Novel fluorocarbon iodides

Copin, Elodie

UNIVERSITY OF DURHAM

A THESIS

entitled

NOVEL FLUOROCARBON IODIDES

Submitted by

ELODIE COPIN

(Graduate Society)

A candidate for the degree of Doctor of Philosophy

Department of Chemistry

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To Patrick and Thibault

"I got off at Durham... and fell in love with it instantly in a serious way. Why, it's wonderful a perfect little city.... If you have never been to Durham, go there at once. Take my car. It's wonderful."

Bill Bryson, Notes from a Small Island, 1995

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Memorandum

The work described within this thesis was carried out at the University of Durham between October 1999 and December 2002. 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 and 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, J. A. Cooper, E. Copin and G. Sandford, *Chem. Commun.*, 2001, 2428
- J. A. Cooper, E. Copin and G. Sandford, *J. Fluorine Chem.*, **115**, 2002, 83

and has been presented at :

- Poster Session, RSC Fluorine Subject Group, Postgraduate Meeting, University of Leicester, September 2001
- Avecia Poster Session, University of Durham, December 2001

Nomenclature and abbreviations

Note that fluorine in the centre of a ring denotes that all of the hydrogen atoms have been replaced by fluorine.

The following abbreviations are used :

AIBN	Azobis(isobutyro)nitrile
DTBP	Di-*tert*-Butyl Peroxide
DBPO	Di-Benzoyl Peroxide
GLC/MS	Gas-liquid Chromatography/ Mass Spectrometry
HFP	Hexafluoropropene
IR	Infrared
NMR	Nuclear Magnetic Resonance
THF	Tetrahydrofuran

Statement of copyright

Abstract

Novel fluorocarbon iodides

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This work describes the three-step synthesis of some new fluorocarbon iodides. First, functionalisations of carbon-hydrogen bonds, using fluorinated alkenes via a free radical chain mechanism, were carried out.

$$RH \xrightarrow[F_2C{=}CFCF_3\ (HFP)]{\text{radical initiator}} RCF_2CFHCF_3$$

The HFP-adducts were then further functionalised by elimination of hydrogen fluoride to yield a series of fluoroalkenes, which were then converted to fluorocarbon iodides by means of a mixture of IF_5/I_2 (corresponding to iodine monofluoride formed *in situ*).

$$RCF_2CFHCF_3 \xrightarrow{-\ HF} RCF{=}CF(CF_3) \xrightarrow[\text{"IF"}]{(IF_5/I_2)} RCF_2CFICF_3$$

Chemistry of the new fluorocarbon iodides was investigated, especially in reactions with thiols.

$$RCF_2\text{-}CFI\text{-}CF_3 \xrightarrow{R'SH} RCF_2\text{-}\underset{\displaystyle SR'}{\underset{|}{CF}}\text{-}CF_3$$

1. Introduction

1.1. General introduction to organofluorine chemistry.

1.1.1. Fluorine in organic chemistry.

Compounds containing fluorine-carbon bonds are extremely rare in nature, and consequently introduction of fluorine into organic compounds leads to a potentially vast 'man-made' organic chemistry.[1] Because of its unique properties (some of them are listed below), fluorine modifies the chemical and biological activities of organic compounds.[2]

1) The fluorine atom is relatively small with its Van der Waals radius close to that of oxygen (H, 1.20 Å ; F, 1.47 Å; Cl, 1.75 Å; O, 1.52 Å).[3] Therefore, steric effects arising from the introduction of a fluorine atom are unlikely to disturb the structure any more than the introduction of oxygen.

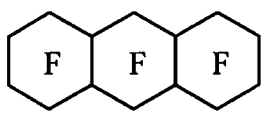
2) The carbon-fluorine bond is the strongest single bond to carbon (485 kJ mol^{-1}) in organic chemistry. This accounts for the chemical and thermal stability of some perfluorocarbons.

3) Fluorine is the most electronegative element and so C-F bonds are polarised.

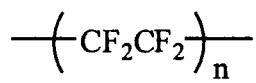
1.1.2. Applications.

Fluorine containing compounds have a wide range of industrial applications, including pharmaceuticals, and some examples are shown below.

Perfluorinated compounds can be used as inert fluids and for coatings.

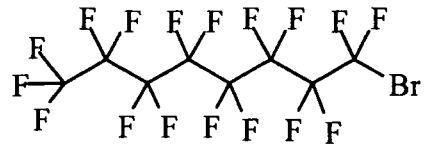


inert fluids



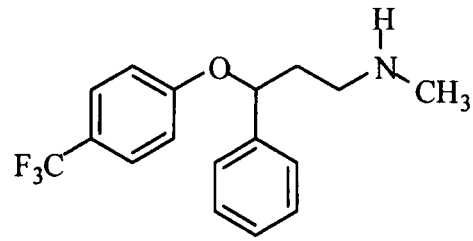
non stick surfaces

Perfluorochemicals (PFCs) have also been used as 'blood substitutes' and oxygen carriers. For example, perflubron is the major component in a commercial O_2-carrying emulsion ("Oxygent") produced in the USA.[4]



Perflubron

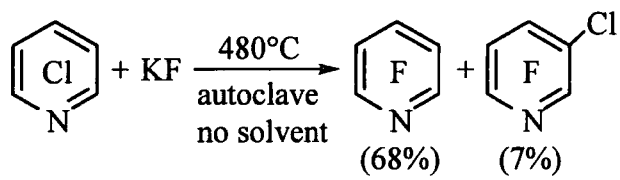
Molecules containing even a single fluorinated group, especially a trifluoromethyl group, can show high biological activity. For example: the antidepressant Prozac™.



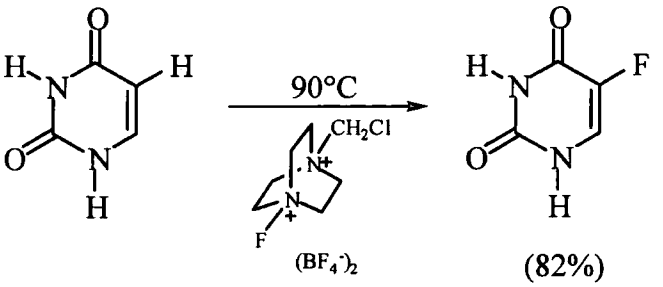
Prozac™

1.1.3. Aims of the project.

Two general approaches may be used to introduce fluorine into organic molecules: fluorination (i.e. creation a new C-F bond) and the introduction of a group that contains fluorine (i.e. creation of a new C-C bond). As a complete discussion of the formation of C-F bonds is beyond the scope of our project, only few examples of fluorination are presented here. Chambers[5] has, for example, developed an efficient route to pentafluoropyridine from pentachloropyridine using potassium fluoride.



Selective fluorination has also been used to form some new C-F bonds and has been successful, for example, in the synthesis of the commercially available 5-fluorouracil, an anti cancer agent.



The second approach to introducing fluorine into an organic compound is the "building block" approach (i.e. introduction of a group that contains fluorine atoms).[6] Fluoroalkyl groups can be introduced by a wide range of methods including electrophilic, nucleophilic and radical processes (For a review see Spink[7]). This project is concerned with the introduction of fluoroalkyl groups *via* radicals. Insertion of fluorinated alkenes into carbon-hydrogen bonds, via a free-radical chain mechanism, have first been performed. A new perfluoroalkyl iodide has also been used in free-radical addition to alkenes and in radical nucleophilic substitution ($S_{RN}1$) by thiols.

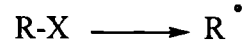
The introduction will therefore include some general principles of free-radical chemistry, a review of free-radical additions to fluoroalkenes, and a review of fluorinated alkyl iodides reactions, with an emphasis on perfluoalkylation of thiols by the $S_{RN}1$ process.

1.2. Free radical chemistry

1.2.1. Mechanism.

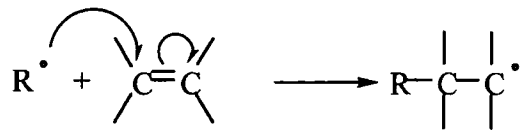
A free-radical chain reaction involves three important steps: initiation, propagation and termination, as represented below.

