	264	0.41
54	8.83	113	7.42	173	11.25	265	0.15
55	16.80	114	2.27	174	1.05	273	0.09
56	1.46	115	4.61	175	0.41	277	0.06
57	9.69	116	1.02	177	3.07	279	0.47
59	23.13	117	1.58	179	1.05	281	0.27
60	1.17	118	0.39	181	0.64	283	0.35
61	8.05	119	1.43	182	0.17	283	0.22
62	2.34	120	0.87	183	1.12	285	0.49
63	11.72	121	3.79	185	2.50	297	0.16
64	6.88	122	0.94	187	0.30	299	0.15
65	24.06	123	3.11	189	0.59	303	0.18
67	21.88	124	0.65	191	3.61	305	0.63
69	100.00	125	1.02	193	11.41	317	0.12
70	1.17	126	1.68	194	1.23	323	0.18
71	4.53	127	10.16	195	1.09	325	1.95
73	9.61	128	1.33	197	1.72	326	0.15
74	1.88	129	2.19	199	1.95	343	0.18
75	8.98	130	0.83	200	0.10	345	17.58
77	60.94	131	2.56	201	0.75	346	1.80
78	4.08	132	2.25	203	1.18	363	0.81
79	14.14	133	4.16	205	1.10	364	0.12
81	32.50	134	0.73	207	0.11	365	0.51
82	15.00	135	1.23	209	0.65	383	0.16
83	6.64	136	0.15	211	1.07		

4. 1-Cyclohexyl-1,1,3,3,3-pentafluoropropane (**12**)



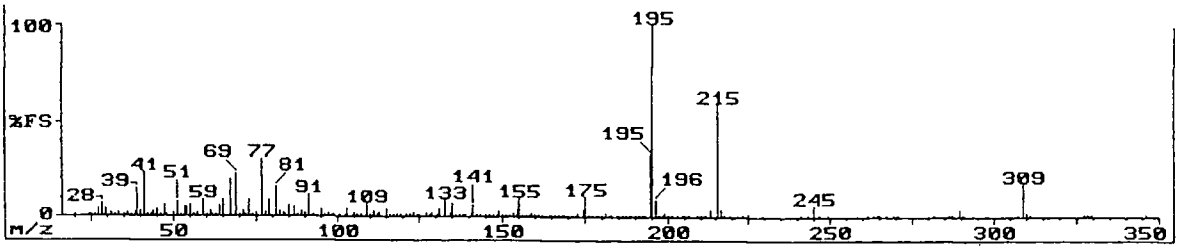
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.02	58	0.31	96	0.35	137	0.97
24	0.01	59	6.67	97	0.87	139	0.24
25	0.03	60	0.46	98	0.14	141	1.13
26	1.21	61	0.74	99	0.25	142	0.09
27	11.43	62	0.28	101	0.95	143	0.03
28	5.16	63	1.28	102	0.24	145	0.16
29	8.07	64	6.11	103	1.65	147	0.06
30	0.21	65	5.41	104	0.37	149	0.44
31	0.43	66	1.04	105	0.55	150	0.04
32	0.25	67	8.97	106	0.04	151	0.09
33	0.98	69	28.70	107	0.16	154	2.07
34	0.02	70	0.77	108	0.20	155	0.95
35	0.01	71	1.66	109	1.02	156	0.06
36	0.07	72	0.71	110	0.20	157	0.33
37	0.21	73	3.53	111	0.60	159	0.09
38	0.99	74	0.14	113	6.92	160	0.02
39	21.52	75	1.46	114	0.66	161	0.04
40	3.70	77	13.45	115	1.27	163	0.01
41	45.29	78	1.07	116	0.13	167	0.15
42	6.75	79	3.17	117	0.46	168	0.07
43	3.95	80	0.57	118	0.05	169	0.03
44	0.43	81	4.23	119	0.20	173	0.10
45	1.93	83	100.00	120	0.06	175	0.31
46	0.62	84	8.74	121	0.34	177	14.01
47	2.49	85	1.74	122	0.12	178	1.13
48	0.07	86	0.21	123	0.47	179	0.07
49	0.08	87	0.43	124	0.03	181	0.07
50	1.77	88	0.30	125	0.08	186	0.04
51	9.64	89	1.09	127	1.09	195	1.33
52	2.27	90	1.10	128	0.09	196	3.22
53	10.31	91	3.11	129	0.30	197	0.24
54	8.07	92	0.25	131	0.29	207	0.02
55	93.72	93	1.72	133	8.97	215	0.07
56	12.33	94	0.28	134	0.20	216	0.55
57	2.66	95	1.38	135	0.64		

5. 1,1,3,3,3-pentafluoro-1-[x-(1,1,3,3,3-pentafluoropropyl)cyclohexyl]propane (x=2,3,4) (**13**)



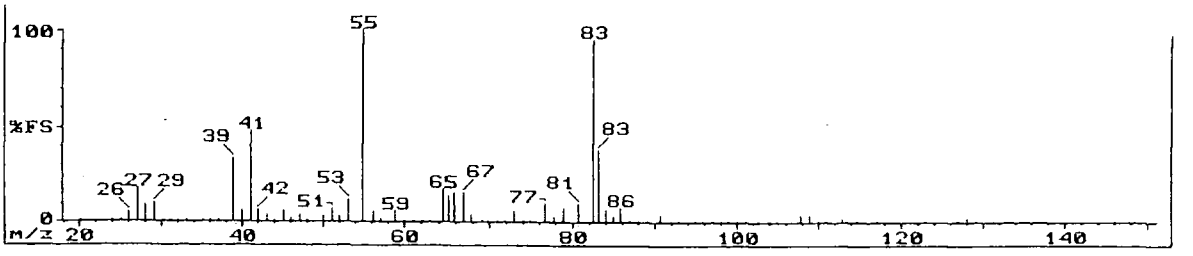
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.05	81	2.78	133	5.79	183	0.28
24	0.07	81	5.02	134	2.03	185	0.19
25	0.16	82	1.06	135	5.94	185	0.33
26	0.77	83	1.09	136	0.73	186	0.28
27	2.16	85	2.26	137	0.50	187	0.18
28	3.86	86	0.63	138	0.32	189	0.08
29	1.81	87	1.81	139	0.81	191	0.26
31	1.02	88	0.45	140	2.87	193	1.31
32	0.96	89	1.27	141	6.48	195	100.00
33	0.72	90	2.22	142	0.50	196	7.02
35	0.47	91	4.84	143	0.11	197	0.57
36	0.67	92	0.41	144	0.22	199	0.78
37	0.43	93	0.33	145	0.73	200	0.26
38	0.56	95	1.64	146	0.36	201	0.13
39	5.02	96	0.53	147	0.79	203	0.59
41	8.95	97	1.43	148	1.10	205	1.16
42	0.71	98	0.29	149	3.20	206	0.15
43	0.43	99	0.33	150	0.59	209	0.08
44	1.16	101	0.82	151	0.86	213	1.91
45	1.52	102	0.96	152	0.71	215	42.90
47	1.89	103	2.51	153	1.81	216	2.99
48	0.08	104	0.91	154	4.53	217	0.35
50	0.43	105	1.60	155	11.88	219	0.17
51	3.14	106	0.29	156	1.02	221	0.09
52	0.52	107	0.30	157	0.20	223	0.67
53	2.22	108	1.87	158	0.88	225	0.83
54	1.13	109	5.17	159	2.06	229	0.14
55	2.99	110	1.29	160	0.55	241	0.11
56	0.31	111	2.62	161	1.11	243	0.23
57	0.90	112	1.11	162	0.23	245	3.51
59	4.61	113	1.91	163	0.19	246	0.46
60	0.41	114	1.22	164	0.18	249	0.41
61	1.22	115	3.03	165	0.41	261	0.11
62	0.08	116	0.63	166	0.69	263	0.33
63	0.98	117	1.03	167	1.68	264	0.09
64	2.99	118	0.17	168	0.36	267	0.21
65	4.24	119	0.25	169	0.32	269	0.79
66	0.28	120	0.34	171	0.16	281	0.10
67	8.80	121	0.80	171	0.33	286	0.17
68	0.34	122	0.89	172	0.72	287	0.16
69	11.50	123	1.93	173	2.01	289	2.89
70	0.56	124	0.26	175	4.28	290	0.23
71	0.78	125	0.24	175	11.19	307	0.25
73	1.33	127	0.95	176	1.35	309	15.12
73	2.33	127	2.41	177	0.54	310	1.76
74	0.56	128	1.06	178	0.36	311	0.07
75	0.61	129	1.76	179	1.01	327	0.82
77	13.27	130	1.25	180	0.70	328	0.24
78	2.24	131	3.57	181	1.70	329	0.06
79	3.03	132	2.68	182	0.21		

6. 1,1,3,3,3-Pentafluoro-1-[*trans*-4-(1,1,3,3,3-pentafluoropropyl)cyclohexyl]propane (**13a**)



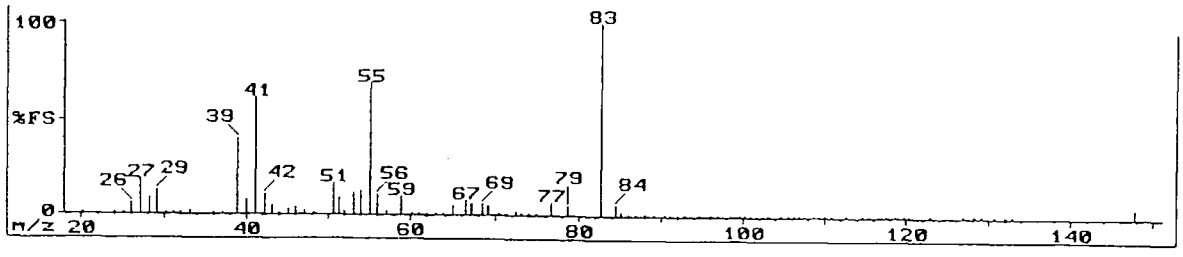
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.29	82	2.54	143	0.11	195	100.00
24	0.08	83	1.83	145	0.55	196	9.16
25	0.34	84	1.05	146	0.24	197	0.63
26	1.42	85	6.00	147	0.71	198	0.71
27	4.33	87	4.76	148	0.88	199	2.41
28	6.44	88	0.78	149	2.65	200	0.26
29	4.21	89	2.88	150	0.43	201	0.12
31	1.79	90	2.04	151	0.62	203	0.30
32	1.31	91	11.51	152	0.53	204	0.45
33	1.62	92	0.58	153	1.59	205	1.30
35	0.72	93	0.72	154	4.08	206	0.18
36	1.98	95	3.43	155	10.09	209	0.10
37	0.96	96	0.87	156	0.89	210	0.03
38	2.20	97	2.31	157	0.11	211	0.09
39	14.11	98	0.31	158	0.67	213	3.85
40	2.89	99	0.36	159	1.59	215	59.16
41	23.27	101	1.35	160	0.39	216	4.08
42	1.42	103	3.62	161	0.68	217	0.27
43	1.22	105	2.26	162	0.10	219	0.29
44	2.57	106	0.21	163	0.09	221	0.06
45	4.33	107	0.31	164	0.14	223	0.37
46	0.76	109	7.12	165	0.32	225	1.69
47	5.69	110	0.70	166	0.53	229	0.08
48	0.10	111	3.20	167	1.25	241	0.16
50	2.07	112	0.60	168	0.26	243	0.43
51	7.30	113	2.27	169	0.21	245	5.57
52	1.41	115	4.21	170	0.12	246	0.48
53	5.14	116	0.36	171	0.28	249	0.24
54	4.46	117	1.31	172	0.59	261	0.12
55	5.82	118	0.14	173	1.55	263	0.33
56	0.32	119	0.24	174	4.27	264	0.06
57	1.72	121	0.68	175	11.08	265	0.31
59	9.03	122	0.67	176	1.33	267	0.15
60	0.53	123	1.52	177	0.43	269	0.43
61	2.44	124	0.17	178	0.48	270	0.11
62	0.38	125	0.26	179	1.07	281	0.05
63	1.41	127	2.37	180	0.88	286	0.04
64	6.19	128	0.75	181	1.70	287	0.12
65	8.85	129	1.69	182	0.20	289	3.57
67	19.06	131	1.10	183	0.22	290	0.29
69	22.03	131	4.08	184	0.25	307	0.22
70	0.97	133	9.22	185	0.73	309	17.08
71	2.51	134	2.18	186	0.28	310	1.78
72	0.91	135	6.99	187	0.33	311	0.11
73	8.85	136	0.77	188	0.07	327	1.11
74	0.73	137	0.53	189	0.09	328	0.35
75	2.04	138	0.21	190	0.12	329	0.12
77	29.70	139	0.72	191	0.31	346	0.06
78	2.13	140	2.13	192	0.46		
79	8.91	141	6.19	193	1.16		
81	15.47	142	0.41	195	33.42		

7. 2-Cyclohexyl-1,1-difluoroethane (**18**)



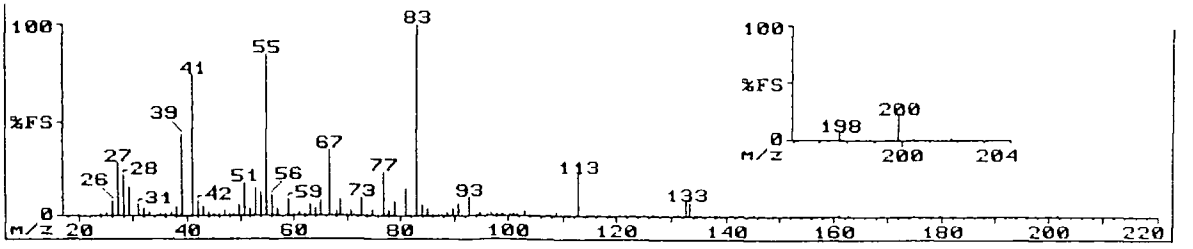
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.17	48	0.16	74	0.52	100	0.33
24	0.30	50	2.71	75	0.66	101	0.12
25	0.90	51	7.17	77	9.50	103	0.61
26	5.04	52	2.46	78	3.17	104	0.14
27	17.00	53	11.67	79	7.67	105	0.44
28	8.79	55	100.00	81	9.54	108	3.42
29	10.04	56	5.42	83	94.67	109	3.83
30	0.28	57	1.47	83	37.83	110	0.39
31	0.91	59	6.21	84	6.38	111	0.24
32	0.86	60	0.97	85	3.38	113	1.78
33	1.36	61	1.06	86	7.83	114	0.14
35	0.02	62	0.28	87	1.19	115	0.04
36	0.21	63	1.39	88	0.09	117	0.03
37	1.23	65	17.50	89	0.13	118	0.04
39	32.67	65	13.83	91	3.62	123	0.03
40	5.92	66	15.67	92	0.45	127	1.29
41	47.33	67	15.50	93	1.40	128	1.77
42	6.17	68	4.21	94	0.10	129	0.39
43	3.46	69	0.92	95	0.40	133	0.12
44	1.44	70	0.47	96	0.30	146	0.06
45	5.71	71	1.45	97	0.71	148	0.30
46	1.57	72	1.42	98	0.17	148	0.16
47	4.17	73	5.96	99	0.51		

8. 1-Cyclohexyl-1,1-difluoroethane (**19**)



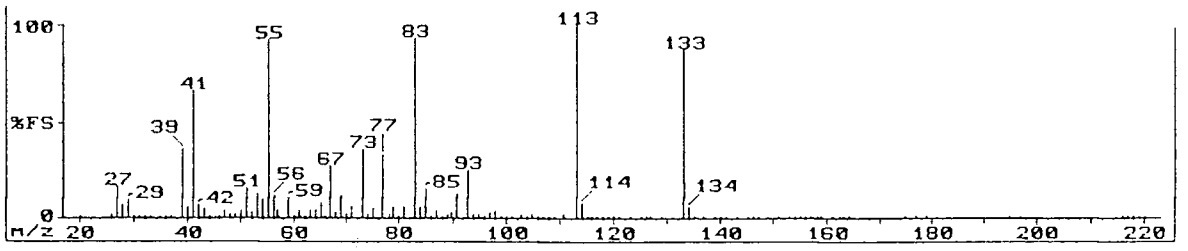
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.19	51	8.33	77	5.76	105	0.24
24	0.33	52	2.40	79	5.12	107	0.33
25	0.94	53	11.27	83	100.00	109	0.66
26	5.88	54	12.16	84	5.74	109	0.32
27	18.73	55	68.63	85	1.91	110	0.09
28	8.33	56	10.39	86	0.64	111	0.04
29	12.55	57	1.56	87	0.70	113	0.08
30	0.20	59	10.00	88	0.06	115	0.04
31	0.94	60	0.70	89	0.12	118	0.18
32	0.70	61	0.75	91	0.99	119	0.21
33	1.57	62	0.36	91	0.64	120	0.38
36	0.22	63	0.94	92	1.08	120	0.11
37	1.35	64	1.45	93	0.37	123	0.01
39	40.00	65	4.61	95	0.64	127	0.67
40	7.84	67	7.84	96	0.24	128	0.08
41	61.57	67	6.27	97	0.62	129	0.08
42	10.59	69	6.27	99	0.53	131	0.08
43	4.39	69	4.56	99	0.45	132	0.01
44	1.11	70	0.92	100	0.11	133	0.01
45	2.70	71	1.07	101	0.14	148	4.88
46	4.02	73	1.79	103	0.35	149	0.21
47	2.40	73	1.18	103	0.19		
48	0.09	74	0.45	105	0.48		
51	16.08	75	0.35	105	0.59		

9. 2-Chloro-1-cyclohexyl-1,1,2-trifluoroethane (**20**)



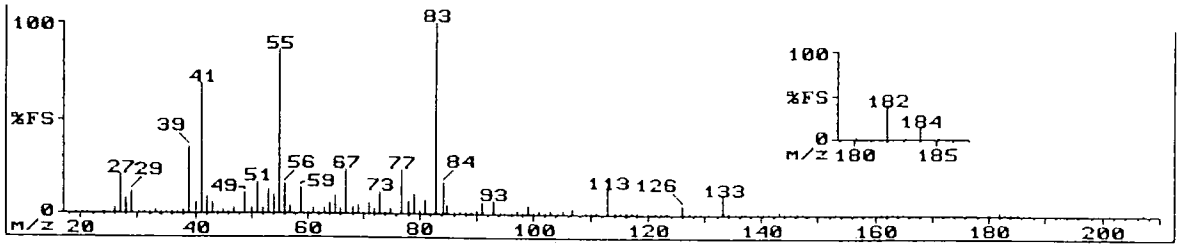
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.55	54	12.17	88	0.47	119	0.21
24	0.54	55	84.13	89	2.22	121	0.10
25	1.55	56	10.58	90	3.47	121	0.12
26	8.07	57	3.94	91	6.81	123	0.27
27	28.31	59	9.13	93	9.79	123	0.24
28	21.43	60	0.66	94	0.47	125	0.58
29	15.61	61	1.82	95	1.88	127	0.24
31	5.49	62	1.12	96	0.26	127	0.17
32	3.70	63	5.36	97	2.07	129	0.06
33	2.01	64	3.90	98	1.03	129	0.07
35	1.00	65	7.51	99	0.61	131	0.75
36	1.25	67	34.92	100	0.16	131	0.97
37	2.25	68	2.81	101	0.73	133	7.64
38	4.99	69	9.13	102	0.16	133	6.61
39	42.86	70	1.40	103	2.68	134	0.43
41	73.54	71	3.21	104	0.51	138	0.10
42	8.20	73	9.52	105	0.96	141	0.11
43	5.16	74	0.86	106	0.08	143	0.10
44	2.04	75	2.98	107	0.25	143	0.09
45	1.36	77	22.88	108	0.09	145	0.25
46	1.14	78	2.48	109	1.50	145	0.19
47	3.34	79	8.10	110	0.07	161	0.03
48	0.78	81	14.81	111	0.64	163	0.13
49	1.35	83	100.00	111	0.51	180	0.18
50	5.36	84	5.72	113	22.75	182	0.07
51	17.59	85	3.47	114	1.22	198	0.25
52	3.74	86	0.38	115	0.47	200	0.84
53	14.15	87	1.04	117	0.77	202	0.16