Initiation (creation of the first radical of the chain)

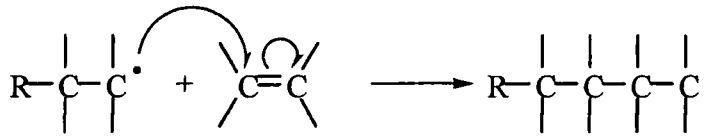


Propagation

Addition

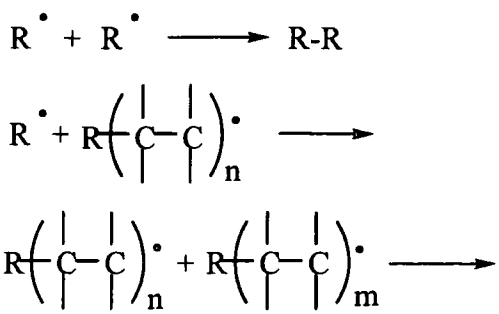


Telomerisation



Chain transfer

Termination (Recombination of two radicals)



In a free-radical chain mechanism, the propagation step consists of a succession of elementary reactions (addition, telomerisation and chain transfer). The first radical gives rise to one or more of those reactions before being regenerated, and we will first discuss the generation and stability of radicals.

1.2.2. Fluoroalkyl radicals

i. How to produce perfluoroalkyl radicals?

The first step of a radical chain reaction is the initiation, in other words: the production of radicals and numerous methods have been developed for this purpose.[8] Methods include thermal, photochemical (UV light) and chemical initiation, as well as chemical reduction, electrochemical methods and γ-irradiation. In this project, γ-rays, chemical initiation (DTBP, AIBN) and SET process (in the perfluoroalkylation of thiols) have been used to initiate the radical reactions.

Gamma irradiation

γ-Rays produced by a cobalt-60 source have been used to initiate some of the radical reactions presented in the current project. With this initiation method, the reaction duration and temperature can be easily varied. γ-Rays do not directly homolytically cleave the substrate, but instead the cobalt-60 source is encased in a steel sheath, which absorbs the radiation and produces secondary electrons. These secondary electrons interact with the organic substrate to produce excited molecules, which dissociate into radicals.

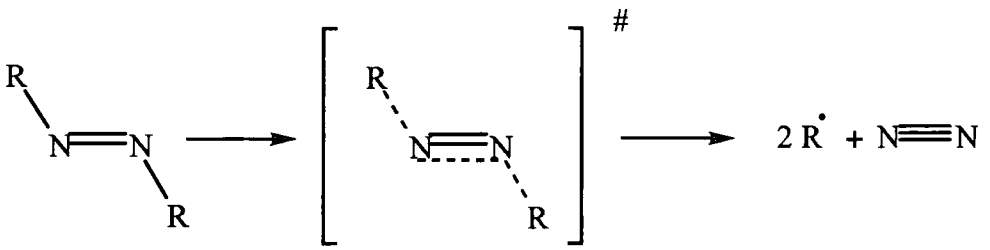
Chemical initiation

Chemical initiation involves thermal decomposition of molecules that have a weak bond, such as in peroxides and azo compounds. The O-O bonds of peroxides are easily cleaved homolytically upon heating to give radicals, which then react with the substrate.

$$^{t}BuO\text{-}O^{t}Bu \xrightarrow{\Delta} 2\ ^{t}BuO\bullet$$

$$^{t}BuO\bullet + R\text{-}H \longrightarrow R\bullet + {}^{t}BuOH$$

Di-benzoyl peroxide (DBPO) and di-*tert*-butyl peroxide (DTBP) are the most commonly used peroxides because of their stability (several months in the refrigerator) and ease of handling. Reactions with DBPO and DTBP are generally carried out at 80°C and 140°C respectively, at which temperature their half-lives are about 4 hours. Azobis(isobutyro)nitrile (AIBN) is also a common initiator because of its moderate decomposition temperature and at 70°C has a half-life of about 5 hours.



Chemical reduction (SET)

Various single electron reductants such as metals or anionic species have been used to initiate addition processes or substitutions processes ($S_{RN}1$). The mechanism will be fully explained later. Perfluoroalkylation of thiols is a good example of such a process.

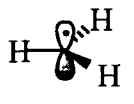
$$M\ (or\ Nu^-) + R_FI \rightarrow M^+\ (or\ Nu^{\bullet}) + R_FI^{\bullet -} \rightarrow R_F^{\bullet}$$

ii. Structure and stability of fluoroalkyl radicals

Fluorine is inductively withdrawing and π-donating. Thus its influence upon structure and reactivity of radicals, usually considered to derive largely from electronic effects, is a complex interplay of disparate interactions.

Structure

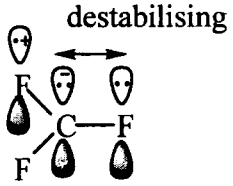
Fluorine substituents have a dramatic effect on the shape of the radical. The methyl radical is planar, whereas substitution of hydrogen atoms by increasing numbers of fluorine results in increasing pyramidal shape, with increasing barriers to inversion.[9]



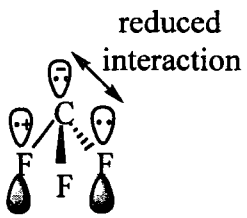
planar $CH_3^{\bullet}$

tetrahedral $CF_3^{\bullet}$

ESR spectroscopy, a useful indicator of a radical's geometry, allowed calculations of some barriers to inversion, with barriers of 1, 7 and 25 kcal mol^{-1} being calculated for CH_2F, CHF_2 and CF_3 respectively[10] and this confirms that fluorine substituents disfavour radical planarity. The loss of planarity may be explained by electron pair repulsion, as represented in the following schemes.



Planar
(e-pair repulsion greater)



Tetrahedral

In terms of frontier orbital theory, pyramidalization of a radical occurs when it can lead to mixing of the SOMO with the LUMO. Being extremely electronegative, fluorine substituents lower the LUMO energy more than any other substituent and consequently have a strong influence on non-planarity.[11]

Radical stabilities.

The influence of fluorine substituents on radical stability results from a 'complex interplay of inductive and resonance effects' and is the subject of much debate.[11, 12] Even if simple orbital theory predicts that anything that would stabilise an anion or a cation will stabilise a radical, fluorine substituents seem to have a more complicated influence on radical stability. Moreover, the influence of multiple fluorine substituents is not additive and cannot be derived from understanding the effect of a single fluorine atom.

Relative values of bond dissociation energies (BDEs) are usually used to provide a measure of the relative inherent stability of free radicals. The higher the BDEs values, the less stable the radical, although it has been claimed that relative BDEs values do not

provide such a measure.[13] The C-H BDEs for fluorinated methanes[14] and ethanes[15] have been reported in the literature and are presented in the following tables (table 1.1 and table 1.2).

Table 1.1 C-H BDEs of fluorinated methanes

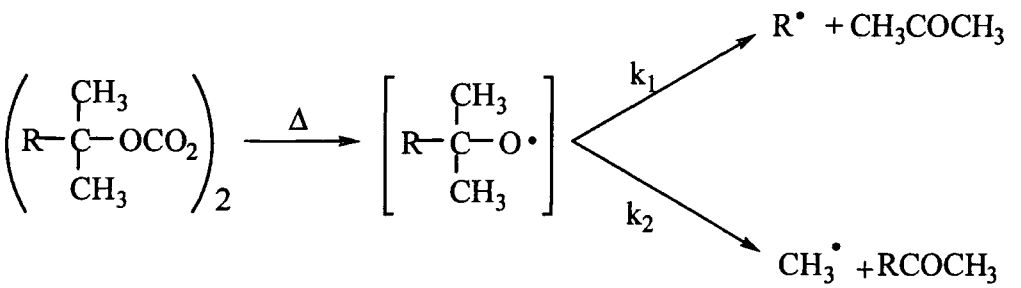
Methane	CH_3-H	CH_2F-H	CHF_2-H	CF_3-H
BDE	104.8 ± 0.2	101.2 ± 2	103.2 ± 2	106.7 ± 1

Table 1.2 Calculated C-H BDEs of fluorinated ethanes

Ethane	CH_3CH_2-H	CH_2FCH_2-H	CHF_2CH_2-H	CF_3CH_2-H
BDE	97.7	99.6	101.3	102

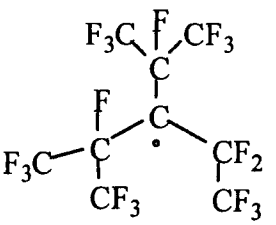
From this data, it can be concluded that a single α-fluorine substituent or two α-fluorine substituents provide a small stabilisation compared to hydrogen, whereas a trifluoromethyl radical is destabilised compared to a methyl radical. Moreover, β-fluorine substituents appear to be destabilising relative to hydrogen.

Radical fragmentation of a series of fluorinated *tert*-butoxy radicals gave experimental support for an order of stability : $CF_3 < CH_3 < CHF_2 \cong CH_2F$.

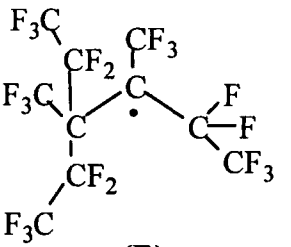


R	CH_3	CH_2F	CHF_2	CF_3
k_{rel} (k_1/k_2)	1.0	9.0	10.2	0.08

Most fluorinated radicals are kinetically reactive and cannot be isolated. However few examples of stable perfluoroalkyl radicals, prepared by addition of elemental fluorine to branched fluoroalkenes, are reported in the literature. For example, Scherer's radical (**A**) persists at room temperature, even in the presence of molecular oxygen.[16] Groβ also reported the persistent (stable over a period of several months at 8°C) tertiary F-4-ethyl-3,4-dimethyl-3-hexyl radical (**B**).[17] The stability of these radicals, represented below, derives from steric effects,which inhibit dimerisation or other reactions.



(A)



(B)

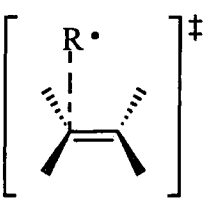
1.2.3. The propagation step.

Free radical reactions involve addition to π-bonds (e.g. addition to alkenes), H-atom abstraction and chain transfer.

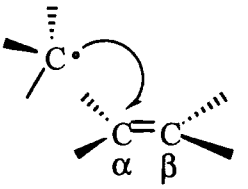
i. Alkene addition reactions.

Reaction rate and polar and steric effects.

The reaction rate of free-radical addition to alkenes depends on a complex interplay of polar effects, steric effects and bond-strength terms.[18-21] Additions of radicals to alkenes are strongly exothermic as a σ-bond is formed while a π-bond is broken. Therefore, according to the Hammond postulate, an early 'reactant-like' transition state is expected.



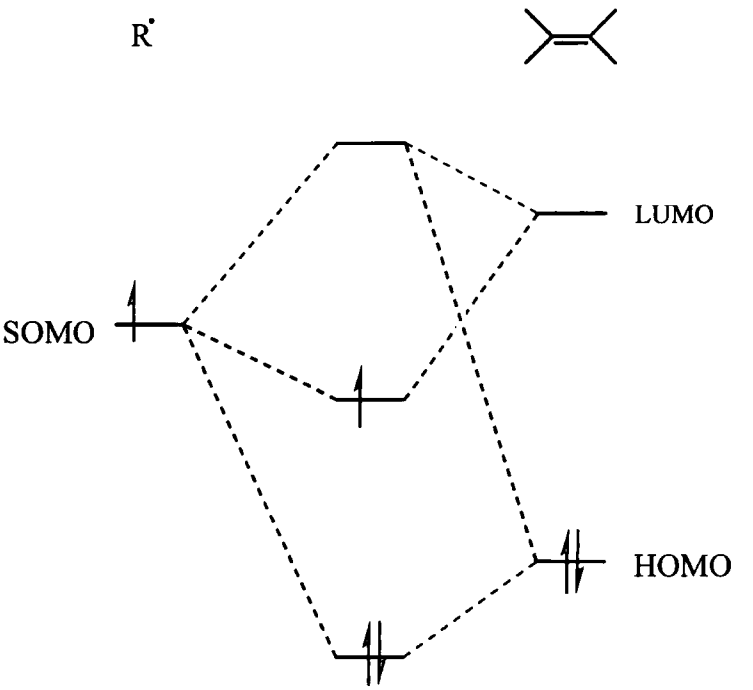
Consequently, polar and steric effects are the dominating factors governing the rate and the regiochemistry of addition rather than stability of the radicals formed. An unsymmetrical transition state could explain the absence of steric β-effects.



The differences between α- and β- substituents have been explained by Giese.[18] Substituents at the carbon atom of the alkene which is not attacked (β-substituents) exert predominantly polar effects on the rate of addition, whereas, substituents at the carbon atom of the alkene which is attacked (α-substituents) and substituents at the attacking radical centre exert both polar and steric effect on the rate of addition.

The early transition state and the absence of steric β-effects allows the polar substituent effects to be described in terms of frontier orbital theory. This theory states that the energy differences between the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of the reactants determine rate variations.[18] The smaller the energy between these frontier orbitals is, the larger is the stabilisation of the transition state when reactants approach one another. The frontier orbital of a free-radical being the singly occupied molecular orbital (SOMO), interaction between the SOMO of the free-radical and the LUMO and HOMO of the alkene are decisive in interpreting polar effects.

Interaction between the SOMO of R• and the HOMO and LUMO of an alkene



Depending on the SOMO-HOMO and SOMO-LUMO energy differences, free-radicals can be regarded as electrophilic or nucleophilic. Strongly electron withdrawing substituents, such as fluorine, decrease the SOMO energy of the radical at which point the SOMO-HOMO interaction becomes predominant. The radical is then considered to be electrophilic. This is to be compared with radicals containing electron-donating groups such as a tertiary alkyl radical. In this case the SOMO energy of the radical is increased and the SOMO-LUMO interaction becomes predominant and therefore a tertiary alkyl radical can be considered as nucleophilic.

Laser flash photolysis (LFP) studies have provided absolute rates of additions of some fluorinated radicals to a range of hydrocarbon alkenes. Those studies showed that perfluoro-n-alkyl radicals are much more reactive than their hydrocarbon counterparts. For example, [n-$C_3F_7^{\bullet}$] adds to 1-hexene 30 000 times faster and to styrene 350 times faster than an n-alkyl radical.[22, 23] This high reactivity can essentially be explained by the high electrophilicities of the very electron deficient fluorinated radicals. The pyramidal shape of fluorinated radicals also accounts for the increased reaction rate. Non-planar fluorinated

radicals have an energetic advantage over planar alkyl radicals as they do not require further bending to reach their transition states.[24]

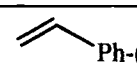
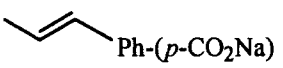
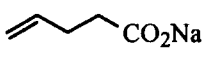
Because of their high electrophilicities and their polar transition states in both H-abstraction and alkene addition reactions, the rates of such reactions of fluorinated radicals are influenced by solvents, with polar solvents stabilising the polar transition states. Additions of perfluoroalkyl radicals to alkenes are faster in CH_3CN than in Freon 113 ($CF_2ClCFCl_2$) as shown in the table below (table 1.3).[25]

Table 1.3 Additions of perfluoroalkyl radicals to alkenes

	k_{add} (10^6 M^{-1} s^{-1}) to styrene	
Radical	F113	CH_3CN
CF_3•	53	171
C_2F_5•	79	127
n-C_3F_7•	43	108

Recently, Dolbier[26] reported the absolute rate constants of $[R_fSO_3Na]^•$ radical addition to a series of water-soluble alkenes bearing carboxylate functionality in aqueous solution. Those rates were larger than those of their counterparts in F113 and few examples are given in the following table (table 1.4).

Table 1.4 Comparison of the rate constants for additions of fluorinated radicals to alkenes in F113 versus H_2O

	k_{H2O}/k_{F113}
	5.4
	8.7
	3.4

Regiochemistry

The regiochemistry of free-radical addition to unsymmetrical alkenes depends on a complex combination of polar and steric effects. Tedder and Walton[19, 21, 27] extensively reviewed the effects determining the site of attack in such reactions. Free radicals preferentially attack the unsubstituted end of the double bond of mono-substituted ethenes as shown below (table 1.5).

Table 1.5 Orientation ratios (α : β) for addition to $C^{\alpha}H_2=C^{\beta}H\text{-}X$

X	$CH_3\bullet$	$CF_3\bullet$
	α : β	α : β
H	1 : 1	1 : 1
CH_3	1: 0.15	1 : 0.1
F	1 : 0.20	1 : 0.99
CF_3	1 : 0.33	1 : >0.02

The electrophilic trifluoromethyl radical and the nucleophilic methyl radical both add preferentially to the α-sites in propene and 1,1,1-trifluoropropene. Therefore the orientation of addition is clearly not governed by polar factors, but steric repulsion override other influences. The orientation ratios for the addition of trifluoromethyl radicals to ethylene, propene and 2-methylpropene are reported in the following table (table 1.6).[19]

Table 1.6 Orientation ratios (α:β) for addition of $CF_3\bullet$

	$C^{\alpha}H_2=C^{\beta}H_2$	$C^{\alpha}H_2=C^{\beta}HCH_3$	$C^{\alpha}H_2=C^{\beta}(CH_3)_2$
α : β	1 : 1	1 :0.1	1 :0.08
$2k_{\alpha}/k_e$	1	2.3	6.0

k_e = rate with ethene

The introduction of a second methyl substituent reduces the proportion of attack at the β-position but enhances the overall rate of attack. Thus, although polarity controls the overall rate of addition, steric effects are predominant in determining the orientation. Steric factors arising from the attacking radical are also important (table 1.7).