10. 2,2-Dichloro-1-cyclohexyl-1,1-difluoroethane (**21**)



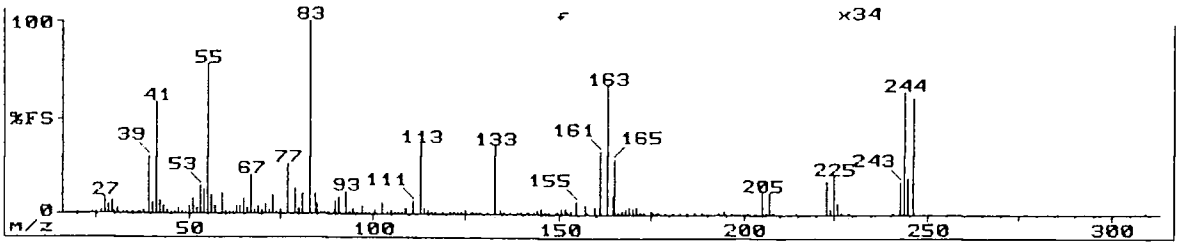
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.01	60	0.74	96	0.66	139	0.28
26	2.10	61	3.67	97	2.46	140	0.03
27	16.20	62	1.23	98	4.11	141	0.78
28	6.79	63	3.60	99	1.05	143	0.58
29	9.57	64	4.27	100	1.40	145	0.16
30	0.22	65	8.16	101	1.23	146	0.03
31	0.69	66	1.30	103	2.23	147	0.04
32	0.18	67	27.55	104	0.52	149	0.02
33	0.68	68	3.25	105	2.33	151	0.05
35	0.64	69	11.61	106	1.04	153	0.06
36	0.46	70	1.71	107	0.49	154	0.04
37	0.77	71	5.64	108	0.36	155	0.08
39	36.22	73	35.71	109	1.16	156	0.04
40	6.03	74	2.10	111	1.49	157	0.06
41	65.82	75	4.97	113	100.00	158	0.04
42	7.21	77	33.16	114	7.53	159	0.18
43	5.04	78	2.39	115	1.01	161	0.32
44	0.88	79	6.09	116	0.26	162	0.06
45	0.88	80	1.31	117	0.54	163	0.16
46	0.53	81	5.87	118	0.15	164	0.03
47	4.11	83	92.86	119	0.62	175	0.02
48	2.36	84	5.48	120	0.13	177	0.06
49	2.03	85	15.82	121	0.33	179	0.23
50	4.30	86	0.35	123	1.08	181	0.07
51	15.31	87	4.02	125	1.43	195	0.10
52	3.28	88	0.61	126	0.12	197	0.06
53	13.01	89	1.67	127	0.62	216	0.70
54	9.95	90	3.35	129	0.25	217	0.07
55	91.84	91	12.50	133	87.24	218	0.46
56	11.35	93	25.38	134	5.45	219	0.03
57	4.08	94	1.77	135	0.70	220	0.08
59	10.71	95	1.65	137	0.37		

11. 2-Chloro-1-cyclohexyl-1,1-difluoroethane (**23**)



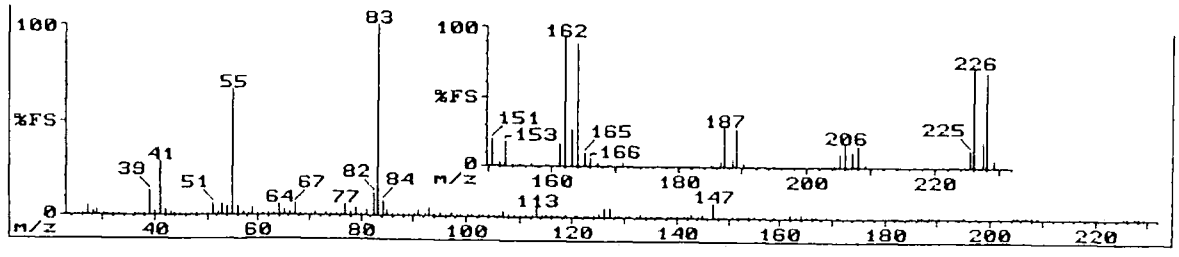
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.05	56	15.98	90	1.76	128	0.13
24	0.04	57	4.14	91	6.03	129	0.05
26	2.79	59	13.14	93	6.37	131	0.02
27	20.49	60	0.88	94	0.48	133	9.80
28	8.04	61	2.57	95	1.04	134	0.58
29	11.27	62	0.90	96	0.79	135	0.04
30	0.29	63	2.84	97	2.03	136	0.01
31	0.61	64	5.96	98	0.79	137	0.01
32	0.24	65	9.71	99	4.66	139	0.04
33	1.51	66	2.77	100	0.34	140	0.02
34	0.02	67	23.14	101	1.81	141	0.09
35	0.28	68	3.43	102	0.23	143	2.33
36	0.54	69	4.75	103	1.67	144	0.19
37	0.59	70	1.28	104	0.39	145	0.87
38	2.13	71	5.78	105	1.69	146	0.09
39	34.90	72	2.55	107	2.89	147	0.04
40	6.27	73	11.57	109	1.09	149	0.01
41	67.84	74	0.93	110	0.19	150	0.01
42	8.33	75	3.09	111	0.56	153	0.01
43	6.08	77	22.94	113	13.14	154	0.02
44	0.93	78	6.37	114	0.89	161	0.47
45	2.03	79	10.49	115	0.29	162	0.56
46	1.26	80	1.50	116	0.09	163	0.17
47	3.09	81	8.24	117	0.24	164	0.18
49	10.20	83	100.00	118	0.14	165	0.02
50	3.11	84	16.08	120	1.15	180	0.01
51	16.57	85	4.53	121	0.24	182	1.74
52	3.14	86	0.85	122	0.33	183	0.15
53	12.65	87	1.25	123	0.33	184	0.57
54	10.00	88	0.37	126	5.29	185	0.05
55	85.88	89	1.02	127	1.33	207	0.01

12. 2-Bromo-1-cyclohexyl-1,1,2-trifluoroethane (**26**)



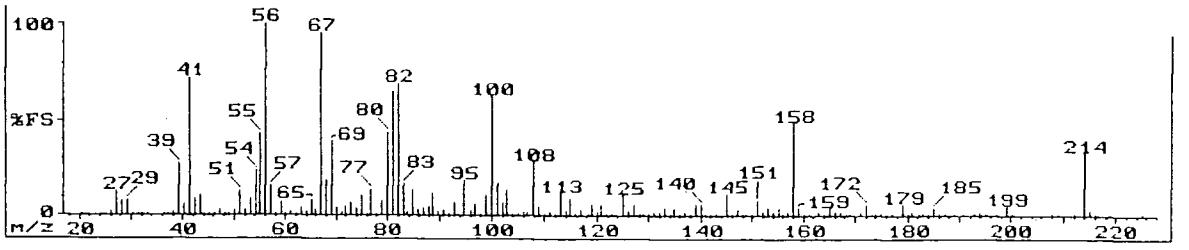
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.04	66	2.48	115	1.52	166	0.04
24	0.13	67	20.39	116	0.36	167	0.04
25	0.31	68	2.28	117	0.44	168	0.07
26	2.13	69	4.00	119	0.42	169	0.12
27	8.92	70	1.69	121	0.86	170	0.07
28	4.73	71	4.93	122	0.18	171	0.11
29	6.96	72	1.89	123	1.26	172	0.01
30	0.11	73	9.51	124	0.16	173	0.03
31	2.57	74	0.77	125	2.08	175	0.05
32	1.02	75	2.35	126	0.30	175	0.02
33	1.08	77	25.88	127	0.63	176	0.01
35	0.50	79	13.63	128	0.07	177	0.03
36	0.67	80	2.45	129	0.50	179	0.02
37	0.77	81	11.08	131	0.40	181	0.04
38	1.48	83	100.00	133	35.69	183	0.03
39	30.20	84	10.29	134	1.99	185	0.04
40	6.00	85	4.61	135	0.20	187	0.02
41	58.43	86	0.48	137	0.39	189	0.01
42	7.06	87	1.06	139	0.31	193	0.01
43	4.22	88	0.74	140	0.02	195	0.04
44	1.48	89	0.67	141	0.29	196	0.01
45	0.94	90	7.25	142	0.49	201	0.02
46	0.89	91	8.73	143	0.98	203	0.04
47	2.55	93	11.86	144	1.81	205	0.34
48	0.18	94	0.70	145	2.65	206	0.01
49	0.44	95	3.26	146	0.27	207	0.33
50	3.43	96	1.12	147	0.05	208	0.02
51	7.94	97	3.80	149	0.08	215	0.02
52	2.99	98	0.46	150	0.05	223	0.50
53	14.61	99	0.83	151	0.08	224	0.09
54	13.04	101	2.38	152	0.10	225	0.61
55	77.65	103	5.56	152	0.04	226	0.16
56	10.00	104	1.08	153	0.06	227	0.03
57	4.31	105	1.69	155	0.19	229	0.01
59	10.29	106	0.25	157	0.14	241	0.02
60	0.68	107	0.38	158	0.01	243	0.52
61	1.40	108	0.39	160	0.11	244	1.86
62	0.80	109	2.57	161	0.97	245	0.55
63	4.26	111	6.96	163	1.96	246	1.79
64	3.68	113	36.86	164	0.29	309	0.02
65	7.94	114	2.62	165	0.86		

13. 2-Bromo-1-cyclohexyl-1,1-difluoroethane (**28**)



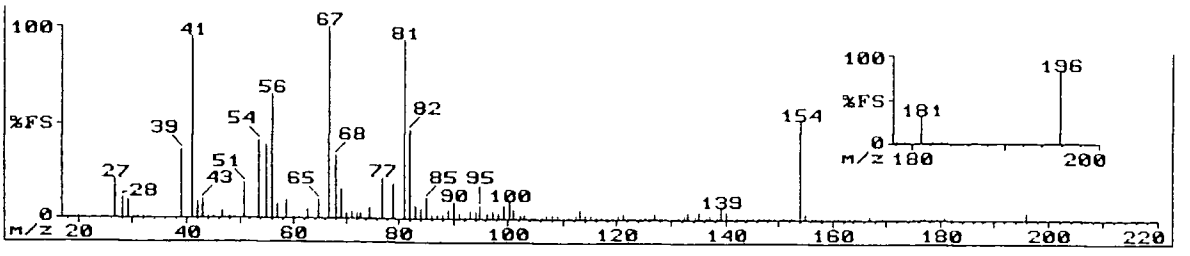
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.68	67	5.74	106	0.61	145	2.36
27	4.65	68	0.74	107	3.34	147	8.11
28	2.20	69	0.84	108	0.47	148	0.70
29	2.93	70	0.56	109	0.82	149	0.07
30	0.07	71	1.50	110	0.26	151	0.37
31	0.14	72	1.08	111	0.60	152	0.06
32	0.16	73	2.03	112	0.71	153	0.34
33	0.52	74	0.25	113	5.11	154	0.02
36	0.02	75	0.50	114	0.48	155	0.02
37	0.17	76	0.88	115	0.20	157	0.03
38	0.82	77	6.17	116	0.04	159	0.02
39	12.58	78	2.11	117	0.14	161	0.31
40	2.34	79	3.76	118	0.03	162	1.79
41	27.70	80	0.93	119	0.21	163	0.51
42	2.72	81	3.04	120	0.02	164	1.71
43	2.30	82	11.74	121	0.20	165	0.17
44	0.42	83	100.00	122	0.17	166	0.10
45	0.99	84	7.77	123	1.11	167	0.05
46	0.70	85	2.47	124	0.30	169	0.04
47	1.17	86	0.43	125	1.79	171	0.04
48	0.05	87	0.41	126	4.69	185	0.02
49	0.11	88	0.18	127	4.98	186	0.08
50	1.39	89	0.38	128	0.46	187	0.54
51	5.91	90	1.03	129	0.10	188	0.09
52	1.71	91	2.64	130	0.02	189	0.52
53	5.91	92	0.81	131	0.18	190	0.05
54	4.86	93	3.51	132	0.34	195	0.02
55	66.22	94	0.62	133	1.58	204	0.03
56	5.00	95	1.88	134	0.15	205	0.18
57	1.69	96	0.76	135	0.08	206	0.31
58	0.23	97	1.52	136	0.02	207	0.21
59	4.35	98	0.36	137	0.20	208	0.28
60	0.29	99	0.40	138	0.02	209	0.03
61	0.56	100	0.06	139	0.20	225	0.23
62	0.39	101	0.27	140	0.02	226	1.37
63	1.14	102	0.23	141	0.06	227	0.35
64	5.83	103	1.11	142	0.65	228	1.31
65	3.27	104	0.44	143	2.34	229	0.12
66	1.52	105	1.20	144	0.65		

14. (1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**)



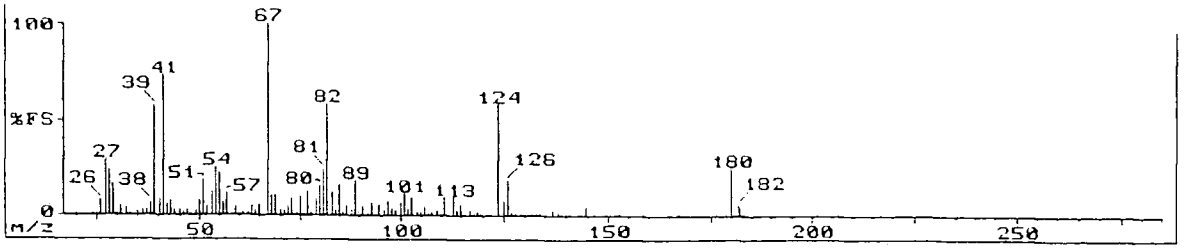
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.03	70	4.04	113	11.28	158	48.12
26	1.93	71	2.06	114	3.24	159	3.90
27	12.97	72	4.70	115	8.74	160	0.22
28	7.61	73	7.05	116	1.26	161	0.31
29	7.66	74	3.99	117	2.49	163	2.40
30	0.21	75	10.95	118	0.99	164	0.26
31	0.93	76	1.33	119	6.25	165	3.43
32	0.18	77	13.72	120	1.68	166	1.47
33	0.57	78	1.17	121	6.20	167	1.95
36	0.02	79	7.80	122	0.92	168	0.67
37	0.46	80	43.61	123	0.76	169	0.40
38	1.95	81	64.66	125	10.29	171	1.87
39	27.44	82	69.17	126	2.85	172	5.78
40	6.06	83	16.35	127	6.02	173	1.37
41	71.43	84	2.21	128	0.65	174	0.13
42	8.55	85	13.72	129	1.37	175	1.42
43	10.39	86	3.34	130	0.36	176	0.15
44	0.60	87	4.04	131	1.67	177	0.28
45	0.75	88	4.42	132	2.06	179	5.83
46	0.59	89	11.61	133	4.14	180	0.39
47	2.67	90	1.80	134	0.90	181	1.76
48	0.09	91	2.55	135	3.85	182	0.15
49	0.21	92	0.35	136	0.48	183	0.05
50	3.01	93	7.14	137	1.76	184	0.45
51	12.22	94	1.05	138	0.63	185	4.09
52	2.43	95	18.05	139	6.06	186	1.01
53	8.69	96	3.05	140	6.16	187	0.10
54	22.93	97	6.16	141	0.87	189	0.08
55	42.67	98	0.57	142	0.07	191	0.05
56	100.00	99	10.34	143	0.48	193	0.60
57	15.41	100	61.65	145	11.37	194	1.95
58	1.21	101	17.11	146	0.89	195	0.35
59	6.91	102	6.34	147	2.85	197	0.13
60	1.12	103	13.91	148	0.47	199	4.61
61	2.11	104	0.95	149	1.42	200	0.33
62	1.29	105	0.95	150	0.41	208	0.38
63	4.14	106	2.17	151	8.18	209	0.05
64	2.28	107	1.86	152	1.66	212	0.01
65	7.47	108	28.57	153	3.85	214	33.08
66	3.05	109	4.84	154	2.07	215	2.73
67	94.74	110	0.48	155	3.57	216	0.12
68	18.42	111	2.26	156	0.33	225	0.06
69	38.53	112	0.61	157	2.08		

15. (1Z)-1-Cyclohexyl-1,3,3,3-tetrafluoroprop-1-ene (**34**)



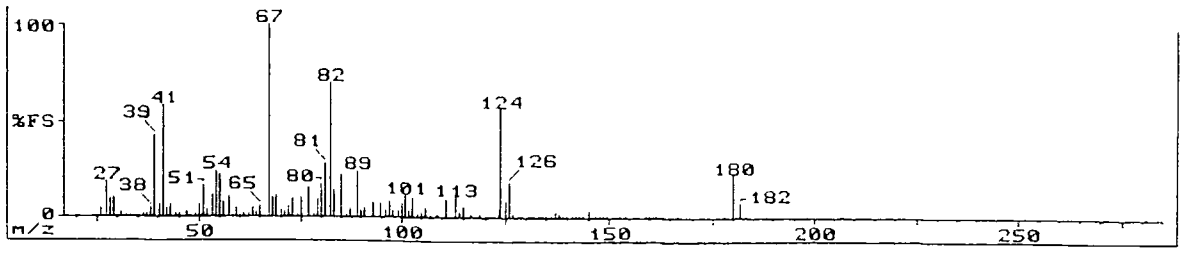
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.04	75	6.05	111	0.51	144	0.31
27	20.14	77	20.95	112	2.26	145	0.65
28	10.95	79	18.11	113	4.43	146	0.43
29	10.14	81	93.51	114	1.92	147	0.89
30	0.21	82	46.49	115	2.05	148	0.59
31	0.90	83	7.06	116	0.50	149	0.76
32	0.78	84	5.07	117	0.74	150	0.46
33	1.00	85	10.95	118	0.63	151	0.21
39	36.22	86	1.64	119	1.26	152	0.36
41	94.59	87	1.65	120	1.53	154	51.35
42	9.19	88	1.97	121	2.77	155	2.64
43	10.00	89	4.56	122	0.74	156	0.58
44	0.72	90	8.65	123	0.21	157	1.38
45	0.96	91	2.97	124	0.15	158	0.22
47	3.68	92	1.39	125	0.33	159	0.20
48	0.09	93	3.72	126	1.32	160	0.29
51	17.97	94	3.45	127	2.67	161	0.73
54	41.08	95	6.69	128	0.45	162	0.23
55	38.38	96	2.80	129	0.49	163	0.47
56	64.86	97	3.85	130	0.10	164	0.17
57	7.53	98	2.50	131	0.29	165	0.08
59	9.32	99	6.93	132	1.66	167	1.52
60	0.64	100	8.58	133	3.41	168	0.76
61	0.91	101	4.76	134	2.36	169	0.08
63	4.73	102	1.94	135	3.65	173	0.06
65	9.73	103	2.33	136	1.22	175	0.49
67	100.00	104	0.53	137	1.82	176	0.92
68	32.97	105	0.38	138	1.92	177	0.84
69	15.14	106	0.82	139	5.51	178	0.09
70	2.74	107	2.07	140	4.36	179	0.03
71	3.95	108	1.92	141	1.03	181	1.49
72	2.94	109	1.93	142	0.12	182	0.07
73	2.53	110	0.39	143	0.09	196	3.95

16. (1*E*)-2-Chloro-1-cyclohexyl-1,2-difluoroethene (**35a**)