Table 1.7 Orientation ratios (α:β) for the addition of branched chain radical to vinyl fluoride (at164°C)

R•	$C^{\alpha}H2=C^{\beta}HF$
	α : β
CF_3•	1 : 0.1
CF_3CF_2•	1 : 0.06
$(CF_3)_2CF$•	1 : 0.02
$(CF_3)_3C$•	1 : 0.005

As the size of the attacking radical was increased, the proportion of addition at the less substituted end also increased. This is due to repulsion between the incoming radical and the alkene substituents. Although orientation appears to be controlled by steric factors, polar effects play a role in the regiochemistry. The extent of attack at the β-position decreases as the radical becomes more electrophilic (table 1.8).

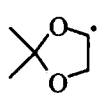
Table 1.8 Orientation ratios (α:β) for the addition to fluoroolefins (at 164°C)

R•	$C^{\alpha}H_2=C^{\beta}F_2$	$C^{\alpha}HF=C^{\beta}F_2$
	α : β	α : β
CH_3•	-	1 : 2.1
CH_2F•	1 : 0.4	1 : 2.0
CHF_2•	1 : 0.1	1 : 0.9
CF_3•	1 : 0.04	1 : 0.5

For trifluoroethylene, the orientation of addition is reversed with the nucleophilic methyl radical attacking at the more substituted carbon.

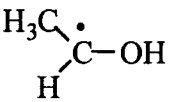
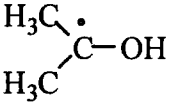
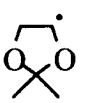
Paleta[28] recently reported the effects of chlorine atoms on the regioselectivity of radical additions to chlorine substituted fluoropropene and some examples are reported in the following table (table 1.9).

Table 1.9 Relative amount of attack at the terminal position of chlorine substituted fluoroolefins (%)

R•	$ClCF_2$-CF=CF_2 (1)	$ClCF_2$-CF=CFCl (2)	$ClCF_2CF=CCl_2$ (3)	$ClCF_2CF=CHCl$ (4)
	99	52	0	76
	100	51	0	76
$H_2\dot{C}(OH)$	100	-	0	-
$CH_3\dot{C}H(OH)$	100	73	0	86
$(CH_3)_2\dot{C}(OH)$	100	95	0	97

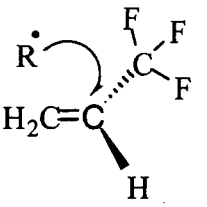
From this data, it can be seen that terminal chlorine atoms in highly fluorinated propenes exert a strong effect on the regioselectivity of addition of nucleophilic radicals. The effect of two chlorine atoms (instead of a fluorine atom) at the terminal position (fluoroalkene (**3**)) is strong enough to reverse completely the regioselectivity of the addition from the Karasch to the anti-Karasch mode. Replacement of fluorine by hydrogen (fluoroalkene (**4**) versus fluoroalkene (**2**)) produces better regioselectivity. This is explained by electronic repulsion between the unshared electron pair on the CFCl fluorine atom and the attacking radical. The exclusive attack by radicals on the terminal position in fluoroalkene (**1**) is explained by the 'tail-effect' (i.e. repulsive field or stereoelectronic effect) of the chlorine atom. Paleta[29, 30] also reported 'tail effects' in the case of perfluoroalkylated chains. A range of nucleophilic radicals were added selectively to perfluoroalkenes R_F-CH=CX_2 (X=F or H) as reported in the following table (table 1.10).

Table 1.10 Regioselectivity of additions of R• to fluoroalkenes

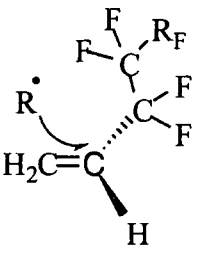
Olefin	Radical R•	Attack to terminal C (%)	Entry
$C_7F_{15}CF=CF_2$	$H_2\dot{C}OH$	100	1
$C_9F_{19}CF=CF_2$		100	2
$CF_3CH=CH_2$	CH_3•	77	3
$CF_3CH=CH_2$	CF_3•	98	4
$C_6F_{13}CH=CH_2$		100	5
$C_6F_{13}CH=CH_2$		100	6
$R_FCH=CH_2$		100	7
$R_FCH=CH_2$		100	8

R_F = C_4F_9, C_6F_{13} and C_8F_{17}

Nucleophilic and non-bulky methyl radicals add partly to the inner carbon atom (entry 3), whereas electrophilic trifluoromethyl radicals add almost exclusively to the terminal carbon (entry 4) and that can be caused by both electronic and steric effects. The high regioselectivities of the additions of nucleophilic radicals to perfluoroalkyl ethylenes (entries 5-8) and longer-chain perfluoroalk-1-enes (entries 1-2) are discussed in terms of the 'tail effect' represented as follows.



3,3,3-trifluoropropene **(A)**



1-(perfluoroalkyl)ethylene **(B)**

The larger number of fluorine atoms in **(B)** than in **(A)** results in more repulsion and consequently in higher regioselectivity.

ii. Hydrogen abstraction.

Most radical processes involve H-abstraction as a key step in the mechanism. It can be H-abstraction from the substrate in the initiation step or H-transfer to complete the free-radical addition process. H-transfer during polymerisation result in polymer inhibition or low molecular weight product.[31] Hence, H-abstractions have been extensively studied. The rate and selectivity of such abstraction depend on steric, polar and electronic effects as well as radical stability.

H-abstraction usually has a large activation energy.[8] Therefore, according to the 'Hammond' postulate, the transition state occurs late in the reaction coordinate. Consequently, the stability of the radical formed must be considered. If there is little polarity or if the polarity is constant, there is a direct relationship between the strength of the C-H bond being broken and the activation energy of hydrogen-abstraction (Evans-Polanyi relationship).[32]

$$E_a = \alpha[BDE_{R\text{-}H}] + \beta$$

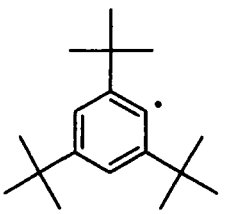
with α, β being constants, E_a being the activation energy and BDE being the bond dissociation energy.

This confirms the importance of the stability of the radical formed. The activation energy of hydrogen abstraction by trifluoromethyl and methyl radicals on alkanes produces evidence of such relationship.[20]

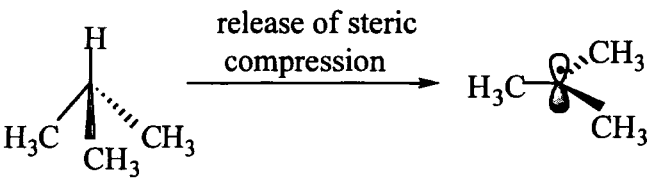
$$R\text{-}H + X\bullet \rightarrow R\bullet + H\text{-}X$$

X	α	β (kcal mol^{-1})
$CH_3\bullet$	0.49	74
$CF_3\bullet$	0.53	84

Steric effects (steric hindrance, steric inhibition of resonance and steric compression) are also important in radical transfer reactions. Steric hindrance prevents a bulky radical (such as 2,4,6-tri-*tert*-butylphenyl radical) from approaching the reaction site.



Steric inhibition of resonance prevents the radical from being stabilised by electron delocalisation. Finally, the release of steric compression on formation of radical, which increases with more substituents, has a beneficial effect on radical stability, and so on the rate of addition.



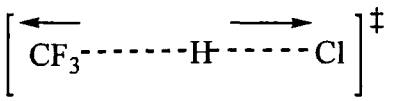
pyramidal planar

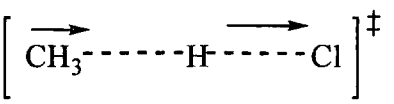
The steric compression factor is the most important steric effect in free-radical chemistry as its release occurs in every abstraction.

Polarity must also be considered in H-abstraction reactions. A 'good match-up' of polarities in an H-abstraction transition state gives beneficial charge transfer interaction.[20] For example, H-abstraction from HCl by trifluoromethyl radical is more exothermic than that of methyl radical and yet has the highest activation energy.

	E_a	$\Delta H°$
$CH_3\bullet + HCl \rightarrow CH_3\text{-}H + Cl\bullet$	3.5	-2
$CF_3\bullet + HCl \rightarrow CF_3\text{-}H + Cl\bullet$	8.0	-4

The 'electronegative' trifluoromethyl radical resists the formation of a polar transition state whereas the 'electropositive' methyl radical facilitates the formation of a polar transition state.





More recently, Dolbier [33, 34] has invoked transition state polar effects to rationalise the relative higher reactivity of perfluoro radicals versus their hydrocarbons counterparts in H-transfer reactions, with electropositive H-atom donors such as silanes and stannanes (e.g. nBu_3SnH, $(TMS)_3SiH$).

1.3. Radical addition to fluorinated alkenes

1.3.1. Radical additions to chlorofluoroethenes

Radical additions to fluoroethenes have been reviewed previously in this group.[35] So we will focus on reactions involving radical additions to 1-chloro-2,2-difluoroethene and 1,1-dichloro-2,2-difluoroethene, the two chlorofluoroethenes that we used in this project.

i. 1-Chloro-2,2-difluoroethene

Only a few papers have been published about radical addition to 1-chloro-2,2-difluoroethene.[36, 37] Haszeldine[37] reported the photochemically initiated addition of trifluoromethyl iodide which gave essentially the 1 :1 adducts with little telomer formed.

$$F_2C{=}CHCl + CF_3I \xrightarrow{\text{UV-light}} CF_3CF_2{-}\underset{Cl}{\overset{H}{C}}{-}I + CF_3CHClCF_2I$$

1 : 2 — 9 : 1

75%

Haszeldine[37] also reported the radical addition of HBr.

$$F_2C{=}CHCl + HBr \xrightarrow{\text{UV-light}} CF_2BrCH_2Cl$$

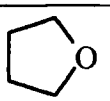
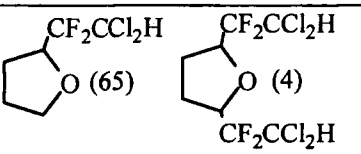
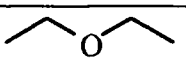
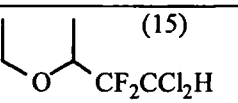
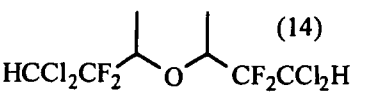
1 : 2 — 97%

Although addition of hydrogen bromide to alkenes usually procceds *via* an ionic mechanism the reaction was, in this case, inhibited in the dark confirming a radical process. Both photochemical additions of trifluoroiodomethane and hydrogen bromide to 1-chloro-2,2-difluoroethene gave essentially the 1 : 1 adducts derived from initial radical attack at the CF_2 site because it is the less sterically hindered and the most electrophilic site.

ii. 2,2-Dichloro-1,1-difluoroethene

Free radical additions of carbon-centred radicals generated from oxygen containing compounds (alcohols,[38] aldehydes,[39] ethers,[40] dialkyl phosphonates[41]) to 2,2-dichloro-1,1-difluoroethene have been reported by Muramatsu, and some examples are shown in the following table (table 1.11).

Table 1.11 Radical additions to 2,2-dichloro-1,1-difluoroethene

Substrate (S)	Ratio S. : CF_2=CCl_2	Initiator	Products and yields (%)	Ref.
CH_3CH_2OH	4 : 1	γ-rays	$HCCl_2CF_2{\cdot}CH(OH)CH_3$ (10) $H(CCl_2CF_2)_2{\cdot}CH(OH)CH_3$ (2)	[38]
$(CH_3)_2CHOH$	4 : 1	γ-rays	$HCCl_2CF_2{-}C(OH)(CH_3)_2$ (15) $H(CCl_2CF_2)_2{-}C(OH)(CH_3)_2$ (7)	[38]
	2 : 1	γ-rays		[40]
	2 : 1	γ-rays	 	[40]
CH_3CHO	2 : 1	DBPO	$H_3C{-}C(=O){-}CF_2CCl_2H$ (38)	[39]
i-C_3H_7CHO	2 : 1	DBPO	i-$C_3H_7{-}C(=O){-}CF_2CCl_2H$ (15)	[39]
$HPO(OCH_3)_2$	2.1 : 1	γ-rays	$CHCl_2CF_2PO(OCH_3)_2$ (3)	[41]
$HPO(OC_2H_5)_2$	2.1 : 1	γ-rays	$CHCl_2CF_2PO(OC_2H_5)_2$ (3)	[41]
$HPO(On\text{-}C_3H_7)_2$	2.1 : 1	γ-rays	$CHCl_2CF_2PO(On\text{-}C_3H_7)_2$ (2)	[41]

DBPO= Di-benzoyl peroxide

Additions to alcohols and ethers gave mixtures of mono and di-adducts, whereas additions to aldehydes and dialkyl phosphonates gave only mono-adducts. Higher molecular weight telomers were also formed accounting for the poor yields. In case of the additions to dialkyl phophonates, formation of chlorofluoroethyl phosphonic acids by hydrolysis of the 1 :1 adducts with atmospheric moisture explained the very low yield.

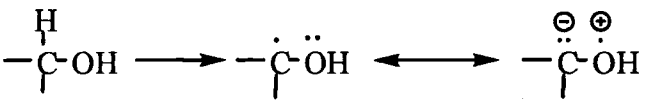
In all cases, radicals were reported to attack at the CF_2 position of CF_2=CCl_2. This was explained by steric effects : the radicals add to the site having less steric hindrance. Moreover the CF_2 site is favoured because it is the most electrophilic site due to the fluorine substituents.

There do not appear to be any reports in the literature detailing reactions between radicals from hydrocarbons and difluoroalkenes .

1.3.2. Radical additions to hexafluoropropene (HFP)

Additions to hexafluoropropene have been extensively used in this project, because HFP is industrially available, cheap and does not readily homopolymerise probably due to steric effects arising from the trifluoromethyl group. HFP is also an extremely electrophilic alkene, very susceptible to radical attack by 'nucleophilic radicals'[42, 43] and therefore polyfluoro-*n*-propyl derivatives are easily formed. HFP has been successfully added to a wide range of oxygen-containing compounds (alcohols and diols,[44-46] aldehydes,[47] ethers[30, 42, 43, 48]), nitrogen-containing compounds[49] and hydrocarbons,[50] using γ-ray, UV-light and peroxide initiations.

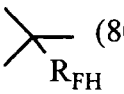
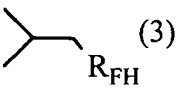
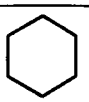
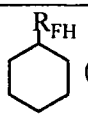
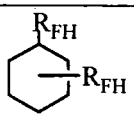
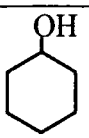
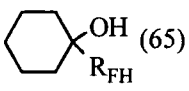
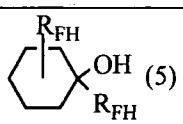
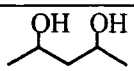
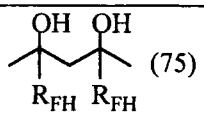
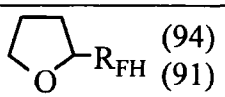
The stabilising interaction of a radical centre with oxygen increases the nucleophilicity of the alkoxy radical.



Thus, reactions with alcohols, aldehydes and ethers are very favourable. Chambers[50] also reported effective reactions with hydrocarbons.

Radical additions to HFP have been extensively reviewed in this group[7, 35, 51] and so only few examples are reported in the following table (table 1.12).

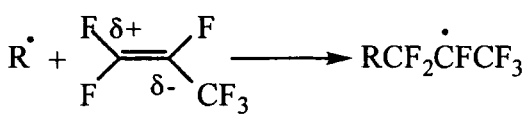
Table 1.12 Radical additions to HFP

Substrate	Ratio substrate : HFP	Initiator	Products and yields (%)	Ref.
	1 : 1.3	DTBP	 (80)  (3)	[50]
	1 : 2	γ-rays	(42) (-)	
	1 : 2	DTBP	 (39)  (53)	[50]
	1 : 1.5	γ-rays	(90) (4)	
	1 : 1.1	DTBP	 (65)  (5)	[44]
	1 : 1.2	γ-rays	(76) (trace)	
	1 : 2.4	γ-rays	 (75)	[44]
	3.3 : 1	hν γ-rays	 (94) (91)	[48] [52]

R_{FH}= CF_2-CFH-CF_3

From this table, it can be seen that hexafluoropropene (HFP) has been added efficiently to a range of hydrocarbons and oxygen containing compounds. Reactions with alcohols and ethers were very favourable owing to the nucleophilicity of the radicals.