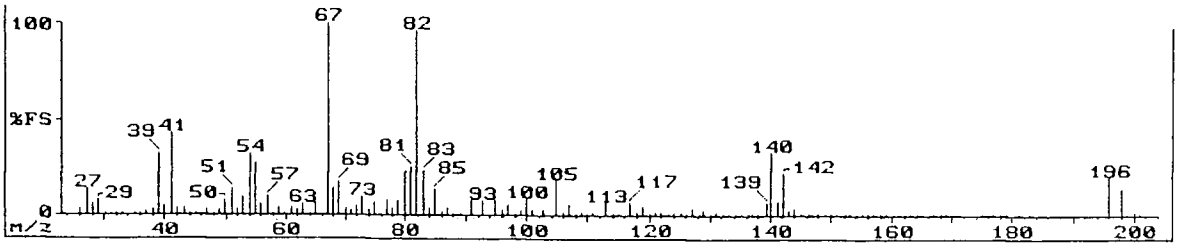
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.53	58	1.39	93	6.64	128	0.14
24	0.57	59	4.63	94	0.91	129	1.14
25	1.40	60	0.96	95	6.20	130	0.12
26	7.92	61	2.21	96	3.14	131	0.75
27	28.74	62	2.21	97	8.17	132	0.25
28	22.83	63	4.77	98	4.33	133	0.27
29	16.93	64	2.53	99	3.15	134	0.13
30	0.51	65	5.81	100	6.84	135	0.47
31	4.53	67	100.00	101	11.76	137	2.58
32	4.08	68	10.38	102	3.49	138	1.85
33	1.28	69	10.58	103	9.84	139	0.82
35	1.60	70	3.35	104	1.71	140	0.43
36	3.03	71	2.74	105	2.29	141	0.09
37	3.20	72	4.92	106	4.92	143	0.40
38	6.79	73	9.01	107	0.85	144	0.34
39	57.48	74	1.85	108	1.53	145	4.58
40	8.81	75	9.69	109	2.66	147	0.36
41	72.44	76	1.39	110	0.34	149	0.05
42	6.05	77	12.35	111	9.65	150	0.06
43	7.33	78	2.18	112	0.56	151	0.26
44	2.82	79	8.42	113	9.99	152	0.09
45	2.73	80	15.75	114	2.63	153	0.07
46	1.77	81	24.02	115	6.25	159	0.04
47	3.08	82	58.27	116	1.16	165	0.19
48	0.77	83	12.99	117	2.53	167	0.08
49	2.52	84	2.52	118	0.28	180	25.20
50	7.68	85	16.34	119	1.75	181	0.95
51	18.50	86	1.59	120	0.55	182	5.71
52	4.38	87	4.43	121	0.62	182	3.79
53	12.25	88	2.82	122	0.79	183	0.26
54	25.59	89	18.50	124	58.27	207	0.11
55	22.24	90	3.11	125	7.73	281	0.34
56	7.09	91	4.97	126	18.90		
57	11.27	92	0.63	127	1.91		

17. (1Z)-2-Chloro-1-cyclohexyl-1,2-difluoroethene (35b)



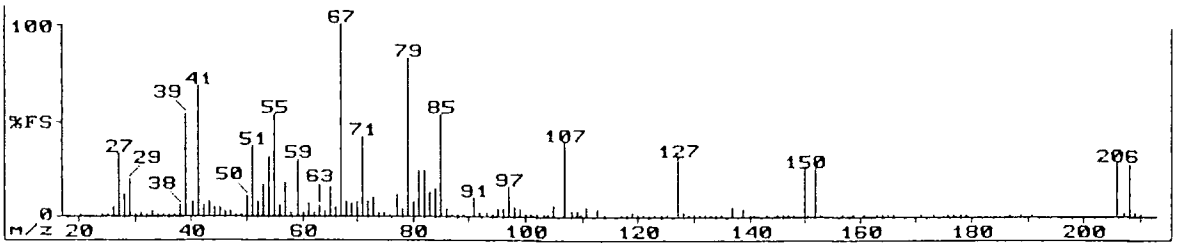
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.21	59	4.65	100	7.38	137	3.22
24	0.36	60	0.87	101	11.37	138	1.78
25	0.92	61	2.19	102	4.11	139	1.25
26	5.32	62	2.04	103	10.24	140	0.62
27	18.35	63	4.52	104	1.81	141	0.18
28	10.04	64	2.48	105	2.63	142	0.04
29	10.84	65	5.78	106	4.52	143	0.43
30	0.34	67	100.00	107	0.52	144	0.64
31	2.83	68	10.70	109	2.01	145	3.74
32	1.10	69	11.50	109	1.40	146	0.31
33	0.79	70	3.51	111	9.57	147	0.27
35	0.80	71	2.73	113	10.70	148	0.09
36	1.66	72	5.39	114	2.73	149	0.09
37	2.26	73	9.57	115	6.12	150	0.06
38	5.05	74	1.81	117	1.94	151	0.38
39	43.09	75	10.70	117	1.21	152	0.14
40	6.72	77	15.23	113	0.41	153	0.14
41	58.51	78	2.43	119	1.71	154	0.05
42	4.52	79	10.04	120	0.54	159	0.08
43	6.38	80	17.55	121	0.64	160	0.10
44	1.98	81	28.46	122	0.81	161	0.03
45	2.19	82	70.21	123	4.59	162	0.03
46	1.45	83	14.10	124	56.38	163	0.06
47	2.46	85	22.07	125	8.58	165	0.19
48	0.62	86	1.85	126	13.62	167	0.05
49	2.13	87	4.99	127	1.71	178	0.03
50	6.45	89	24.20	128	0.28	180	22.61
51	16.42	90	3.82	129	1.15	181	1.13
52	3.86	91	5.32	130	0.10	182	8.05
53	11.50	93	7.91	131	0.80	183	0.51
54	24.20	95	7.65	132	0.37	207	0.05
55	22.34	96	3.59	133	0.40	281	0.12
56	7.31	97	8.64	134	0.22		
57	10.64	98	4.32	135	0.45		
58	1.23	99	3.62	136	0.27		

18. (1Z)-2.2-Dichloro-1-cyclohexyl-1-fluoroethene (36)



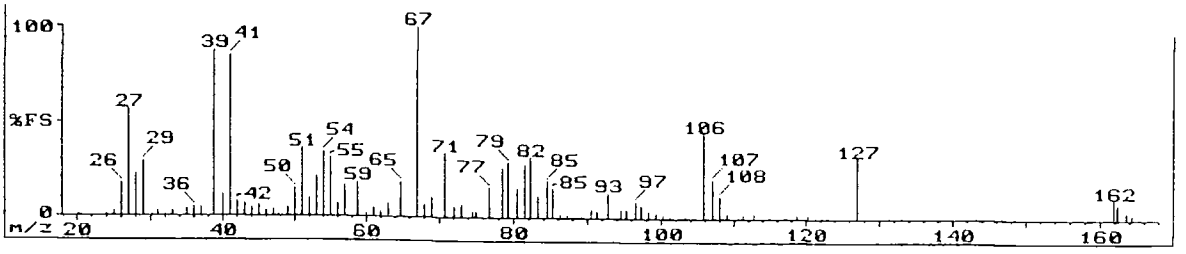
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	2.73	65	5.67	109	2.31	149	0.36
27	13.55	67	100.00	110	0.42	150	0.23
28	5.78	68	14.54	111	1.49	151	0.36
29	7.82	69	17.40	113	6.91	152	0.37
30	0.23	70	3.61	114	1.34	153	1.39
31	1.05	71	3.00	115	0.92	154	0.82
32	0.12	72	5.18	117	6.83	155	0.87
33	0.60	73	9.25	118	2.04	156	0.47
35	0.83	74	2.62	119	4.54	157	0.21
36	0.42	75	7.27	120	1.07	158	0.11
37	1.48	76	0.81	121	1.55	159	0.14
38	3.39	77	7.93	122	2.26	160	0.23
39	32.16	78	3.88	123	1.08	161	0.67
40	4.76	79	8.04	124	1.82	162	0.16
41	42.73	80	23.57	125	2.26	163	0.33
42	3.72	81	25.44	126	1.43	164	0.07
43	4.05	82	96.04	127	4.32	165	0.09
44	0.94	83	23.46	128	0.92	166	0.11
45	1.05	84	4.21	129	3.00	167	0.27
46	0.61	85	13.55	130	0.83	168	0.10
47	2.62	86	1.90	131	1.84	169	0.17
48	0.35	87	3.69	132	0.59	170	0.05
49	2.78	88	0.58	133	1.05	171	0.04
50	7.93	89	0.81	134	0.34	175	0.01
51	13.88	91	7.38	135	0.65	176	0.03
52	3.33	93	8.15	136	0.12	177	0.03
53	9.69	95	7.93	137	0.36	178	0.02
54	32.16	96	3.00	138	0.23	179	0.02
55	27.42	97	5.40	139	7.27	180	0.02
56	5.64	98	1.14	140	32.60	181	0.07
57	10.02	99	3.39	141	7.60	183	0.04
58	0.88	100	8.26	142	22.03	196	19.93
59	4.19	101	2.95	143	2.51	198	14.32
60	1.37	103	3.06	144	3.85	199	0.94
61	3.72	105	18.06	145	0.44	200	2.06
62	3.14	106	2.04	146	0.15	201	0.16
63	6.22	107	5.53	147	0.45		
64	1.26	108	0.70	148	0.16		

19. (1Z)-2-Bromo-1-cyclohexyl-1-fluoroethene (**37**)



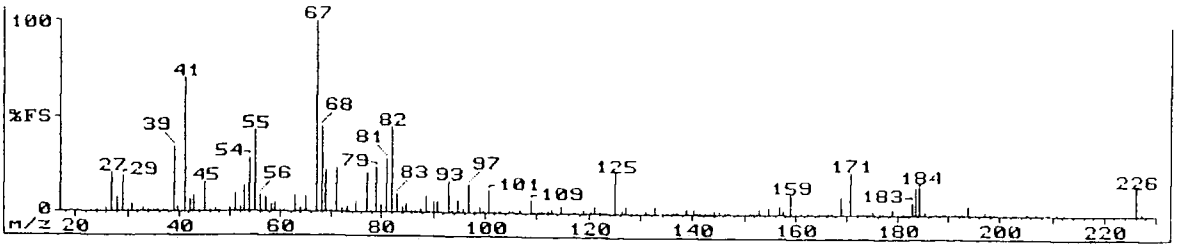
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.05	59	29.66	96	3.40	139	4.20
24	0.04	60	1.63	97	15.11	140	0.09
25	0.29	61	6.72	98	4.48	141	0.07
26	4.66	62	2.36	99	3.87	143	0.06
27	32.65	63	5.97	100	0.76	145	0.13
28	11.71	64	3.17	101	0.34	146	0.06
29	19.40	65	15.11	102	0.24	147	0.07
30	0.40	66	4.43	103	0.43	148	0.10
31	2.11	67	100.00	104	0.27	150	25.56
32	0.42	68	7.70	105	5.83	151	0.16
33	2.45	69	6.81	107	38.62	152	25.37
34	0.03	70	7.84	108	3.13	153	1.15
35	0.02	71	41.79	109	3.26	157	0.11
36	0.14	72	7.70	110	0.56	159	0.12
37	1.42	73	9.98	111	4.76	161	0.11
38	5.55	74	1.49	113	3.68	163	0.79
39	52.99	75	2.11	114	0.06	164	0.90
40	7.84	76	0.64	117	0.67	165	0.68
41	67.91	77	12.13	118	0.14	166	0.87
42	5.41	78	3.87	119	1.60	171	0.05
43	7.37	79	82.09	120	0.19	173	0.04
44	4.48	80	7.93	121	0.74	175	0.04
45	5.13	81	24.07	122	0.26	177	0.06
46	2.45	82	24.07	123	1.05	178	0.05
47	2.74	83	12.69	124	0.42	179	0.05
48	0.29	84	14.18	125	0.84	187	0.04
49	0.94	85	52.99	127	31.16	189	0.03
50	10.31	86	3.54	128	2.37	191	0.03
51	36.75	87	0.60	129	0.26	206	28.36
52	8.21	88	0.28	130	0.06	207	2.03
53	16.60	89	0.55	131	0.59	208	27.05
54	31.53	91	9.79	132	0.94	209	1.95
55	53.73	92	1.47	133	0.23	210	0.09
56	6.25	93	2.11	134	0.59		
57	17.54	94	0.72	135	0.54		
58	2.11	95	3.82	137	4.57		

20. (1Z)-2-Chloro-1-cyclohexyl-1-fluoroethene (**38**)



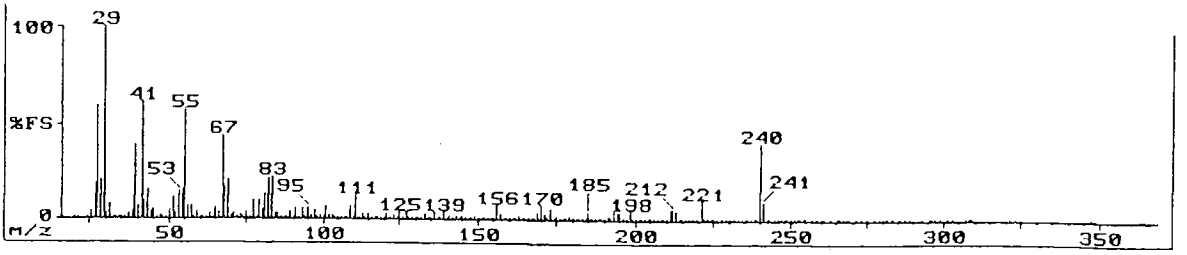
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.41	50	14.49	80	15.44	108	12.03
24	1.12	51	36.36	81	28.03	109	2.94
25	2.89	52	9.47	82	32.20	110	1.31
26	17.23	53	21.12	83	12.12	111	1.50
27	56.44	54	33.71	85	19.70	113	2.68
28	21.97	55	30.68	85	15.15	115	0.32
29	29.55	56	6.63	86	2.39	117	0.33
30	0.69	57	16.86	87	2.13	119	2.08
31	3.08	59	13.84	88	1.26	120	1.68
32	0.71	60	1.96	89	0.99	121	0.53
33	2.91	61	4.52	91	4.78	122	0.50
35	4.19	62	3.24	91	4.29	123	0.22
36	5.23	63	6.44	93	14.02	127	31.82
37	5.09	65	18.75	95	4.62	131	0.08
39	87.12	67	100.00	95	4.64	133	0.20
40	12.03	68	7.10	97	8.71	143	0.30
41	84.47	69	10.89	97	7.20	143	0.17
42	7.39	71	33.71	98	3.46	145	0.13
43	6.44	72	5.97	99	3.24	147	0.10
44	4.40	73	6.53	100	1.73	162	10.23
45	5.75	74	3.15	101	0.97	162	7.58
46	3.20	75	2.53	102	0.91	164	3.79
47	3.43	77	16.00	103	0.65	164	2.44
48	1.12	79	26.52	106	44.32	165	0.22
49	4.50	79	28.79	107	20.64		

21. (1Z)-1-Cyclohexyl-1-methoxy-2,3,3,3-tetrafluoroprop-1-ene (**39a**)



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.08	67	100.00	111	1.39	159	10.91
24	0.02	68	44.20	111	0.84	160	0.50
26	1.86	69	22.10	112	1.03	161	0.27
27	20.86	70	1.42	113	1.99	163	0.52
28	7.60	71	22.93	115	4.25	163	0.18
29	18.65	72	2.24	116	0.29	165	0.92
30	0.75	73	2.73	117	0.40	166	1.38
31	4.28	75	5.66	119	1.61	166	0.58
32	0.47	77	20.86	120	1.92	167	1.18
33	1.85	78	1.11	121	4.28	169	9.39
34	0.03	79	23.20	122	0.53	171	22.79
35	0.26	80	3.63	123	1.40	172	1.16
36	0.03	81	28.45	125	21.41	173	0.58
37	0.39	82	44.20	126	2.21	175	1.77
39	33.98	83	9.94	127	4.21	176	0.10
40	2.49	84	3.25	128	1.06	177	0.30
41	70.17	85	5.01	129	1.40	179	3.25
42	7.08	86	0.92	131	1.52	180	0.16
43	8.39	87	0.45	133	3.80	181	0.18
44	0.28	88	1.51	134	0.47	183	6.60
45	15.06	89	8.49	135	1.29	184	14.23
46	0.76	90	5.35	136	0.36	184	16.85
47	1.70	91	5.52	137	0.69	185	1.56
48	0.04	93	16.57	139	2.69	186	0.17
50	2.31	94	0.78	140	2.45	187	0.10
51	9.81	95	7.01	141	1.31	189	0.01
52	2.45	96	1.49	142	0.10	191	0.11
53	13.54	97	14.50	143	0.55	193	0.23
54	28.31	98	1.39	144	1.61	194	4.39
55	43.09	99	2.59	145	1.67	195	0.51
56	8.84	100	1.02	146	0.42	197	1.80
57	8.11	101	11.46	147	0.99	198	0.49
58	3.49	102	1.26	149	1.13	205	0.18
59	5.11	103	1.34	150	0.28	207	0.34
60	0.33	105	1.23	151	0.78	209	0.03
61	0.52	105	0.99	153	3.07	211	0.95
63	8.29	107	1.55	155	4.35	212	0.06
64	1.67	109	7.04	157	5.04	226	14.78
65	7.35	110	0.33	158	3.35	227	1.47

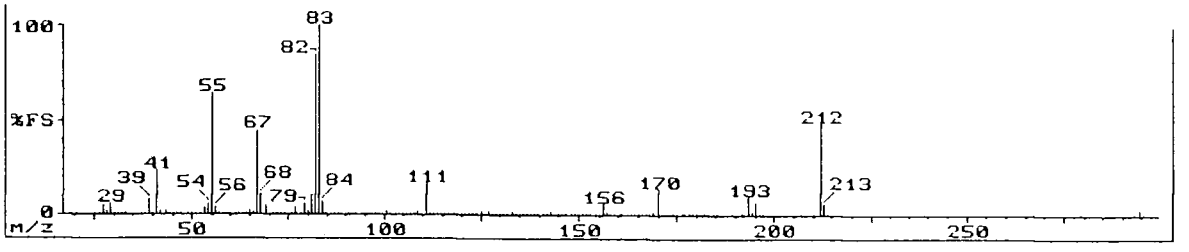
22. (1Z)-1-Cyclohexyl-1-ethoxy-2,3,3,3-tetrafluoroprop-1-ene (33)