The orientation of radical additions to HFP is well established,[1] with regioselective addition to the difluoromethylene group occuring, in most cases, as it is the less sterically hindered and the most electrophilic site.



Although, depending on the system and the reaction conditions, 1-5% of the opposite isomer can be formed.[30]

We have just seen that a carbon-hydrogen bond can be functionalised by radical addition to fluorinated alkenes, such as HFP. The HFP-adduct can be further functionalised by elimination of hydrogen fluoride to give some fluoroalkenes. In this project, addition of iodine monofluoride to the newly formed fluoroalkenes gave some new fluorocarbon iodides. Therefore, the next part of the introduction will include a review of synthesis and reactivity of perfluoroalkyl iodides.

1.4. Perfluoroalkyl iodides

1.4.1. Synthesis

Perfluoroalkyl iodides (R_FI) occupy an unique place in organofluorine chemistry as they constitute 'building blocks' for the synthesis of various organic compounds containing fluorine.[53, 54] For example, they are crucial components in the synthesis of surface treatment compounds, herbicides and polymers on the industrial scale. Therefore, many routes have been developed for their preparation and some examples are presented here.

i. Preparation from perfluorocarboxylic acid derivatives.

Formerly, perfluoroalkyl iodides were prepared by the Hunsdiecker reaction.[55]

$$R_FCOOAg + I_2 \longrightarrow R_FI + AgI + CO_2$$

$R_F = C_nF_{2n+1}$, n=1 to 10

Higher perfluoroalkyl iodides have been prepared by reaction of the corresponding acids with iodine and BPO.[53]

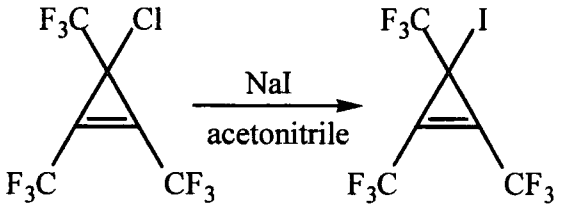
$$F(CF_2)_7COOH \xrightarrow[Br(CH_2)_2Br,\ 110°C]{I_2 + (C_6H_5COO)_2} F(CF_2)_7I \quad 60\%$$

ii. Halogen exchange.

Another method for preparing perfluoroalkyl iodides is halogen exchange. For example, addition of iodine to TFE gives ICF_2CF_2I and selective fluorination of one iodine atom gives 1-iodopentafluoroethane.[53]

$$CF_2{=}CF_2 \xrightarrow{I_2} ICF_2CF_2I \xrightarrow{F_2} CF_3CF_2I \quad 75\text{-}100\%$$

Replacement of allylic chlorine atoms by iodine in chloroperfluoroalkenes is achieved by treatment with sodium iodide in solution at room temperature and an example is reported as follows.[56]



77%

iii. Preparation from perfluoroalkenes.

Because of the commercial availability of perfluoroalkenes, the synthesis of perfluoroalkyliodides from perfluoroalkenes (by electrophilic iodofluorination, nucleophilic iodofluorination and telomerisation) is of great interest.[53] The nucleophilic iodofluorination is initiated by the addition of fluoride ion to a perfluoroalkene. Thus, for example, 2-iodoperfluoropropane is prepared by reaction of HFP, iodine and potassium fluoride.[57]

$$CF_3CF{=}CF_2 \xrightarrow[CH_3CN,\ 100°C]{KF,\ I_2} CF_3CFICF_3$$

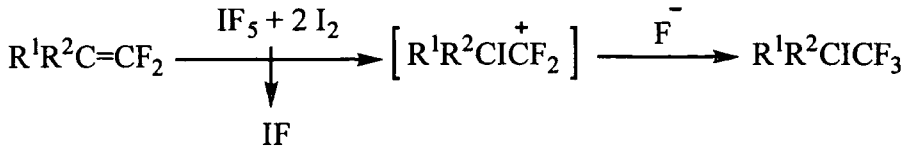
60%

Chambers [58] first reported the electrophilic iodofluorination of tetarafluoroethylene (TFE) using a mixture of iodine and iodine pentafluoride. The reaction is suitable for a wide range of alkenes and gives high yields of products, as reported in the following table (table 1.13).

Table 1.13 Yields of products of the iodofluorination of $R^1R^2C{=}CF_2$

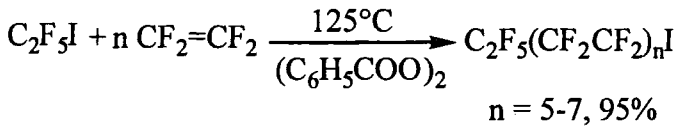
R^1	R^2	Yield (%)
H	F	76
F	F	99
Cl	F	95
F	CF_3O	94
F	CF_3	69

The reaction may proceed *via* a carbocation on addition of iodine to the alkene.



In the electrophilic iodofluorination reactions, iodine monofluoride is produced *in situ* as it is an unstable species, which disproportionates to I_2 and IF_3.[59] Methods to generate iodine monofluoride include reaction of iodine pentafluoride with iodine,[58] N-iodosuccinimide (NIS) or iodine with hydrogen fluoride,[60] triethylamine trihydrofluoride with NIS,[61] ammonium hydrogen fluoride and aluminium fluoride with NIS,[62] iodine and silver fluoride,[63] direct reaction of elemental fluorine with iodine[64] and reaction of xenon difluoride with iodine or NIS.[65] Catalysts, such as metals or their salts, can also be added to the iodofluorinating mixture to increase the product yields.[66]

Synthesis of iodoperfluoroalkanes with long carbon chains are performed by radical addition of iodoperfluoroalkanes to perfluoroalkenes. For example, Moore[67] reported the oligomerisation of tetrafluoroethylene with C_2F_5I in the presence of peroxides.

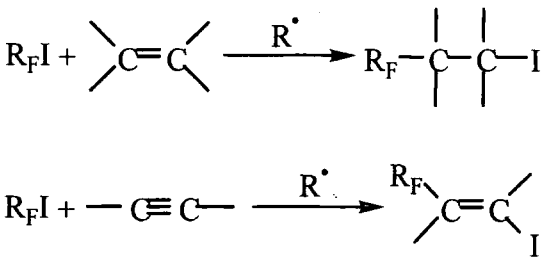


Thus, iodoperfluoroalkanes can be prepared in different ways from a large variety of compounds and they can then undergo reactions with a wide range of substrates. Therefore, the aim of the next paragraphs will be to give an overview of perfluoroalkyl iodide reactivity.

1.4.2. Radical additions of perfluoroalkyl iodides to unsaturated compounds

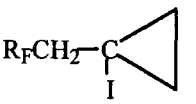
Radical additions of perfluoroalkyl radicals generated from perfluoroalkyl iodides to unsaturated compounds have opened an enormous area of synthesis that has been extensively reviewed by Brace,[54, 68, 69] and therefore, only some examples are presented here. Radical additions of perfluoroalkyl to unsaturated compounds are usually carried out in the presence of 1-2 % of azobis(isobutyro)nitrile (at its decomposition temperature) to

give specific compounds with R_F groups attached in precise positions in a large variety of alkenes and alkynes. Since iodine may be removed (by elimination or by substitution), this provides another point of reactivity.



Addition of perfluoroalkyliodides to mono-substituted 1-alkenes or 1,1-di-substituted alkenes occur with Markownikoff orientation, and some examples are reported in the following table (table 1.14).[54]

Table 1.14 Addition of R_FI to alkenes

R_FI	Alkene	Ratio R_FI : alkene	Product and yield (%)
n-C_3F_7I	1-heptene	1 :1	$R_FCH_2CHIC_5H_{11}$ (98)
n-C_3F_7I	methylenecyclopropane	1 :1	 (96)
n-C_3F_7I	isobutene	1 :1	$R_FCH_2CI(CH_3)_2$ (44)