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.92	76	0.69	130	0.65	184	0.49
21	0.07	77	9.60	131	0.62	185	3.45
24	1.24	78	1.03	132	0.61	186	0.31
25	3.41	79	10.14	133	2.92	187	0.21
26	18.83	80	5.03	134	0.63	188	0.07
27	59.45	81	13.87	135	1.43	189	0.23
28	20.73	82	21.34	136	3.81	190	0.14
29	100.00	83	21.95	137	1.26	191	2.23
30	3.20	84	3.09	138	0.59	192	0.85
31	7.32	85	2.48	139	3.94	193	4.73
32	1.37	86	0.45	140	0.91	194	3.72
33	1.41	87	1.15	141	1.54	195	4.04
34	0.08	88	1.16	142	0.29	196	0.53
35	0.23	89	3.77	143	2.25	197	1.16
36	0.38	90	1.18	144	0.79	198	5.34
37	2.74	91	5.49	145	2.25	199	0.72
38	5.11	92	0.78	146	0.41	200	0.16
39	39.02	93	5.49	147	0.97	201	0.32
40	6.33	94	1.09	148	0.56	202	0.12
41	61.59	95	6.25	149	1.81	203	0.34
42	9.38	96	1.98	150	0.48	204	0.06
43	16.01	97	5.18	151	1.03	205	0.21
44	4.10	98	0.98	152	0.42	206	0.03
45	4.71	99	1.35	153	1.41	207	0.28
46	0.69	100	1.24	154	0.40	208	0.07
47	2.31	101	7.01	155	0.99	209	0.14
48	0.33	102	1.54	156	7.70	210	0.15
49	1.06	103	2.15	157	3.24	211	5.87
50	5.03	104	0.42	158	0.46	212	6.25
51	11.36	105	1.35	159	0.98	213	5.03
52	3.24	106	0.71	160	0.16	214	0.54
53	14.56	107	1.15	161	0.53	215	0.34
54	15.55	108	1.41	162	0.49	216	0.07
55	57.01	109	7.09	163	1.66	217	0.11
56	6.78	110	1.17	164	0.62	218	0.10
57	6.55	111	13.03	165	0.73	219	0.14
58	0.76	112	1.28	166	0.81	221	10.82
59	3.72	113	2.71	167	0.63	222	1.35
60	0.50	114	1.10	168	0.23	223	1.19
61	0.74	115	2.71	169	3.81	224	0.17
62	0.98	116	0.60	170	7.39	225	0.32
63	3.11	117	1.04	171	3.05	226	0.07
64	1.43	118	0.28	172	1.00	227	0.12
65	5.56	119	1.45	173	5.79	228	0.05
66	4.19	120	0.45	174	0.81	229	0.20
67	43.29	121	2.65	175	1.60	230	0.07
68	16.16	122	0.59	176	0.29	231	0.14
69	20.43	123	2.23	177	0.58	232	0.05
70	2.15	124	1.04	178	0.15	233	0.18
71	2.63	125	4.25	179	2.10	234	0.11
72	0.70	126	0.79	180	0.31	235	0.91
73	1.87	127	3.53	181	0.51	236	0.14
74	0.52	128	1.10	182	0.27	237	0.09
75	3.49	129	1.13	183	1.28	238	0.08

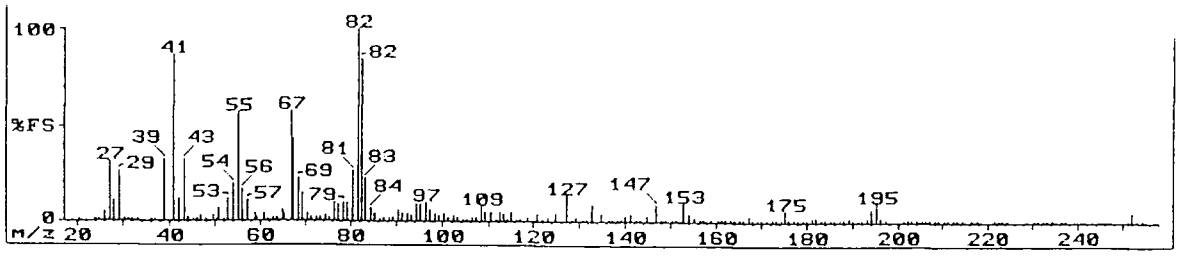
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
239	0.79	254	0.04	273	0.02	299	0.03
240	41.16	255	0.06	275	0.09	301	0.03
241	9.45	257	0.07	277	0.04	303	0.03
242	0.93	258	0.03	279	0.16	307	0.17
243	0.12	259	0.06	280	0.04	308	0.09
245	0.12	260	0.02	281	0.07	309	0.03
246	0.05	261	0.04	283	0.06	321	0.09
247	0.10	263	0.09	285	0.03	323	0.04
248	0.08	265	0.06	287	0.03	347	0.03
249	0.59	266	0.04	289	0.08	363	0.05
250	0.10	267	0.50	293	0.04	364	0.05
251	0.09	268	0.08	295	0.13		
252	0.03	269	0.12	296	0.04		
253	0.21	271	0.07	297	0.02		

23. (1Z)-1-Cyclohexyl-1-cyclohexyloxy-2,3,3,3-tetrafluoroprop-1-ene (**40**)



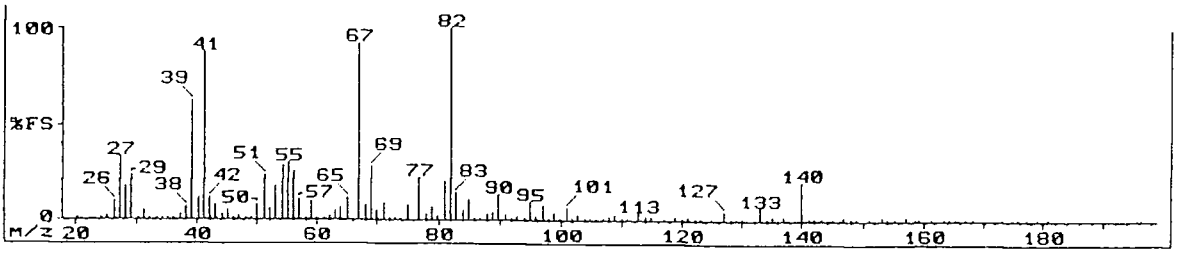
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.01	72	0.13	117	0.20	161	0.15
25	0.02	73	0.35	118	0.03	162	0.09
26	0.28	74	0.08	119	0.45	163	0.73
27	4.43	75	0.70	120	0.07	164	0.50
28	1.73	76	0.08	121	0.63	165	0.22
29	6.13	77	4.00	122	0.07	166	0.69
30	0.15	78	0.59	123	0.79	167	0.22
31	0.20	79	5.95	124	0.46	168	0.10
32	0.09	80	1.84	125	2.32	169	1.61
33	0.05	81	10.74	126	0.24	170	13.35
37	0.04	82	84.47	127	1.61	171	0.84
38	0.12	83	100.00	128	0.37	172	0.14
39	8.07	84	6.55	129	0.50	173	0.45
40	1.18	85	0.60	130	0.16	174	0.18
41	23.30	86	0.06	131	0.19	175	0.42
42	1.90	87	0.18	132	0.22	176	0.04
43	2.37	88	0.25	133	1.71	177	0.31
44	0.20	89	0.57	134	0.29	178	0.02
45	0.09	90	0.21	135	0.49	179	1.14
46	0.03	91	0.77	136	1.37	180	0.11
47	0.12	92	0.08	137	0.39	181	0.18
49	0.05	93	1.41	138	0.36	182	0.07
50	0.25	94	0.23	139	0.28	183	0.58
51	0.97	95	1.14	140	0.20	184	0.22
52	0.48	96	0.32	141	0.56	185	0.08
53	3.88	97	0.99	142	0.06	189	0.05
54	5.76	98	0.23	143	1.50	191	0.08
55	64.08	99	0.60	144	0.33	192	0.66
56	4.07	100	0.28	145	1.05	193	9.41
57	1.09	101	1.49	146	0.14	194	2.11
58	0.13	102	0.30	147	0.41	195	7.10
59	0.47	103	0.49	148	0.35	196	0.53
60	0.05	104	0.07	149	0.77	197	0.34
61	0.12	105	0.31	150	0.42	207	0.02
62	0.08	106	0.09	151	0.46	210	0.05
63	0.37	107	0.20	152	0.16	212	48.79
64	0.17	108	0.24	153	0.82	213	6.01
65	2.55	109	1.49	154	0.06	214	0.41
66	1.64	111	16.75	155	0.51	267	0.03
67	44.90	112	1.20	156	6.01	279	0.02
68	10.92	113	0.88	157	1.37	293	0.16
69	4.85	114	0.24	158	0.09	294	2.85
70	0.74	115	0.55	159	0.25	295	0.38
71	0.56	116	0.13	160	0.02		

24. (2*E*)-3-Cyclohexyl-1,1,1,2-tetrafluorohept-2-ene (**41a**)



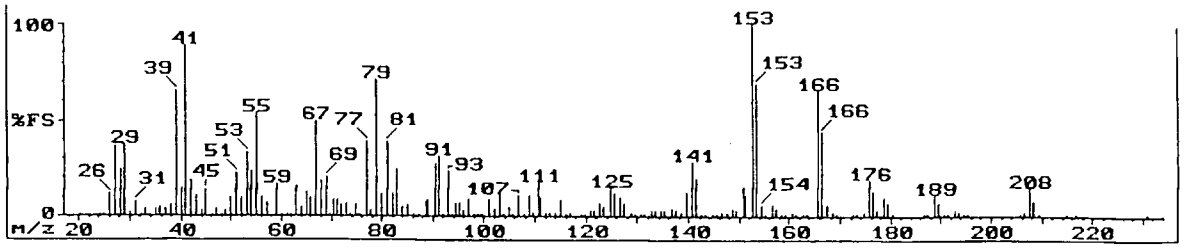
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.20	75	1.59	127	13.35	181	1.46
24	0.24	77	9.94	128	0.50	182	1.60
25	0.89	77	8.70	129	1.62	183	0.52
26	4.87	79	9.80	131	1.11	184	0.07
27	30.97	79	9.80	131	0.50	185	0.03
28	10.94	81	25.99	133	8.35	186	0.03
29	25.85	82	100.00	135	4.30	187	0.08
30	0.67	82	84.66	136	0.44	188	0.66
31	1.07	83	22.59	137	0.71	189	2.23
32	0.58	84	6.64	138	0.79	190	0.41
33	0.59	85	3.62	139	1.40	191	0.16
36	0.25	87	1.25	140	3.16	192	0.18
37	1.43	87	1.54	141	4.30	193	1.62
39	31.96	88	2.01	142	0.27	194	6.89
41	86.36	89	2.03	143	0.41	195	9.66
42	11.51	91	5.50	145	2.77	196	2.16
43	32.24	91	3.37	147	8.59	197	0.21
44	1.56	93	3.44	148	1.14	201	0.03
45	0.59	93	2.88	149	1.45	202	0.15
46	0.28	95	8.91	150	0.58	203	0.49
47	2.73	95	8.70	151	1.24	204	0.07
48	0.09	97	9.80	153	9.38	205	0.02
50	2.63	97	5.58	154	3.59	206	0.02
50	1.12	99	3.69	155	1.46	207	0.11
51	7.07	99	2.91	156	0.23	208	0.38
52	1.46	101	3.94	157	0.46	209	0.90
53	11.93	101	2.41	159	1.30	210	1.06
54	19.18	103	3.05	160	0.49	211	0.16
55	56.25	103	1.59	161	0.59	212	0.04
56	16.90	105	1.14	162	0.56	213	0.09
57	10.80	105	1.06	163	0.36	214	0.02
59	3.98	107	2.24	164	0.38	216	0.02
59	1.80	107	1.56	165	0.74	217	0.03
61	3.44	109	7.53	166	1.29	221	0.02
62	0.39	109	4.55	167	2.63	222	0.07
63	1.84	111	4.97	168	1.36	223	0.22
63	1.72	112	0.24	169	0.33	224	0.06
65	5.58	113	4.51	170	0.22	230	0.06
65	3.73	113	3.69	171	0.39	231	0.26
67	56.82	114	1.15	172	0.17	232	0.10
67	42.61	115	4.72	173	0.48	233	0.07
69	22.16	116	0.24	174	1.45	234	0.02
69	14.35	117	0.91	175	6.29	236	0.01
70	4.33	119	2.01	176	0.84	237	0.05
71	1.91	121	4.01	177	0.47	252	4.72
73	2.31	122	1.27	178	0.36	253	0.48
73	2.02	123	2.15	179	1.00	254	0.04
75	2.52	125	3.98	180	0.59		

25. (1*Z*) and (1*E*)-1-Cyclohexyl-2,3,3,3-tetrafluoroprop-1-ene (**45a**) and (**45b**)



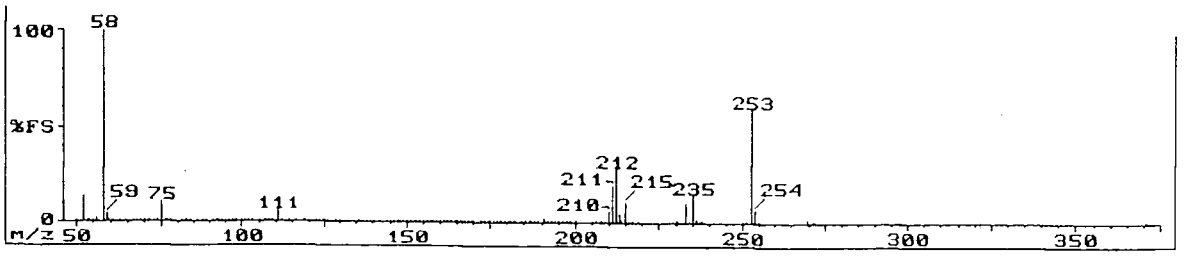
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.06	57	11.08	93	2.27	134	1.02
24	0.78	58	1.37	94	1.18	135	1.54
25	2.01	59	9.73	95	9.57	137	2.28
26	9.93	60	0.60	96	2.37	140	20.25
27	32.75	61	1.24	97	7.36	141	1.12
28	17.41	62	1.57	98	1.33	142	0.10
29	23.73	63	5.14	99	3.64	143	0.07
30	0.65	64	7.00	100	0.43	145	1.06
31	4.47	65	11.39	101	6.49	147	1.96
32	0.68	67	92.41	102	1.30	148	0.28
33	1.29	68	7.71	103	3.05	149	0.38
34	0.03	69	28.01	104	0.42	151	0.52
35	0.11	70	4.43	105	0.38	153	1.89
36	0.39	71	8.54	106	0.62	154	1.15
37	3.20	72	1.10	107	1.29	155	0.39
38	6.65	73	1.43	108	1.55	157	1.64
39	62.03	74	1.10	109	2.69	159	0.26
40	11.71	75	7.99	110	0.41	159	0.20
41	87.34	77	22.63	111	0.94	161	0.15
42	11.23	78	2.81	113	3.88	163	0.07
43	7.56	79	7.16	114	2.40	164	0.03
44	2.97	80	1.98	115	1.99	165	0.12
45	4.43	81	20.73	117	1.37	166	0.08
46	1.03	82	100.00	119	1.90	167	0.61
47	1.92	83	14.24	120	0.51	168	0.57
48	0.39	84	5.30	121	1.74	173	0.04
49	1.21	85	10.44	122	0.24	175	0.27
50	7.83	86	0.82	123	0.21	176	0.05
51	23.10	87	0.51	125	0.42	177	0.10
52	5.46	88	2.57	127	4.59	179	0.08
53	17.09	89	3.88	128	0.34	181	0.65
54	27.69	90	13.29	129	0.51	196	0.53
55	30.06	91	2.93	130	0.07	196	0.46
56	25.63	92	0.47	133	7.20		

26. (1*Z*) and (1*E*)-1-Cyclohexyl-1-methoxy-3,3,3-trifluoroprop-1-ene (**46**)



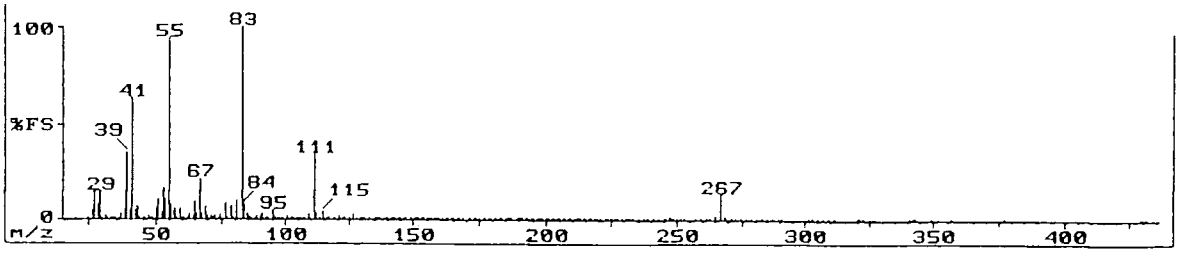
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.19	69	20.46	111	17.44	154	6.12
24	0.47	70	0.64	111	9.68	155	0.97
25	1.30	71	8.27	112	2.29	157	5.52
26	11.59	71	8.67	113	2.07	157	4.08
27	36.29	72	5.37	114	2.29	159	1.06
28	24.70	73	6.45	115	8.77	159	0.55
29	37.10	74	0.50	116	1.02	161	2.27
30	2.32	75	6.05	117	2.02	161	1.39
31	7.46	76	0.81	119	1.14	163	0.91
32	1.36	77	39.11	120	0.32	163	0.67
33	3.70	78	2.80	121	3.20	166	64.92
35	3.88	79	70.97	121	3.02	166	43.95
36	4.91	80	11.19	123	7.16	167	6.00
37	3.98	81	39.11	123	5.24	169	1.56
38	6.25	82	11.79	125	14.11	169	0.71
39	65.32	83	23.99	125	11.19	173	0.34
40	14.11	84	5.19	127	9.27	173	0.21
41	88.71	85	6.25	127	6.55	175	2.17
42	18.85	86	0.76	129	1.54	176	18.55
43	10.38	87	1.03	129	0.76	176	12.30
44	3.25	88	8.06	131	1.40	177	2.67
45	13.21	89	8.87	131	1.26	179	9.27
46	0.71	90	27.02	133	3.18	179	6.85
47	3.83	91	31.05	133	3.23	180	1.12
48	0.56	92	1.21	135	2.72	187	0.38
49	2.67	93	23.39	135	2.52	187	0.24
50	9.27	94	0.86	137	3.53	189	10.48
51	22.28	94	7.06	137	2.90	189	6.33
52	9.38	95	7.06	139	1.81	190	0.72
53	32.66	96	3.05	140	12.70	191	0.08
54	22.88	97	8.77	141	28.23	193	3.18
55	53.63	98	1.27	141	19.35	193	2.09
56	9.38	99	1.13	142	1.18	194	0.47
57	6.65	100	0.16	143	0.22	195	0.10
59	16.83	101	8.77	145	1.17	206	0.14
60	0.90	102	4.01	145	0.91	207	2.24
61	1.17	103	10.79	147	1.89	208	14.72
62	0.57	104	1.37	147	2.19	209	7.36
63	15.52	105	4.46	149	3.88	209	1.21
64	5.02	106	0.42	149	2.65	215	0.15
65	12.50	107	10.38	151	15.83	217	0.17
66	9.27	108	0.94	151	10.99	231	0.10
67	49.60	109	10.38	153	100.00		
68	18.55	110	1.84	153	69.35		

27. 1-Cyclohexyl-2-fluoro-2-(trifluoromethyl)pent-4-en-1-one (48)



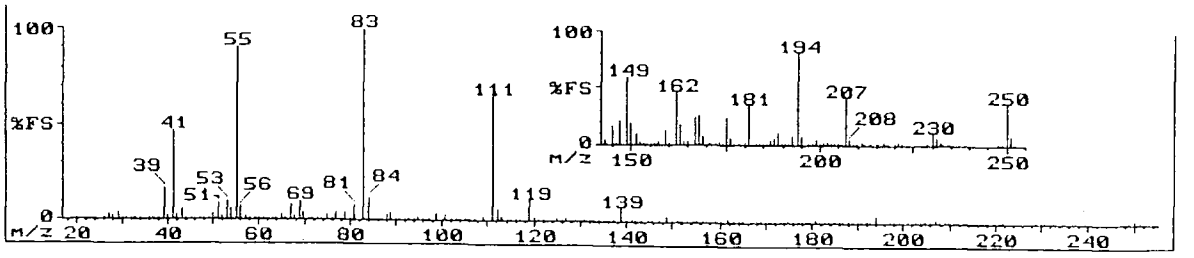
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
50	0.06	101	0.11	151	0.39	195	1.13
52	13.66	102	0.15	152	0.11	196	0.26
53	0.44	103	0.03	153	0.23	197	0.13
54	0.52	105	0.08	154	0.20	198	0.14
55	1.16	107	0.06	155	0.15	200	0.11
56	1.72	108	0.22	156	0.23	205	0.06
58	100.00	109	0.43	157	0.10	206	0.04
59	3.58	111	5.93	158	0.17	207	0.08
60	0.61	112	0.66	159	0.03	208	0.05
61	0.19	114	0.26	160	0.05	209	0.34
63	0.18	116	0.08	161	0.16	210	5.93
65	0.11	118	0.05	162	0.11	211	19.33
67	0.22	119	0.06	163	0.58	212	28.35
68	0.15	120	0.06	164	0.07	213	5.09
69	0.28	121	0.19	165	0.41	214	0.30
70	0.10	122	0.13	166	0.13	215	10.89
71	0.21	123	0.25	167	0.81	216	1.27
72	0.66	124	0.08	168	0.29	217	0.26
73	0.16	125	0.32	169	0.21	219	0.03
74	0.47	126	0.20	170	0.26	224	0.06
75	10.50	127	0.35	172	0.13	228	0.37
76	0.66	128	0.95	173	0.73	229	0.08
77	0.25	129	0.06	174	0.22	230	2.40
78	0.09	130	0.39	175	0.37	231	0.21
79	0.13	132	0.03	176	0.23	233	10.89
81	1.08	133	0.06	177	0.35	234	0.83
82	0.33	134	0.05	178	0.16	235	14.18
83	1.11	135	0.09	179	0.39	236	1.58
84	0.31	136	0.10	180	0.10	237	0.18
86	0.34	137	0.16	181	0.29	238	0.03
88	0.21	138	0.05	182	0.23	250	0.89
89	0.03	139	0.14	184	0.64	251	0.13
91	0.11	140	0.13	185	0.21	253	59.54
92	0.07	142	0.46	186	0.23	254	6.44
93	0.11	144	0.38	187	0.07	255	0.63
94	0.17	145	0.43	188	0.43	270	2.21
95	0.25	146	0.09	189	0.10	271	0.29
96	0.15	147	0.06	191	1.72	272	0.06
97	0.03	148	0.05	192	0.49	298	0.04
98	0.27	149	0.23	193	1.35	371	0.04
100	0.85	150	0.12	194	0.38		

28. 1-Cyclohexyl-2-fluoro-3-methyl-2-(trifluoromethyl)pent-4-en-1-one (**49**)



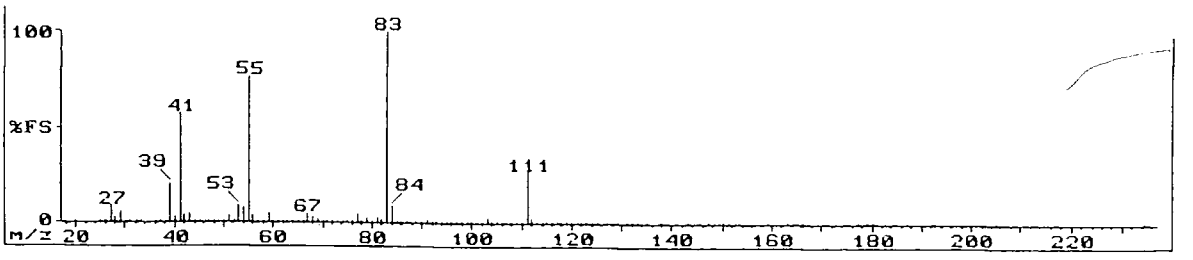
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.05	78	0.87	144	0.22	201	0.10
24	0.34	79	6.67	145	0.29	203	0.14
25	0.76	80	0.82	146	0.17	203	0.22
26	4.69	81	9.53	147	0.22	205	0.09
27	14.30	83	100.00	149	0.52	205	0.10
28	7.94	84	8.16	150	0.13	207	0.11
29	14.52	85	3.02	151	0.18	207	0.16
30	0.46	86	1.30	152	0.04	208	0.07
31	1.99	87	0.37	153	0.19	209	0.10
32	0.34	88	1.23	154	0.27	210	0.16
33	0.92	89	2.07	155	0.37	211	0.19
34	0.03	90	1.46	156	0.14	212	0.09
35	0.03	91	3.10	157	0.14	213	0.09
36	0.17	92	0.29	158	0.02	214	0.04
37	2.52	93	1.20	159	0.15	215	0.05
38	4.48	95	4.48	159	0.14	217	0.07
39	34.75	96	0.56	161	0.16	217	0.13
40	5.01	97	0.75	163	0.52	219	0.07
41	63.14	99	0.76	163	0.49	219	0.09
42	4.71	101	2.07	164	0.49	221	0.14
43	7.20	102	0.25	165	0.34	223	0.06
44	1.35	103	0.76	167	0.16	224	0.03
45	1.24	104	0.38	167	0.13	225	0.22
46	0.46	105	1.33	169	0.11	226	0.03
47	1.85	106	0.10	171	0.14	227	0.20
48	0.35	107	0.79	171	0.13	227	0.25
49	0.89	109	2.70	173	0.11	229	0.50
50	5.48	111	33.90	173	0.12	230	0.05
51	11.02	112	2.49	175	0.22	231	0.16
52	3.76	113	0.81	177	0.21	232	0.04
53	16.95	115	3.95	177	0.20	233	0.13
54	10.81	116	0.29	178	0.13	235	0.24
55	94.07	117	0.83	179	0.10	237	0.07
56	7.84	119	0.93	181	0.09	239	0.08
57	5.48	121	1.85	181	0.11	241	0.03
58	0.54	122	0.28	183	0.13	243	0.04
59	5.91	123	0.39	183	0.14	245	0.17
60	0.50	125	0.23	185	0.97	246	0.33
61	0.48	127	2.52	185	1.19	247	1.57
62	0.79	128	0.42	186	0.19	248	0.17
63	3.15	129	0.28	187	0.13	249	1.22
64	1.56	130	0.07	189	0.22	250	0.05
65	10.06	131	0.18	190	0.15	251	0.26
66	2.54	133	0.75	191	0.16	253	0.45
67	21.19	135	1.21	191	0.18	257	0.02
68	3.31	135	0.30	192	0.14	259	0.02
69	6.73	136	0.88	193	0.14	261	0.05
70	1.49	137	0.42	195	0.07	263	0.03
71	2.15	138	0.22	195	0.10	265	1.62
72	0.25	139	0.79	196	0.08	267	13.98
73	1.77	140	1.34	197	0.11	268	1.63
74	0.21	141	0.52	198	0.14	269	0.16
75	2.57	142	0.19	199	0.18	271	0.03
77	8.90	143	0.16	201	0.05	273	0.02

29. 1-Cyclohexyl-2-fluoro-2-(trifluoromethyl)penta-3,4-dien-1-one (**50**)



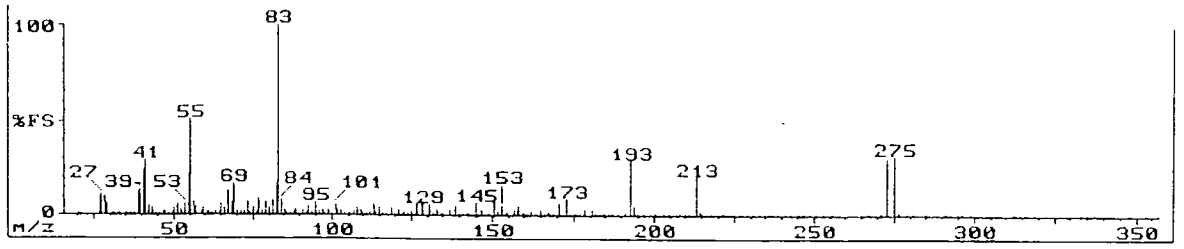
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.02	74	0.22	129	0.40	184	0.01
24	0.00	75	2.53	130	0.09	185	0.03
26	0.37	76	0.13	131	0.31	186	0.02
27	3.35	77	3.72	132	0.25	187	0.23
28	1.48	78	0.78	133	1.18	188	0.29
29	3.60	79	4.11	134	0.19	189	0.56
30	0.09	80	0.70	135	0.17	190	0.09
31	0.16	81	8.11	136	0.03	191	0.05
32	0.56	83	100.00	137	0.15	192	0.04
33	0.12	84	11.37	139	7.09	193	0.39
34	0.01	85	0.61	140	0.47	194	3.91
36	0.02	86	0.12	141	0.37	195	0.39
37	0.23	87	0.32	142	0.10	197	0.10
38	0.90	88	2.53	143	0.20	198	0.01
39	16.44	89	4.25	145	0.82	199	0.23
40	2.25	90	0.43	146	0.08	200	0.02
41	46.85	91	1.38	147	1.00	201	0.13
42	3.18	92	0.27	149	2.90	202	0.18
43	5.35	93	0.87	150	0.98	203	0.04
44	0.40	94	0.52	151	0.46	204	0.01
45	0.26	95	1.71	152	0.19	205	0.01
46	0.08	96	0.75	153	0.11	206	0.04
47	0.22	97	1.10	154	0.04	207	1.97
48	0.03	99	4.03	155	0.11	208	0.26
49	0.26	100	0.27	156	0.04	209	0.06
50	2.65	101	2.53	157	0.13	210	0.03
51	8.90	102	0.22	159	0.62	211	0.14
52	1.74	103	0.46	160	0.08	212	0.02
53	9.57	104	0.12	162	2.20	213	0.05
54	5.83	105	0.49	163	0.87	214	0.01
55	90.54	106	0.15	164	0.13	215	0.10
56	7.15	107	0.29	165	0.13	216	0.01
57	1.86	109	2.34	167	1.17	217	0.15
58	0.18	111	65.32	168	1.27	218	0.02
59	0.69	112	5.35	169	0.43	220	0.01
60	0.09	113	1.79	170	0.03	221	0.12
61	0.32	114	0.29	171	0.09	222	0.02
62	0.31	115	0.57	172	0.04	229	0.03
63	1.08	116	0.12	173	0.12	230	0.47
64	0.40	117	0.28	174	0.05	231	0.34
65	2.45	119	10.36	175	1.17	232	0.13
66	1.10	120	1.97	176	0.34	233	0.03
67	8.00	121	0.63	177	0.06	235	0.03
68	2.00	122	0.10	178	0.03	248	0.01
69	10.14	123	0.39	179	0.06	249	0.04
70	3.74	125	2.42	180	0.17	250	1.77
71	0.69	126	0.27	181	1.68	251	0.42
72	0.11	127	1.55	182	0.07	252	0.05
73	0.35	128	0.28	183	0.03		

30. 1-Cyclohexyl-2-(trifluoromethyl)pent-4-en-1-one (**52**)



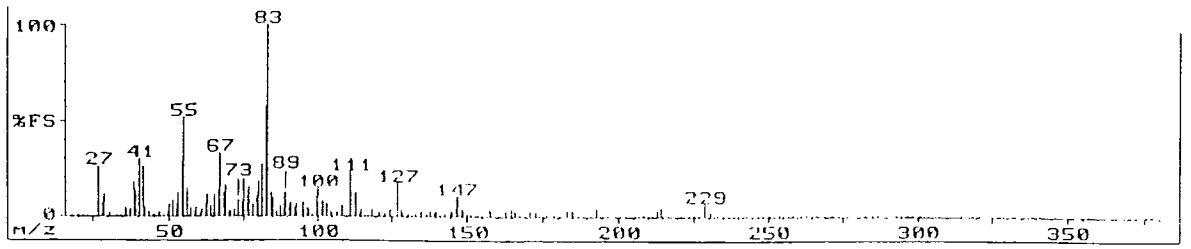
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.03	59	4.54	92	0.17	125	0.04
25	0.03	60	0.19	93	0.36	127	0.11
26	0.82	61	0.07	94	0.53	128	0.02
27	8.95	62	0.07	95	1.41	129	0.03
28	2.78	63	0.34	96	0.24	130	0.04
29	5.66	64	0.24	97	0.36	131	0.14
30	0.14	65	1.20	98	0.06	132	0.02
31	0.18	66	0.62	99	0.10	133	0.04
32	0.09	67	5.07	100	0.02	135	0.04
33	0.23	68	3.13	101	0.63	138	0.03
36	0.03	69	1.88	102	0.22	141	0.03
37	0.07	70	0.30	103	2.93	143	0.03
38	0.65	71	0.28	104	0.30	145	0.02
39	20.79	72	0.23	105	0.22	147	0.04
40	2.78	73	0.39	106	0.06	149	0.03
41	57.37	74	0.05	107	0.17	150	0.19
42	3.45	75	0.48	108	0.10	151	0.12
43	4.47	76	0.20	109	0.42	153	0.03
44	0.29	77	4.41	110	0.31	159	0.05
45	0.09	78	0.44	111	27.63	163	0.03
46	0.30	79	2.45	112	3.09	164	0.03
47	0.44	80	0.42	113	0.23	165	0.03
48	0.03	81	3.27	114	0.05	166	0.03
49	0.08	82	1.96	115	0.17	167	0.02
50	0.97	83	100.00	116	0.03	177	0.02
51	4.21	84	8.62	117	0.06	179	0.18
52	1.58	85	0.42	118	0.05	180	0.01
53	8.75	86	0.04	119	0.12	192	0.03
54	7.43	87	0.04	120	0.03	205	0.02
55	76.84	88	0.13	121	0.17	234	0.05
56	3.88	89	0.27	122	0.17		
57	1.13	90	0.14	123	0.94		
58	0.18	91	2.01	124	0.07		

31. 1,2-Dibromo-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (53)



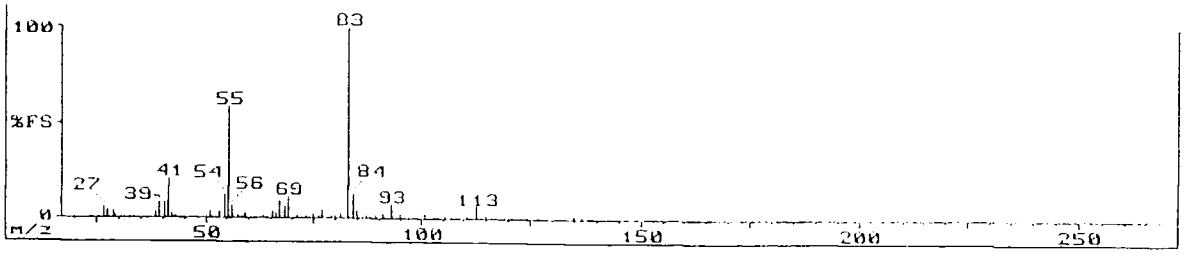
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.01	79	6.75	139	4.43	210	0.86
27	10.04	80	3.79	140	0.56	211	0.39
27	10.26	81	7.94	141	1.40	213	20.26
29	10.08	82	16.06	142	0.31	214	1.70
29	5.79	83	100.00	143	1.09	215	0.46
31	0.81	84	8.12	145	6.93	217	0.86
31	0.56	85	3.19	147	2.92	218	0.33
33	0.49	86	0.64	148	0.31	219	0.87
33	0.29	87	1.41	149	1.45	220	0.37
35	0.04	88	2.19	151	6.80	221	0.22
35	0.15	89	3.19	152	1.82	222	0.24
36	0.28	90	0.81	153	5.20	223	0.15
38	0.97	91	2.76	154	0.33	224	0.13
39	12.96	92	0.91	155	1.54	225	0.16
39	13.69	93	5.34	157	2.79	227	0.18
41	24.45	94	2.03	158	4.47	229	0.14
41	29.20	95	7.16	159	1.31	231	0.31
42	5.02	96	1.87	160	1.72	233	1.12
43	3.83	97	2.92	161	0.61	235	0.92
44	0.43	98	0.59	162	1.69	236	0.09
45	0.47	99	2.55	163	1.00	237	0.24
46	1.48	100	1.27	164	0.24	239	0.25
47	2.37	101	5.61	165	3.06	241	0.07
48	0.12	102	2.79	166	0.33	243	0.04
49	0.75	103	2.66	167	2.42	245	0.14
50	3.65	104	0.29	168	0.57	247	0.17
51	5.43	105	0.62	169	0.60	249	0.09
52	3.24	106	0.96	171	7.03	251	0.89
53	6.25	107	2.25	173	9.12	253	1.41
54	21.35	108	3.83	174	1.35	255	0.55
55	50.36	109	3.06	175	1.22	256	0.06
56	7.12	110	0.56	176	0.08	265	0.04
57	3.56	111	1.29	177	0.33	267	0.04
58	1.54	112	1.68	179	3.10	271	0.03
59	3.74	113	5.38	181	2.83	273	30.47
60	0.78	114	1.77	182	0.14	275	31.39
61	2.24	115	4.01	183	0.39	276	2.25
62	0.98	116	0.65	184	0.11	277	0.12
63	1.84	117	0.53	185	0.98	279	0.02
64	2.00	119	3.65	186	0.17	281	0.02
65	6.16	120	0.99	187	0.53	285	0.02
66	3.70	121	3.24	189	0.59	289	0.07
67	12.23	122	0.20	191	2.01	291	0.39
68	6.61	123	1.84	193	28.83	293	1.04
69	16.61	124	0.74	194	4.38	295	0.79
70	1.79	125	1.76	195	0.40	296	0.07
71	1.93	127	5.70	197	0.30	299	0.02
72	2.04	129	6.02	199	0.30	313	0.02
73	7.07	131	5.57	200	0.07	333	0.02
74	1.43	132	1.14	201	0.25	335	0.03
75	4.01	133	3.01	203	0.25	337	0.02
76	1.62	134	0.46	205	0.87	353	0.02
77	8.94	135	1.38	207	0.84		
78	1.77	137	3.01	208	0.05		

32. 1-Chloro-1-cyclohexyl-1,2,3,3,3-pentafluoro-2-iodopropane (55)