$R_F = C_3F_7$

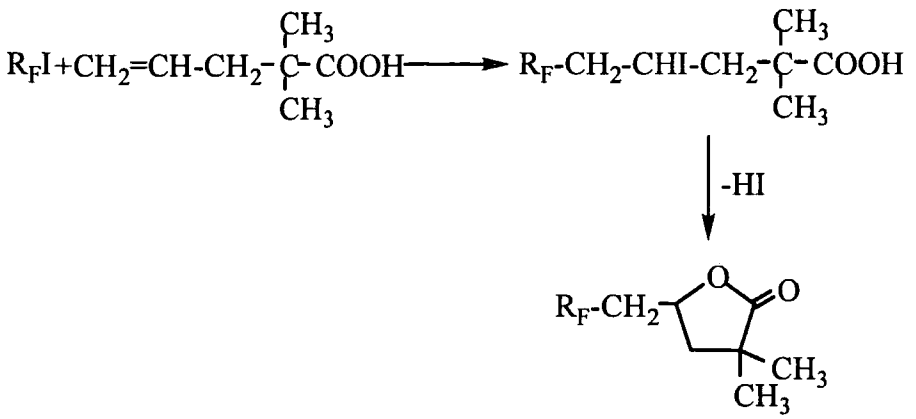
Radical reaction of iodoperfluoroalkanes with alkenes containing functional groups is a useful synthetic tool, because the addition occurs exclusively to the double bond without affecting the functional groups. For example, addition of perfluoroalkyliodides to a series of ω-alkenoic carboxylic acids or ω-alkenoate esters provides the adducts $R_FCH_2CHI(CH_2)_nCO_2R$ (R= H or alkyl ; n=1-14) in good to excellent yields.[70-73]

$$R_FI + CH_2{=}CH(CH_2)_nCO_2H \xrightarrow{\text{AIBN, 70°C}} R_FCH_2CHI(CH_2)_nCO_2H \quad (95\text{-}100\%)$$

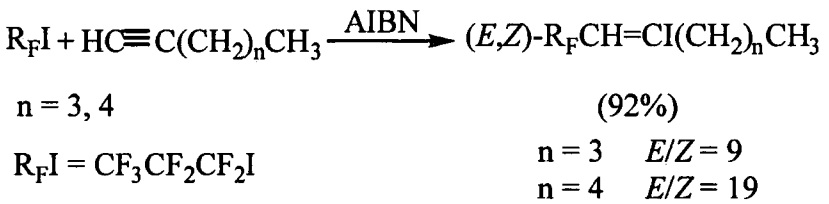
$R_F = C_3F_7\text{-}C_{10}F_{21}$

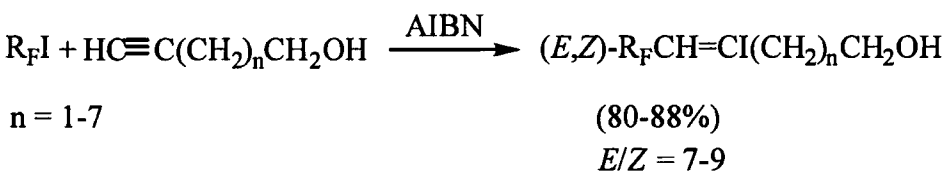
n = 1-14

Carboxylic acids with two or three methylene groups between the carboxyl group and the double bond constitute an exception, as lactonisation occurs through intramolecular nucleophilic dehydroiodination.[71] The process is assisted by *gem*-substitution.



Perfluoroalkyliodides also react with alkynes,[74] and alkynyl alcohols[75-77] to give good to excellent yields of mono-adducts in *Z*- and *E*- configurations, and these reactions are summarised in the following schemes.





In all cases, the *E*-isomers (with R_F and I *trans* to each other) were formed preferentially for steric reasons.

There are of course many other examples of addition of perfluoroalkyliodides to unsaturated compounds but a complete discussion is beyond the scope of our project, and

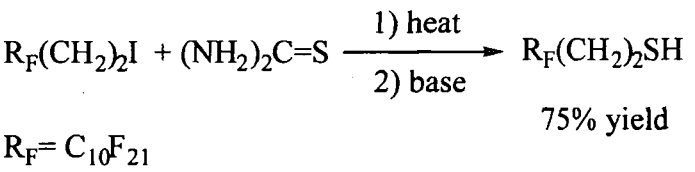
we will rather detail the reactions of perfluoroalkyl iodides with thiols in the next paragraph.

1.4.3. Reactions of perfluoroalkyl iodides with thiols.

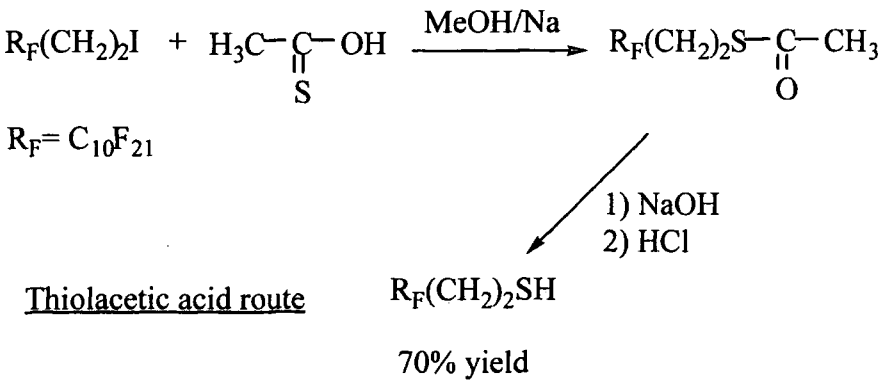
i. Synthesis

Thiols derived from perfluoroalkyliodides are of great interest in organofluorine chemistry.[78, 79] For example, ω-(perfluoroalkyl)-ethanethiols ($R_F(CH_2)_nSH$, n=2-15) adsorb onto smooth surfaces to give oriented monolayers that are highly repellent to wetting by various liquids. Many routes to synthesise $R_F(CH_2)_nSH$ from R_FI have been developed and Brace[54] extensively reviewed this field. The reader is so directed to the literature and only some examples are presented here with an emphasis on perfluoroalkylation of thiols by $S_{RN}1$ process.

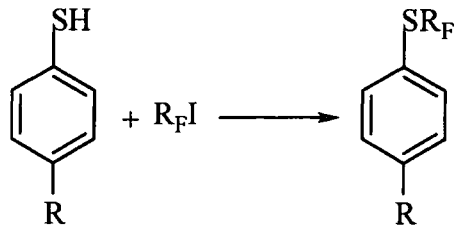
ω-(Perfluoroalkyl)ethanethiols $R_F(CH_2)_nSH$ (n=2-15) can be prepared in high yields from $R_F(CH_2)_nI$ (n=2, 4, 6...) and thiourea.[80] For example:



Calas[78] concluded, from a comparison of five synthetic routes, that methods based on thioacetic acid and thiourea appear to be the most effective for thiol synthesis. For example:



Homolytic perfluoroalkylation of thiols by perfluoroalkyl iodides is also a useful method to prepare fluorinated thiols. Perfluoroalkylation of aromatic, heteroaromatic and aliphatic thiols were formerly conducted in liquid ammonia under UV-irradiation.[81-83] Phase transfer catalysed perfluoroalkylation of thiols was then developed. Popov[84] reported the perfluoroalkylation of a range of aromatic thiols in water/organic solvent media under UV irradiation, in the presence of triethyl benzyl ammonium chloride.



50-80 % yield

R_F	R
CF_3	H, Cl, CH_3, CH_3O
C_3F_7	H, Cl, CH_3, CH_3OOC
$(CF_3)_2CF$	Cl
n-C_6F_{13}	Cl

Feiring[85] reported some successful perfluoroalkylation without irradiation or initiator. The reactions reported gave also better results when using DMF rather than phase transfer procedure and few examples are given in the following table (table 1.15). Although the reported perfluoroalkylations occurred in good yields, long reaction times were required (17 hours).

Table 1.15 Reaction of perfluoroalkyl iodides with thiolates

R_FI	thiolate	solvent	conditions	products (GC yield) [isolated yield]
$C_8F_{17}I$	PhSNa	DMF	25°C, 17 hrs	$PhSC_8F_{17}$ (92) [90] $C_8F_{17}I$ (5)
$C_8F_{17}I$	$C_4H_9SN(Bu)_4$	C_6H_6/H_2O	25°C, 4 hrs	$C_8F_{17}SC_4H_9$ (12) $(C_4H_9S)_2$ (35) $C_8F_{17}I$ (47)
$C_8F_{17}I$	C_4H_9SNa	DMF	25°C, 17 hrs	$C_8F_{17}SC_4H_9$ (36) [35] $(C_4H_9S)_2$ (15) $C_8F_{17}I$ (47)
$(CF_3)_2CFI$	PhSNa	DMF	25°C, 17 hrs	$PhSCF(CF_3)_2$ (76) [40] $(PhS)_2$ (16) $CF_3CF=CFSPh$ (6)

Boiko and Shchupak[86] perfluoroalkylated thiols with R_FI in the presence of Et_3N (base), which considerably reduced the amount of disulfides formed (only 3-12%). Such reactions occurred spontaneously under daylight or ordinary laboratory light, at 20-22°C and were complete in less than 3 hours depending on the thiol nucleophilicity. Boiko also reported the reactions to be dependant on the temperature (inhibition at 0-5°C), lighting (inhibition in the dark), solvent polarity and structure of both perfluoroalkyl radical and thiol substituents (discussed later). Some examples are reported in the following table (table 1.16).