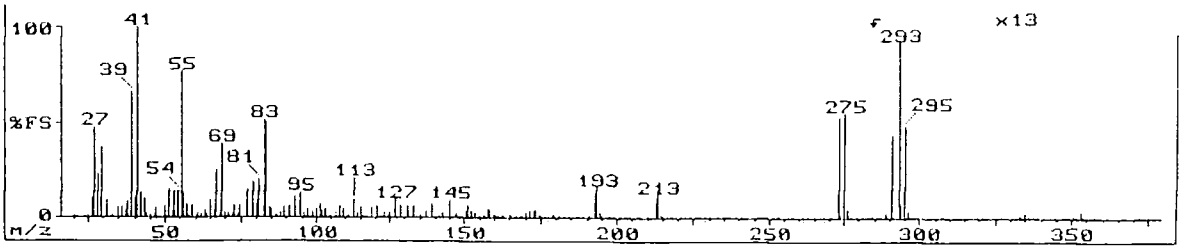
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	[illegible]	80	18.78	142	0.60	217	0.07
27	25.81	81	27.65	143	1.87	219	0.20
28	6.83	82	57.14	145	2.71	221	0.07
29	11.75	83	100.00	145	2.45	224	0.08
31	[illegible]	84	12.67	147	10.60	225	0.07
33	[illegible]	85	9.56	147	10.37	227	1.11
35	[illegible]	86	2.91	149	4.41	229	6.83
36	4.90	87	5.93	149	3.77	231	2.62
36	[illegible]	88	12.33	151	2.04	232	0.17
38	[illegible]	89	13.02	151	2.30	233	0.09
39	[illegible]	90	6.91	152	1.20	235	0.07
39	[illegible]	91	7.60	153	1.07	237	0.03
41	[illegible]	92	5.04	154	0.14	239	0.16
41	26.50	93	6.74	155	0.46	240	0.24
42	[illegible]	94	6.65	157	4.06	242	0.20
43	[illegible]	95	8.06	158	3.31	243	0.05
44	[illegible]	96	4.81	159	0.66	245	0.08
45	[illegible]	97	3.80	161	0.77	247	1.07
46	[illegible]	98	1.87	163	3.31	249	0.46
47	[illegible]	99	11.06	165	3.57	250	0.04
48	[illegible]	100	14.52	166	2.51	251	0.07
49	[illegible]	101	7.72	167	1.04	254	2.28
50	[illegible]	102	8.99	168	0.81	255	0.04
51	[illegible]	103	7.06	169	0.49	257	0.03
52	[illegible]	104	2.45	171	2.45	258	0.03
53	[illegible]	105	2.19	173	2.82	259	0.02
54	[illegible]	106	1.90	174	0.49	261	0.03
55	[illegible]	107	2.62	175	0.37	263	0.08
56	[illegible]	108	5.50	177	1.55	265	0.07
57	[illegible]	109	5.90	179	0.94	266	0.06
58	[illegible]	111	23.39	181	0.47	267	0.08
59	[illegible]	113	12.56	183	4.26	269	0.04
60	[illegible]	114	1.59	185	3.40	272	0.12
61	[illegible]	115	4.21	187	0.71	274	0.03
62	[illegible]	116	1.41	189	0.46	283	0.39
63	[illegible]	117	1.08	191	1.30	285	0.35
64	[illegible]	119	3.54	193	4.61	287	0.03
65	[illegible]	121	3.08	194	1.27	293	0.08
66	[illegible]	123	2.19	195	0.17	295	0.02
67	[illegible]	125	3.57	197	0.41	297	0.03
68	[illegible]	127	17.51	199	0.44	299	0.04
69	[illegible]	128	3.66	201	0.28	301	0.03
70	[illegible]	129	2.30	203	0.20	315	0.03
71	[illegible]	131	2.39	206	0.43	319	0.05
72	[illegible]	132	0.94	207	0.40	321	0.71
73	[illegible]	133	1.74	208	0.33	339	1.25
74	[illegible]	135	3.31	209	0.42	341	0.10
75	[illegible]	137	2.33	210	0.31	355	0.33
76	[illegible]	138	4.26	211	1.23	357	0.11
77	[illegible]	139	1.87	213	3.80	376	1.99
78	[illegible]	140	3.54	214	4.52	377	0.11
79	[illegible]	141	1.39	215	0.42	378	0.58

33. 1,2-Dichloro-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (**56**)



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.02	64	1.18	111	1.99	165	0.15
24	0.01	65	4.09	113	6.67	166	0.21
26	0.69	66	2.79	114	0.79	167	0.17
27	5.39	67	10.00	115	1.84	169	0.27
28	4.88	68	6.37	116	1.16	171	0.87
29	4.09	69	11.37	117	0.56	173	0.81
29	1.86	70	1.05	119	1.07	174	0.17
31	0.36	71	1.91	120	0.09	175	0.10
31	0.21	72	1.10	121	0.82	177	0.13
32	0.18	73	2.35	123	0.71	179	0.12
33	0.14	74	0.98	124	0.70	181	0.05
35	0.13	75	2.94	125	0.37	183	0.11
35	0.24	76	1.46	127	1.31	185	0.10
36	0.30	77	4.56	129	0.78	187	0.08
37	0.40	78	1.06	131	1.17	189	0.17
38	4.00	79	2.40	132	0.69	191	0.30
39	8.82	80	1.79	133	0.48	193	0.50
40	3.53	81	4.00	135	2.28	194	0.02
41	21.76	83	100.00	135	1.74	195	0.05
42	3.31	84	13.43	137	2.28	197	0.06
43	2.28	85	5.22	138	0.06	199	0.02
44	0.20	86	0.72	139	0.53	201	0.33
45	0.09	87	1.94	139	0.34	203	0.22
46	0.45	88	0.84	140	0.11	206	0.51
47	1.10	89	1.46	141	0.19	207	0.08
48	0.16	91	2.94	143	0.30	208	0.13
49	0.69	93	7.55	143	0.18	209	0.13
50	1.83	94	1.21	145	0.69	211	0.10
51	3.60	95	3.04	145	0.65	213	0.11
52	1.36	96	0.87	147	1.17	223	0.03
53	4.04	97	1.45	149	0.59	225	0.02
54	12.45	98	0.36	151	1.35	227	0.04
55	58.04	99	0.77	153	0.58	229	0.82
56	6.67	101	2.99	155	0.31	231	0.32
57	2.23	102	0.73	157	0.21	245	0.04
58	0.61	103	0.85	157	0.19	247	0.22
59	1.43	104	0.18	158	0.27	249	0.06
60	0.35	106	1.74	159	0.07	253	0.02
61	0.96	107	1.15	161	0.51	265	0.02
62	1.86	108	1.24	163	0.25		
63	1.05	109	1.32	165	0.28		

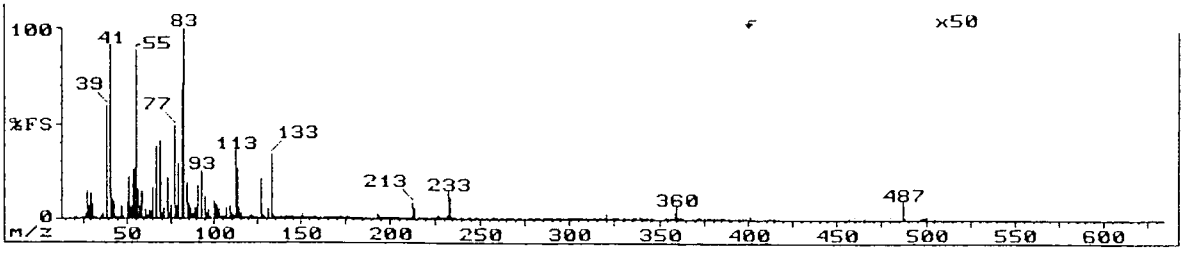
34. 1-Bromo-1-cyclohexyl-1,2,3,3,3-pentafluoro-2-iodopropane (**57**)



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.27	80	7.98	148	0.98	201	0.17
21	0.07	81	20.64	149	1.23	202	0.15
24	0.84	83	51.79	150	4.20	203	0.12
25	1.81	83	50.25	151	5.44	204	0.37
26	11.67	84	5.67	152	4.07	205	0.44
27	47.18	85	4.68	153	3.17	206	0.39
28	23.21	86	0.71	154	1.31	207	0.34
29	36.92	87	1.98	155	1.18	209	0.87
31	9.62	88	3.17	156	1.55	210	1.03
32	0.67	89	5.99	157	4.90	211	1.30
33	2.05	91	6.70	158	4.52	213	10.51
35	6.12	93	12.05	159	2.08	213	12.56
36	6.25	95	13.21	160	1.51	214	2.02
37	4.94	96	3.27	161	0.18	215	0.38
38	8.72	97	4.87	161	1.41	216	0.44
39	66.15	98	1.11	162	1.81	217	0.56
40	11.92	99	3.53	163	1.15	218	0.65
41	100.00	100	5.16	165	2.04	219	0.74
42	13.85	101	8.17	165	1.96	220	0.35
43	10.38	102	4.36	166	1.28	221	0.29
44	1.47	103	4.42	167	1.35	222	0.22
45	1.84	104	0.56	168	0.71	223	0.17
46	1.27	105	1.03	169	0.82	224	0.18
47	5.80	106	1.34	171	3.40	225	0.12
48	0.35	107	2.95	171	3.53	226	0.02
49	0.95	108	7.28	173	4.20	226	0.11
50	6.83	109	4.97	173	4.46	227	0.13
51	15.13	110	1.05	174	1.70	228	0.09
52	4.13	111	2.02	175	0.90	229	0.12
53	14.10	113	9.36	176	0.47	230	0.15
54	14.62	114	2.95	177	0.43	231	0.18
55	76.92	115	6.09	178	1.75	232	0.46
56	13.97	116	1.00	179	1.80	233	0.70
57	7.82	117	0.80	180	1.36	234	0.43
58	1.07	119	5.42	181	1.58	235	0.53
59	6.57	121	6.70	182	0.37	236	0.03
60	0.69	122	0.92	183	0.43	236	0.20
61	3.04	123	3.17	184	0.68	237	0.23
62	2.03	124	1.34	185	0.57	238	0.19
63	3.69	125	2.95	186	0.33	239	0.22
64	2.00	127	10.13	187	0.29	240	0.07
65	9.49	129	5.44	189	0.39	241	0.07
66	3.69	131	7.05	189	0.15	243	0.05
67	25.26	133	6.47	190	1.39	245	0.21
68	2.04	134	1.19	191	1.59	246	0.01
69	38.97	135	1.50	193	13.46	246	0.12
70	3.01	137	3.72	193	16.54	247	0.13
71	3.01	139	7.76	194	3.21	248	0.01
72	1.96	140	1.20	195	0.55	249	0.14
73	7.28	141	2.21	196	0.34	250	0.02
74	1.84	143	2.44	197	0.27	250	0.42
75	6.96	145	9.74	198	0.36	251	0.65
77	15.64	146	2.00	199	0.32	252	0.83
79	19.10	147	2.47	200	0.21	253	1.11

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
255	0.91	283	0.03	315	0.05	347	0.01
256	0.11	284	0.01	317	0.02	348	0.01
257	0.03	285	0.05	319	0.01	349	0.01
258	0.01	286	0.01	321	0.01	351	0.15
259	0.03	287	0.04	325	0.02	352	0.01
261	0.04	289	0.19	326	0.01	353	0.28
263	0.04	291	3.37	327	0.03	354	0.02
265	0.05	293	7.15	329	0.01	355	0.10
267	0.06	294	0.58	331	0.02	356	0.02
269	0.04	295	3.75	332	0.01	357	0.01
269	0.05	296	0.34	333	0.12	366	0.00
271	0.34	299	0.04	334	0.01	371	0.05
273	53.85	301	0.03	335	0.21	372	0.01
274	1.79	303	0.02	336	0.01	373	0.08
275	54.87	305	0.01	337	0.06	374	0.02
276	4.71	307	0.02	338	0.01	375	0.04
277	0.18	308	0.01	339	0.01		
279	0.06	311	0.03	341	0.01		
281	0.05	313	0.07	345	0.01		

35. 1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**58**)



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.23	88	2.52	147	1.15	200	0.10
21	0.02	89	5.56	147	0.69	201	0.06
24	0.14	90	5.66	148	0.33	202	0.17
25	0.34	91	17.84	150	1.35	203	0.37
26	3.33	93	25.10	150	2.57	204	0.40
27	14.71	95	11.27	151	1.35	205	0.21
28	6.76	96	2.77	153	1.02	206	0.10
29	13.73	97	5.27	153	0.98	207	0.78
31	8.14	98	0.91	154	0.85	208	0.64
32	0.67	100	9.31	155	0.53	209	0.32
33	1.18	101	7.55	156	0.48	211	0.72
35	1.19	102	6.57	158	1.54	211	1.10
36	1.57	103	4.83	158	1.62	213	8.73
37	2.52	104	1.26	159	0.64	213	5.98
39	59.22	105	1.57	161	0.19	214	0.76
41	91.37	106	0.68	161	0.11	215	0.12
42	10.20	108	5.49	163	0.44	217	0.38
43	8.53	109	7.06	163	0.39	217	0.21
44	1.31	110	0.36	165	0.78	218	0.05
45	1.29	111	2.48	165	0.63	219	0.06
46	0.73	111	2.18	167	1.07	220	0.09
47	6.76	113	36.08	167	0.88	221	0.09
48	0.33	113	26.67	168	0.86	223	0.13
50	8.43	114	5.39	169	0.55	225	0.05
51	22.45	115	2.75	171	0.69	225	0.05
52	6.67	116	1.10	171	0.65	226	2.01
53	25.88	117	0.61	173	1.96	227	1.72
54	26.67	119	1.24	173	1.22	228	0.22
55	88.63	119	1.16	174	0.34	229	0.09
56	15.78	121	2.43	175	0.22	230	0.10
57	6.86	121	1.94	177	2.23	231	1.44
59	14.31	123	1.45	177	1.19	231	2.13
60	1.25	123	0.90	178	0.29	233	14.51
61	5.12	125	0.71	179	0.21	233	11.96
62	2.03	125	0.63	180	0.21	234	1.12
63	4.80	127	21.18	181	0.23	235	0.10
64	4.07	128	1.99	182	0.34	237	0.02
65	16.57	129	1.22	183	0.25	238	0.26
67	38.04	131	5.83	185	0.50	239	0.30
67	25.88	131	3.82	185	0.38	240	0.04
69	40.39	133	33.73	186	0.28	241	0.06
70	2.45	133	21.67	187	0.16	243	0.14
71	5.37	134	2.23	189	0.34	244	0.02
73	21.27	135	0.38	189	0.43	245	0.30
74	2.75	137	0.45	191	0.65	247	0.17
75	6.96	137	0.35	191	0.55	248	0.01
77	49.02	139	1.15	193	2.65	249	0.10
78	7.06	139	1.21	193	3.06	249	0.08
79	29.02	141	1.20	194	1.64	251	0.03
81	70.98	141	1.57	195	0.64	253	0.93
83	100.00	142	1.21	196	0.37	254	0.72
84	18.53	143	0.48	197	0.18	256	0.01
85	7.45	145	1.79	198	0.14	257	0.36
87	5.59	145	1.31	199	0.08	258	0.34

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
259	0.19	293	0.08	330	0.02	379	0.01
260	0.02	294	0.02	331	0.03	381	0.03
261	0.07	295	0.05	333	0.02	383	0.01
263	0.03	296	0.01	335	0.05	385	0.02
265	0.03	297	0.03	336	0.02	386	0.01
266	0.14	299	0.48	337	0.02	387	0.02
267	0.09	300	0.03	339	2.08	389	0.02
267	0.14	301	0.07	340	0.18	393	0.02
268	0.10	302	0.02	341	0.32	395	0.01
269	0.09	303	0.02	342	0.04	397	0.01
271	0.08	304	0.06	343	0.05	399	0.04
272	0.02	305	0.03	345	0.05	401	0.03
273	0.13	306	0.06	346	0.01	411	0.01
275	0.03	307	0.02	354	0.64	413	0.02
275	0.04	309	0.02	355	0.02	415	0.01
277	0.32	311	0.04	357	0.15	457	0.01
278	0.39	313	0.05	358	0.17	465	0.01
279	0.07	314	0.02	359	3.82	487	0.19
281	0.31	316	0.06	360	6.96	488	0.02
282	0.02	317	0.04	361	0.57	497	0.01
283	0.03	318	0.03	362	0.04	498	0.01
285	0.36	319	0.09	363	0.02	499	0.03
286	0.04	321	3.33	369	0.03	500	0.01
287	0.09	322	0.23	371	0.02	501	0.05
288	0.02	323	0.02	372	0.02	505	0.01
289	0.05	325	0.08	373	0.02	625	0.01
291	0.03	326	0.01	375	0.03	627	0.01
292	0.01	327	0.02	377	0.01		

C. IR Spectra

Chapter 2

1. 1-Cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**)
2. 1,1,2,3,3,3-Hexafluoro-1-[x-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl]propane (x=2,3,4) (**9**)
3. 1,1,2,3,3,3-Hexafluoro-1-[*trans*-4-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl]propane (**9a**)
4. 1-Cyclohexyl-1,1,3,3,3-pentafluoropropane (**12**)
5. 1,1,3,3,3-Pentafluoro-1-[x-(1,1,3,3,3-pentafluoropropyl)cyclohexyl]propane (x=2,3,4) (**13**)
6. 1,1,3,3,3-Pentafluoro-1-[*trans*-4-(1,1,3,3,3-pentafluoropropyl)cyclohexyl]propane (**13a**)

Chapter 3

7. 2-Cyclohexyl-1,1-difluoroethane (**18**) and 1-Cyclohexyl-1,1-difluoroethane (**19**)
8. 2-Chloro-1-cyclohexyl-1,1,2-trifluoroethane (**20**)
9. 2,2-Dichloro-1-cyclohexyl-1,1-difluoroethane (**21**)
10. 2-Chloro-1-cyclohexyl-1,1-difluoroethane (**23**)
11. 2-Bromo-1-cyclohexyl-1,1,2-trifluoroethane (**26**)
12. 2-Bromo-1-cyclohexyl-1,1-difluoroethane (**28**)

Chapter 4

13. (1*Z*)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**)
14. (1*Z*)-1-Cyclohexyl-1,3,3,3-tetrafluoroprop-1-ene (**34**)
15. (1*E*) and (1*Z*)-2-Chloro-1-cyclohexyl-1,2-difluoroethene (**35a**) and (**35b**)
16. (1*Z*)-2,2-Dichloro-1-cyclohexyl-1-fluoroethene (**36**)
17. (1*Z*)-2-Chloro-1-cyclohexyl-1-fluoroethene (**38**)

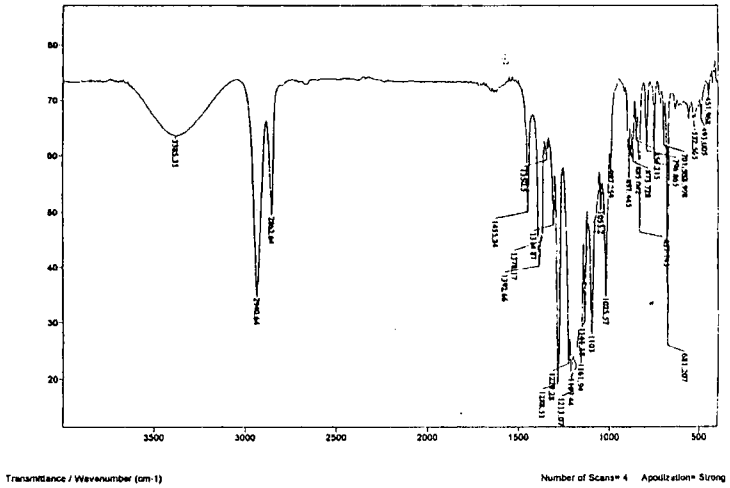
Chapter 5

18. (1*Z*)-1-Cyclohexyl-1-methoxy-2,3,3,3-tetrafluoroprop-1-ene (**39a**)
19. (1*Z*)-1-Cyclohexyl-1-ethoxy-2,3,3,3-tetrafluoroprop-1-ene (**33**)
20. (1*Z*)-1-Cyclohexyl-1-cyclohexyloxy-2,3,3,3-tetrafluoroprop-1-ene (**40**)
21. (2*E*)-3-Cyclohexyl-1,1,1,2-tetrafluorohept-2-ene (**41a**)
22. (1*Z*) and (1*E*)-1-Cyclohexyl-2,3,3,3-tetrafluoroprop-1-ene (**45a**) and (**45b**)
23. (1*Z*) and (1*E*)-1-Cyclohexyl-1-methoxy-3,3,3-trifluoroprop-1-ene (**46**)
24. 1-Cyclohexyl-2-fluoro-2-(trifluoromethyl)pent-4-en-1-one (**48**)
25. 1-Cyclohexyl-2-fluoro-3-methyl-2-(trifluoromethyl)pent-4-en-1-one (**49**)
26. 1-Cyclohexyl-2-fluoro-2-(trifluoromethyl)penta-3,4-dien-1-one (**50**)
27. 1-Cyclohexyl-2-(trifluoromethyl)pent-4-en-1-one (**52**)

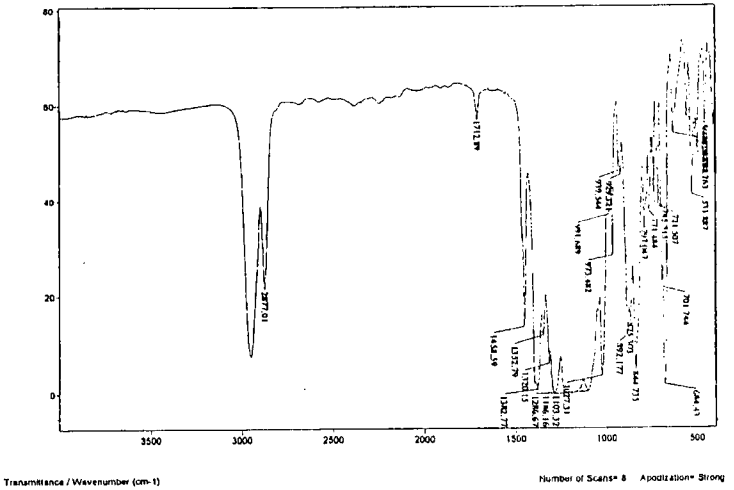
Chapter 6

28. 1,2-Dibromo-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (**53**)
29. 1-Chloro-1-cyclohexyl-1,2,3,3,3-pentafluoro-2-iodopropane (**55**)
30. 1,2-Dichloro-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (**56**)
31. 1-Bromo-1-cyclohexyl-1,2,3,3,3-pentafluoro-2-iodopropane (**57**)
32. 1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**58**)

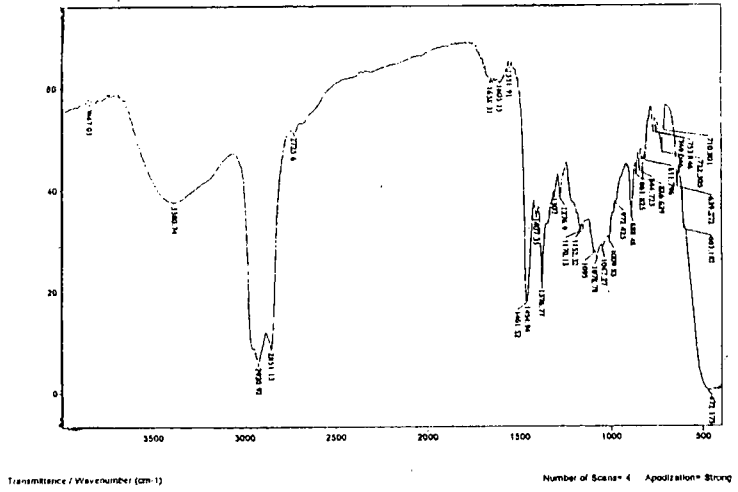
1. 1-Cyclohexyl-1,1,2,3,3,3-hexafluoropropane (**8**)



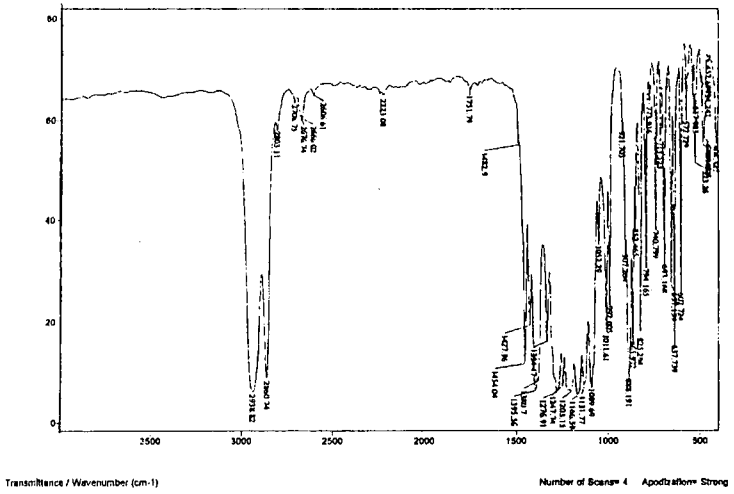
2. 1,1,2,3,3,3-Hexafluoro-1-[x-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl]propane (x=2,3,4) (**9**)



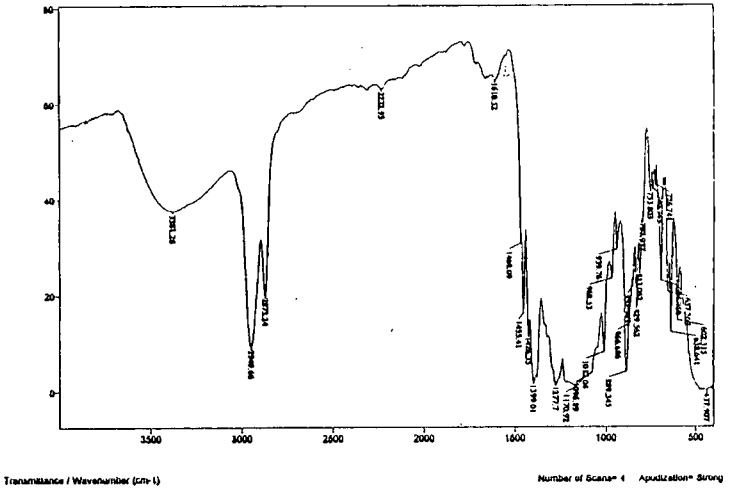
3. 1,1,2,3,3,3-Hexafluoro-1-[*trans*-4-(1,1,2,3,3,3-hexafluoropropyl)cyclohexyl]propane (**9a**)



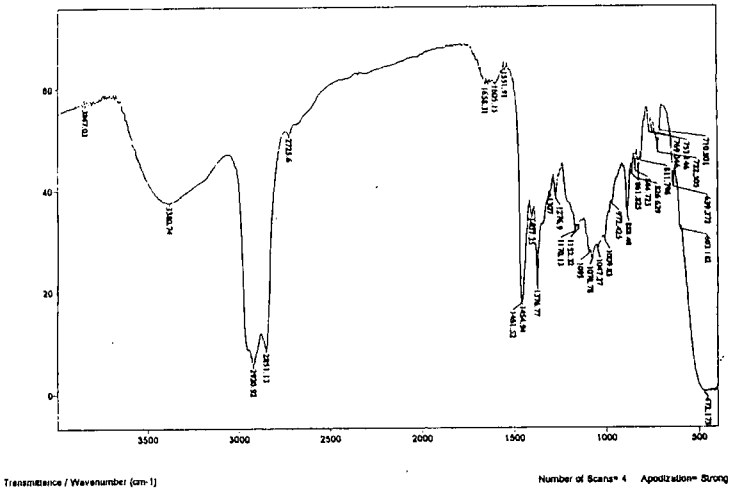
4. 1-Cyclohexyl-1,1,3,3,3-pentafluoropropane (**12**)



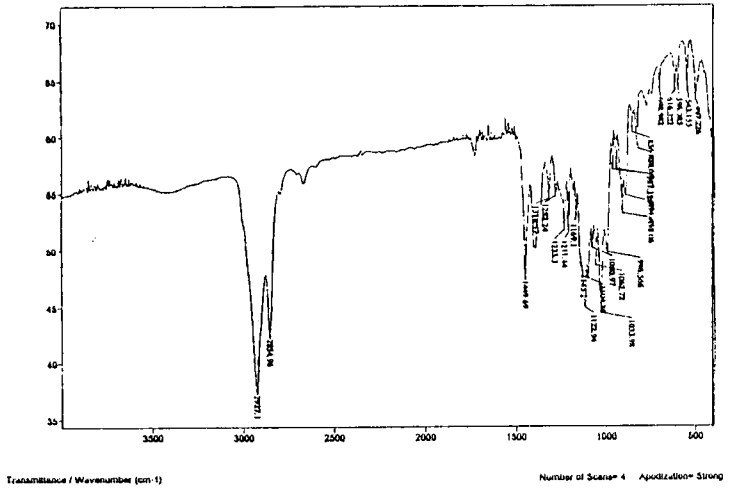
5. 1,1,3,3,3-Pentafluoro-1-[x-(1,1,3,3,3-pentafluoropropyl)cyclohexyl]propane (x=2,3,4) (**13**)



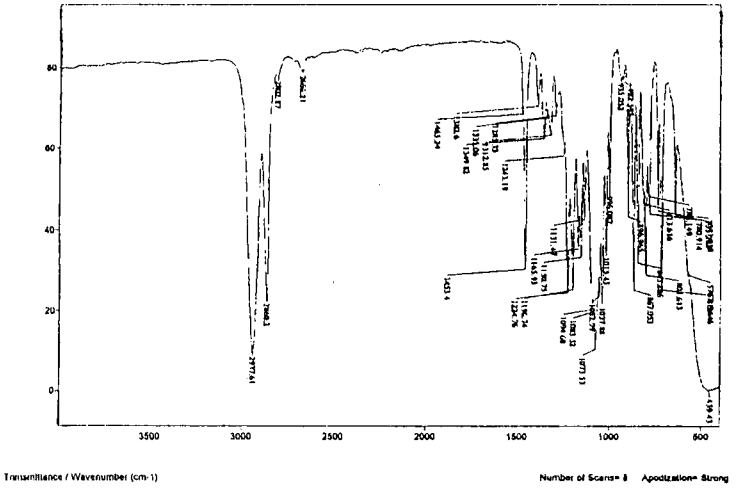
6. 1,1,3,3,3-Pentafluoro-1-[*trans*-4-(1,1,3,3,3-pentafluoropropyl)cyclohexyl]propane (**13a**)



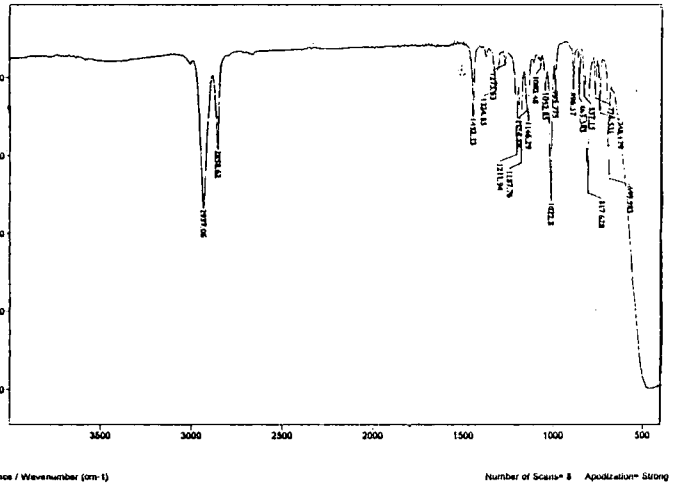
7. 2-Cyclohexyl-1,1-difluoroethane (**18**) and 1-Cyclohexyl-1,1-difluoroethane (**19**)



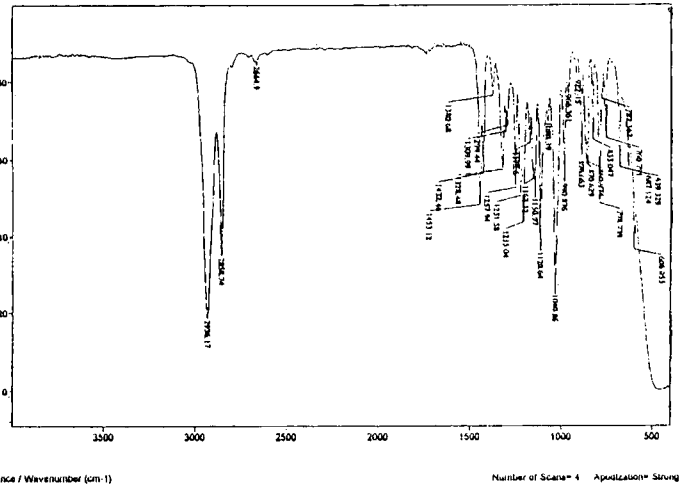
8. 2-Chloro-1-cyclohexyl-1,1,2-trifluoroethane (**20**)



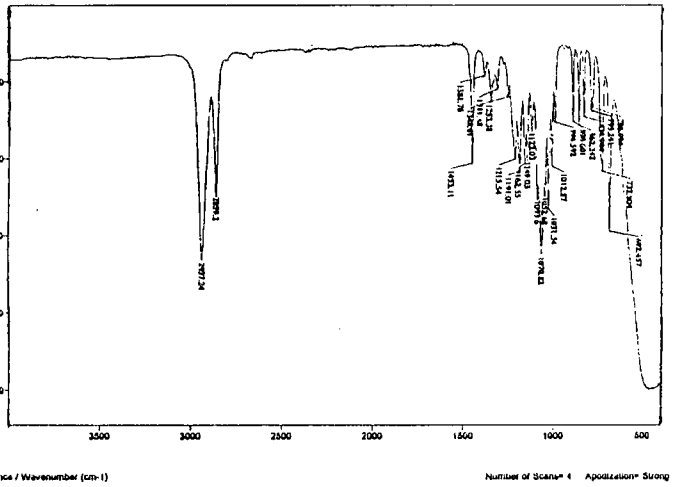
9. 2,2-Dichloro-1-cyclohexyl-1,1-difluoroethane (**21**)



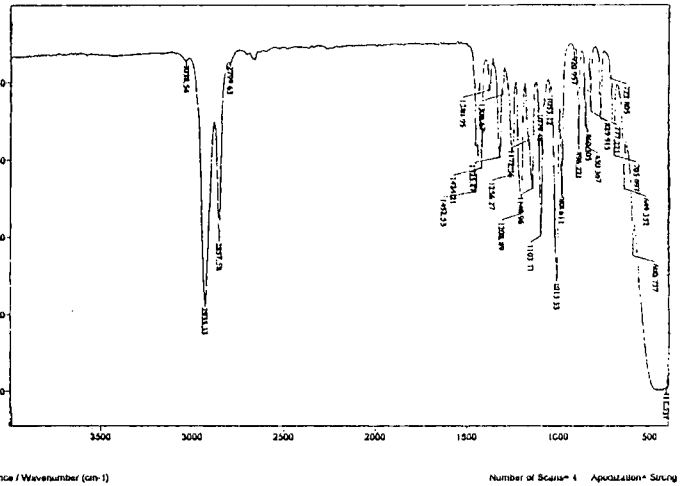
10. 2-Chloro-1-cyclohexyl-1,1-difluoroethane (**23**)



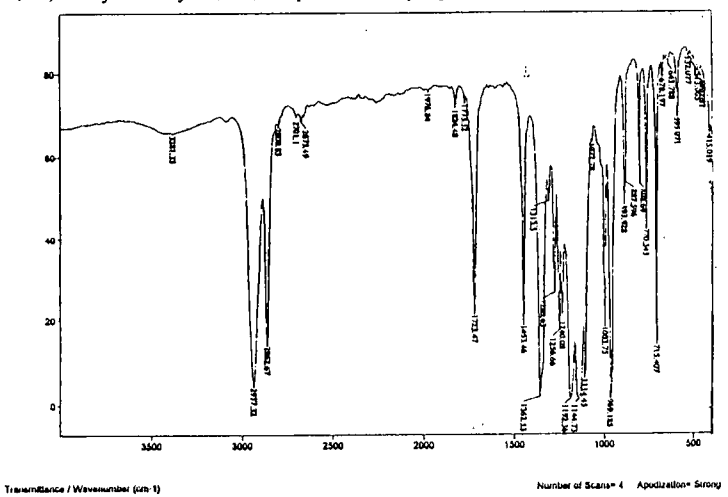
11. 2-Bromo-1-cyclohexyl-1,1,2-trifluoroethane (**26**)



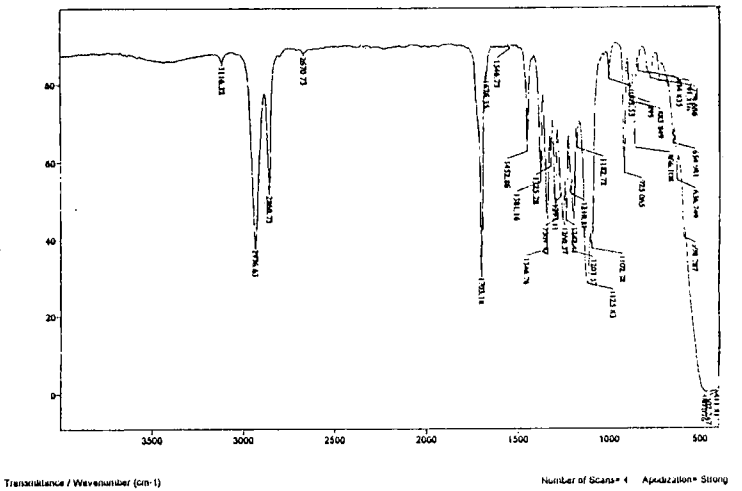
12. 2-Bromo-1-cyclohexyl-1,1-difluoroethane (**28**)



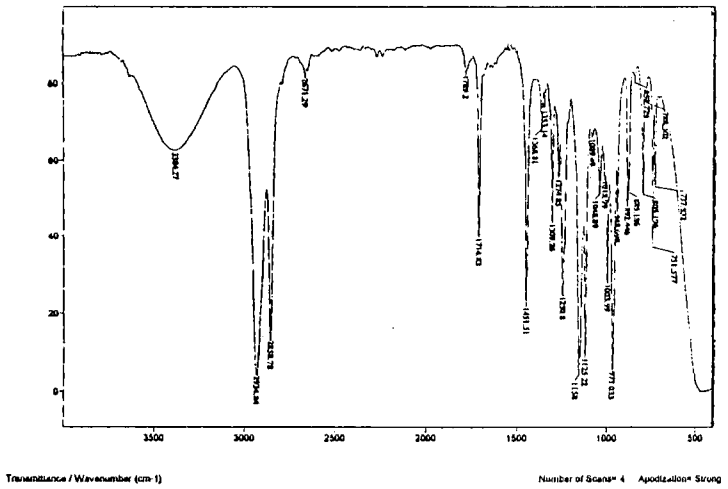
13. (1*Z*)-1-Cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**32a**)



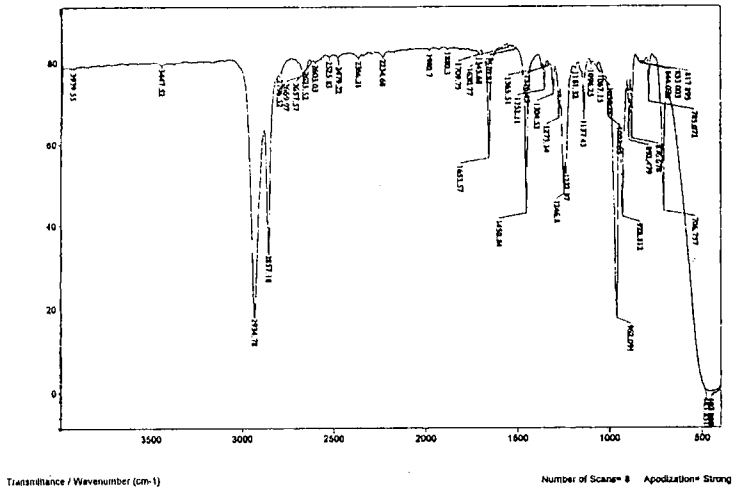
14. (1Z)-1-Cyclohexyl-1,3,3,3-tetrafluoroprop-1-ene (**34**)



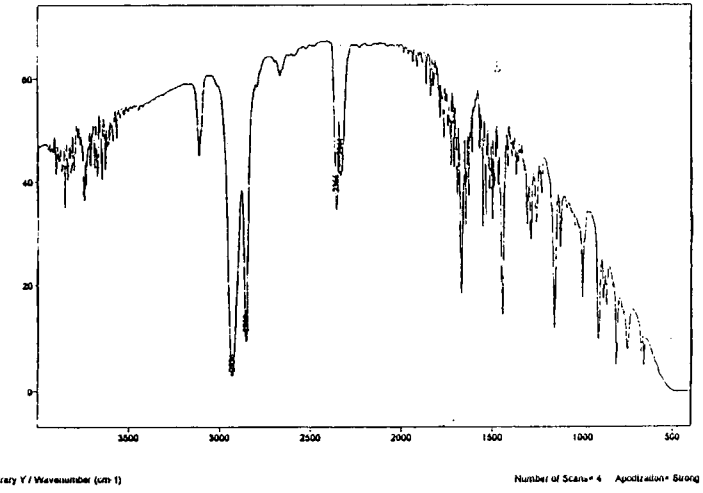
15. (1*E*) and (1Z)-2-Chloro-1-cyclohexyl-1,2-difluoroethene (**35a**) and (**35b**)



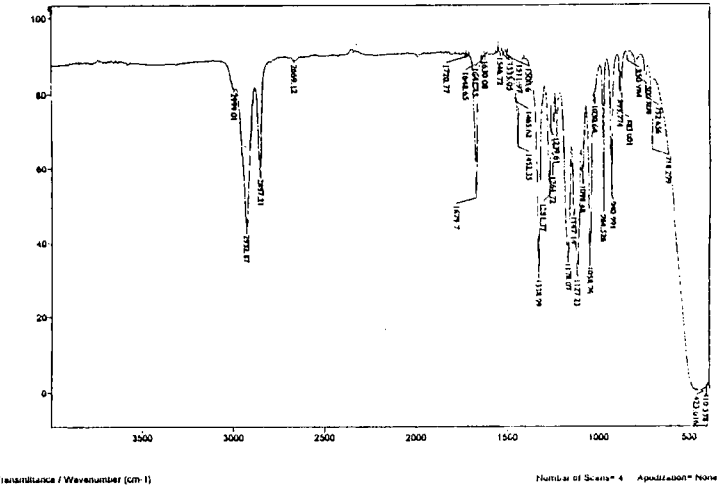
16. (1Z)-2,2-Dichloro-1-cyclohexyl-1-fluoroethene (**36**)



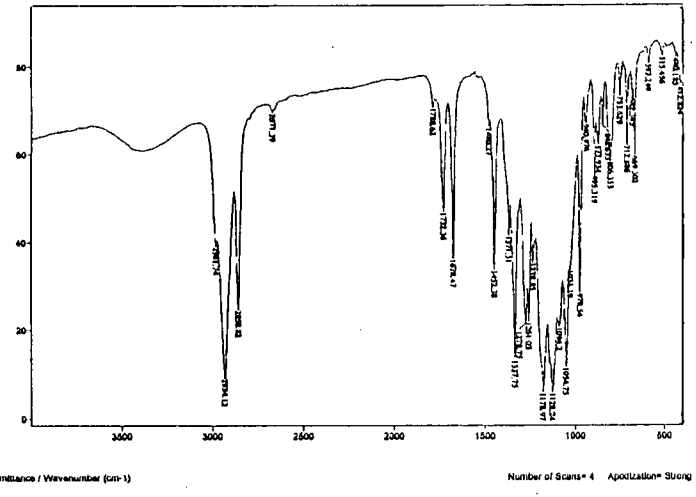
17. (1Z)-2-Chloro-1-cyclohexyl-1-fluoroethene (**38**)



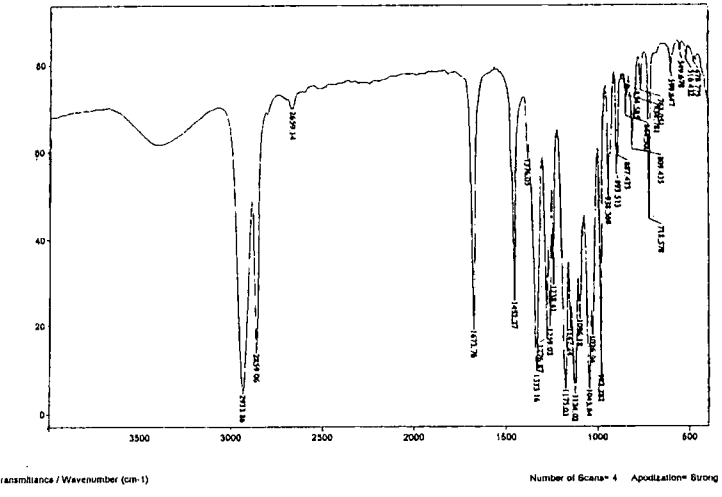
18. (1Z)-1-Cyclohexyl-1-methoxy-2,3,3,3-tetrafluoroprop-1-ene (**39a**)



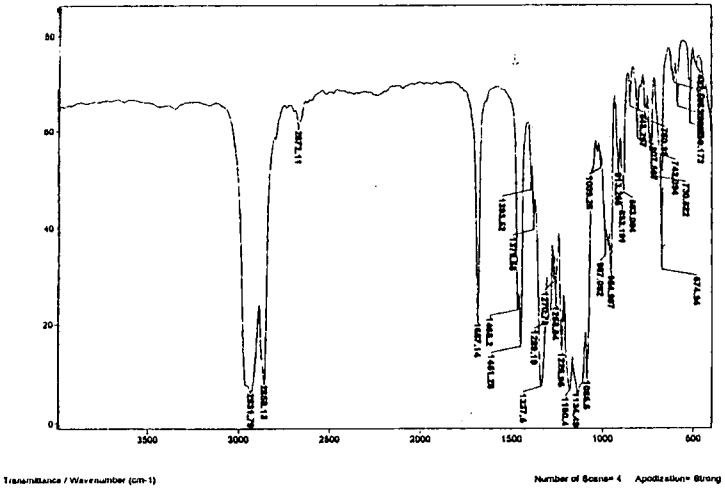
19. (1Z)-1-Cyclohexyl-1-ethoxy-2,3,3,3-tetrafluoroprop-1-ene (**33**)



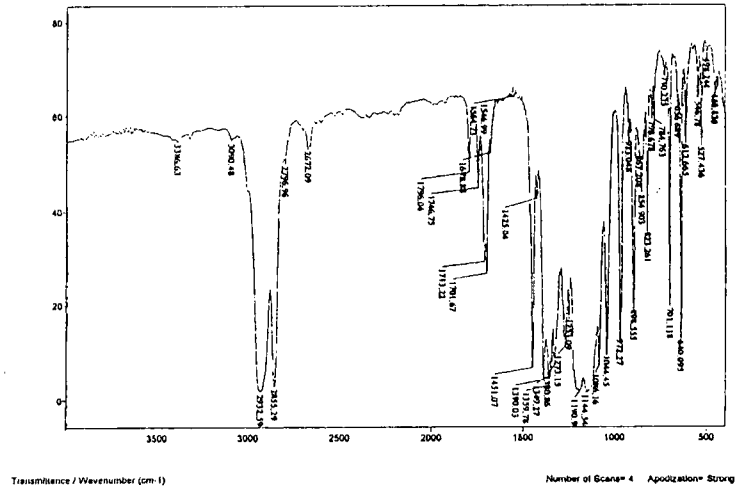
20. (1Z)-1-Cyclohexyl-1-cyclohexyloxy-2,3,3,3-tetrafluoroprop-1-ene (**40**)



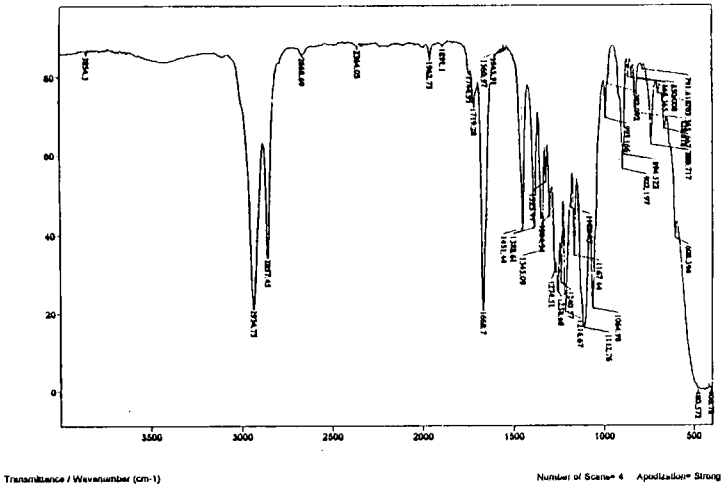
21. (2*E*)-3-Cyclohexyl-1,1,1,2-tetrafluorohept-2-ene (**41a**)



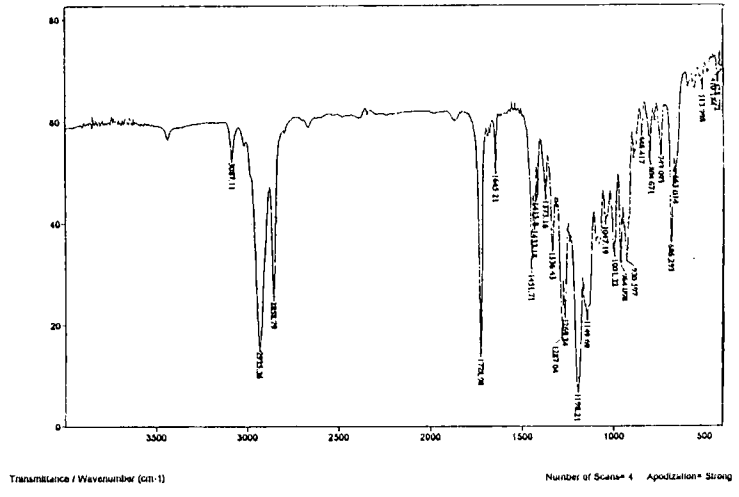
22. (1*Z*) and (1*E*)-1-Cyclohexyl-2,3,3,3-tetrafluoroprop-1-ene (**45a**) and (**45b**)



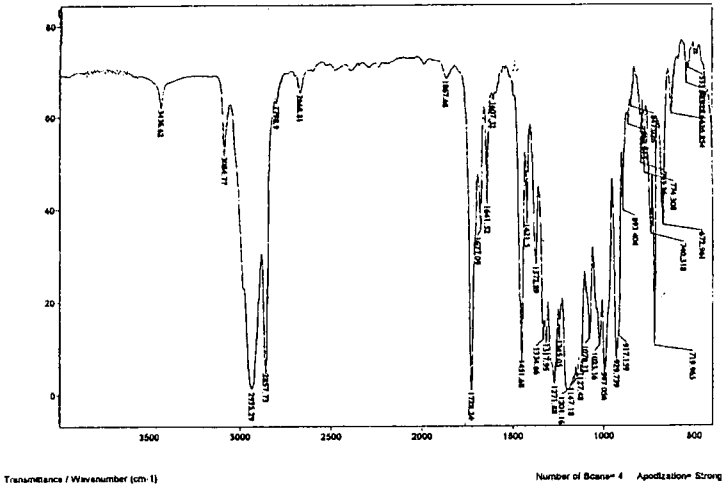
23. (1*Z*) and (1*E*)-1-Cyclohexyl-1-methoxy-3,3,3-trifluoroprop-1-ene (**46**)



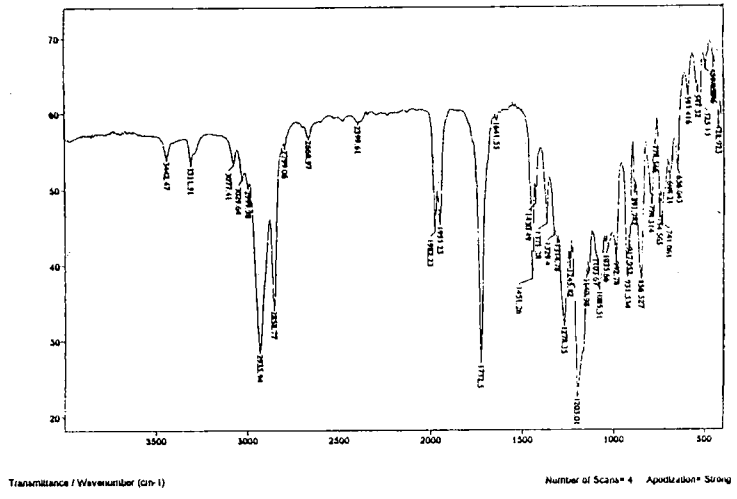
24. 1-Cyclohexyl-2-fluoro-2-(trifluoromethyl)pent-4-en-1-one (**48**)



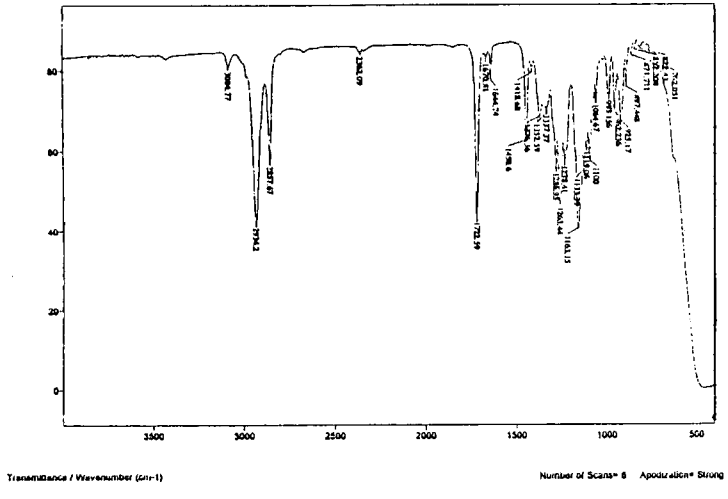
25. 1-Cyclohexyl-2-fluoro-3-methyl-2-(trifluoromethyl)pent-4-en-1-one (**49**)



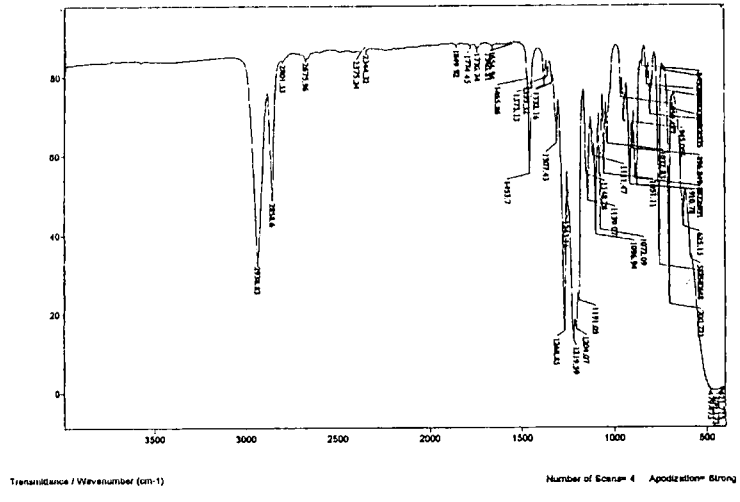
26. 1-Cyclohexyl-2-fluoro-2-(trifluoromethyl)penta-3,4-dien-1-one (**50**)



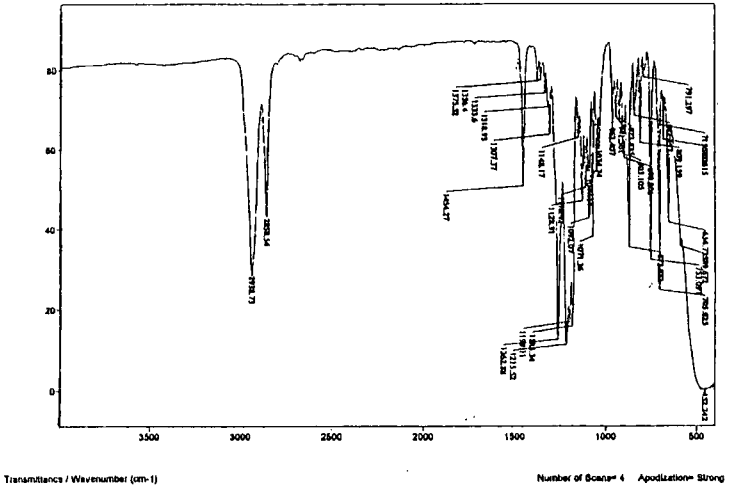
27. 1-Cyclohexyl-2-(trifluoromethyl)pent-4-en-1-one (**52**)



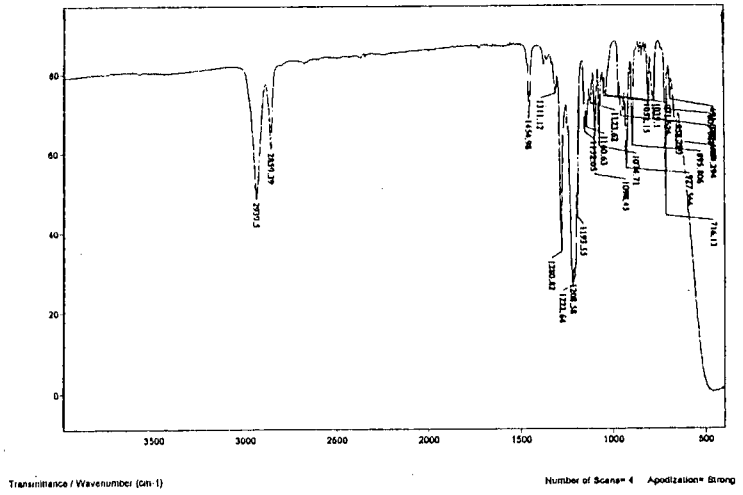
28. 1,2-Dibromo-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (**53**)



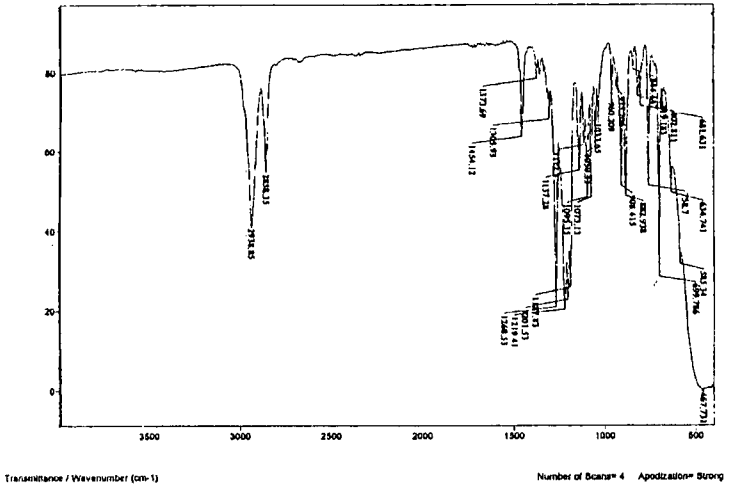
29. 1-Chloro-1-cyclohexyl-1,2,3,3,3-pentafluoro-2-iodopropane (55)



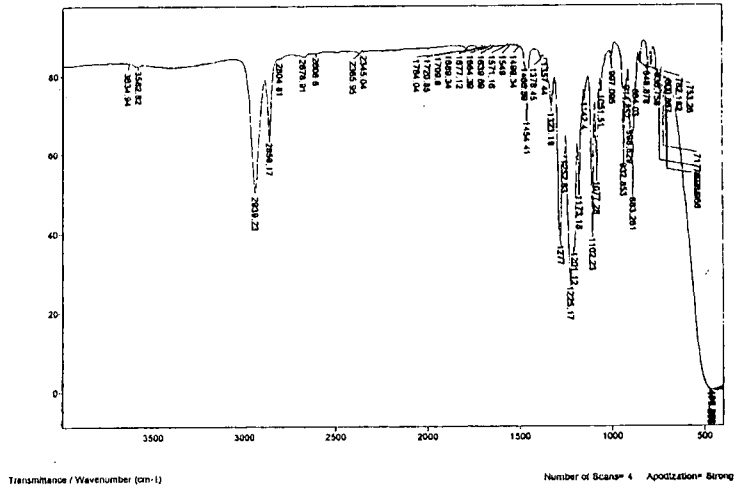
30. 1,2-Dichloro-1-cyclohexyl-1,2,3,3,3-pentafluoropropane (56)



31. 1-Bromo-1-cyclohexyl-1,2,3,3,3-pentafluoro-2-iodopropane (57)



32. 1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (58)



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