Table 1.16 The reaction of arenethiolates $XC_6H_4SNHEt_3$ with C_3F_7I.

X	solvent	conditions	Yield of products (%)
H	DMF	19-20°C, 2 hrs	RSR_F (83)
			RSSR (3)
			R_FI (-)
4-$NHCO_2CH_3$	CH_3CN	21-22°C, 0.5 hrs	RSR_F (98)
			RSSR (trace)
4-$NHCO_2CH_3$	DMF	21-22°C, 0.5 hrs	RSR_F (89)
			RSSR (3)
			R_FI (-)
4-Cl	DMF	22°C, 2 hrs	RSR_F (72)
			RSSR (3)
			R_FI (-)
4-COOH	DMF	22-30°C, 0.5 hrs	RSR_F (72)
			RSSR (trace)
			R_FI (trace)

$R = X\text{-}C_6H_4$

$R_F = C_3F_7$

ii. $S_{RN}1$ mechanism

Thiol perfluoroalkylation is believed to proceed by an $S_{RN}1$ mechanism.[85]

$$RS^- + R_FI \longrightarrow RS^{\bullet} + R_FI^{-\bullet} \quad \textbf{step (1)}$$

$$R_FI^{-\bullet} \longrightarrow R_F^{\bullet} + I^- \quad \textbf{step (2)}$$

$$RS^- + R_F^{\bullet} \longrightarrow RSR_F^{-\bullet} \quad \textbf{step (3)}$$

$$RSR_F^{-\bullet} + R_FI \longrightarrow RSR_F + R_FI^{-\bullet} \quad \textbf{step (4)}$$

A single electron transfer (SET) from the thiolate to the perfluoroalkyl iodide initiates this chain mechanism (step (1)). The anion radical formed decomposes into a perfluoroalkyl

radical (step (2)), which adds to the thiolate anion giving a new anion radical (step (3)). Electron transfer from the last anion radical to the perfluoroalkyl iodide completes the process by giving the desired product and regenerating the perfluoroalkyl iodide anion radical (step (4)).

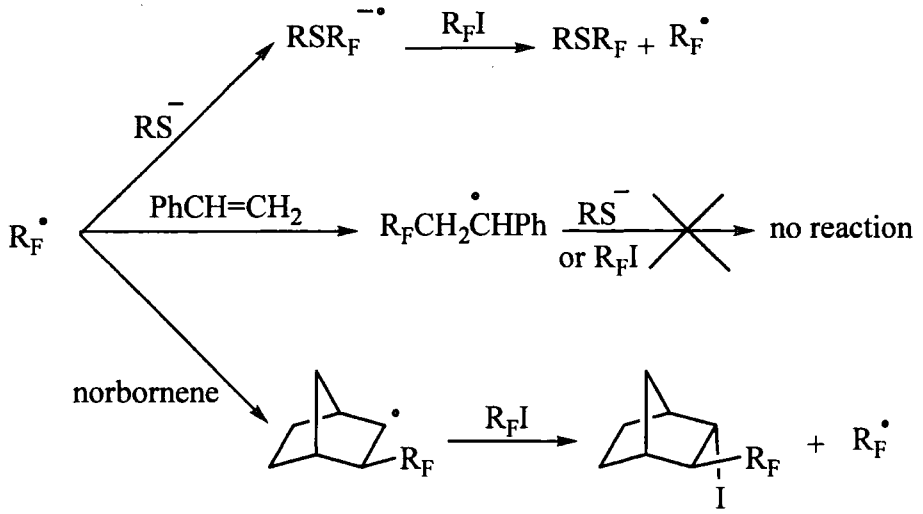
iii. Evidence for a radical chain process

Feiring[85] gave evidence for a radical process by inhibition and trapping studies, with added alkenes (styrene and norbornene) and some examples are reported in the following table (table 1.17).

Table 1.17 Reaction of perfluoroalkyl iodides with thiolates in the presence of added alkenes

R_FI	Thiolate	Additive	Product (GC yield)
$C_8F_{17}I$	PhSNa	___	$PhSC_8F_{17}$ (92) $C_8F_{17}I$ (5)
$C_8F_{17}I$	PhSNa	styrene	no reaction
$C_8F_{17}I$	PhSNa	norbornene	$PhSC_8F_{17}$ (77) 2-iodo-3-perfluorooctyl-norbornane (6) $C_8F_{17}I$ (16)

Styrene inhibits the perfluoroalkylation process by scavenging the perfluoroalkyl radicals. The resulting benzyl radical is not reactive enough to abstract iodine from R_FI or to add to RS^-. Use of norbornene as an additive resulted in the formation of 2-iodo-3-perfluorooctyl norbornane. This species is formed by addition of the perfluoroalkyl radical to norbornene, followed by iodine-abstraction from R_FI. Those results are summarised in the following scheme.



iv. Limiting step

The very fast fragmentation of the radical anion $R_FI^{\bullet -}$(step (2)) and the coupling of the electrophilic radical [$R_F^\bullet$] with the anion RS^- (step (3)) occur at ionic reaction speed and are not limiting. Boiko also showed that, as disulfide formation (due to recombination of radicals $RS^\bullet$ produced in the first step) is not affected by the reaction conditions, the first step is not limiting. From his studies, Boiko[86] concluded that the limiting step is the single electron transfer from $RSR_F^{\bullet -}$ to the perfluoroalkyl iodide (step (4)).

The structure of the perfluoroalkyl iodides influences the rate-determining step. Perfluoroalkylation is facilitated (considering both rate and products yield) when heptafluoropropyl iodide is employed rather than trifluoromethyl iodide (table 1.18).

Table 1.18 Reaction of R_FI with XC_6H_4SH at room temperature

R_F	X	solvent	time (h)	Products yield (%)	
				RSR_f	RSSR
C_3F_7	4-$NHCO_2CH_3$	DMF	0.5	89.2	3.4
CF_3	4-$NHCO_2CH_3$	DMF	1	69.9	9.5
C_3F_7	2-NH_2	CH_3CN	0.5	84.1	—
CF_3	2-NH_2	DMF	1	66.4	6.8

R = X-C_6H_4

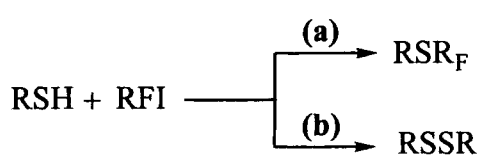
Boiko[86] also reported that solvent affected the reaction rate. A decrease in the solvent polarity (e.g. when CH_3CN is used instead of DMF) causes inhibition and reduces the RSR_F yield. Surprisingly, thiol perfluoroalkylation is also inhibited in HMPA (a highly donating solvent) because it forms donor-acceptor complexes with the perfluoroalkyl iodide and so reduces its electrophilic properties. Consequently, the perfluoroalkylation process in HMPA is slowed down compare to the reaction in DMF, as shown in the following table (table 1.19).

Table 1.19 Reaction of R_FI with XC_6H_4SH

R_FI	X	solvent	condition	Yield of products (%)	
				RSR_F	RSSR
C_3F_7I	$C_6H_4NHCOOCH_3$-p	DMF	21°C, 0.5 hrs	89.2	3.4
C_3F_7I	$C_6H_4NHCOOCH_3$-p	HMPA	21-22°C, 3hrs	74.5	2.7

v. Disulfide formation.

Condensation of alkyl thiolates with perfluoroalkyl halides can produce a notable amount of disulfides. With aliphatic thiolates, disulfide formation often limits the yield of perfluoroalkylated thiols.



According to Boiko,[86] disulfides are formed by recombination of RS•, when the chain reaction is too slow, whereas, Wakselman[87] concluded, from his studies on perfluoroalkylation of aliphatic thiols in the presence of sodium hydroxymethanesulfinate, that the disulfide is first formed and then perfluoroalkylated.

$$R_FI + HS(CH_2)_2SH \xrightarrow[DMF,\ H_2O]{NaO_2SCH_2OH} \underset{30\%}{R_FS(CH_2)_2SR_F} + \underset{3\%}{R_FS(CH_2)_2SH}$$

$$+ \underset{8\%}{R_FS(CH_2)_2SS(CH_2)_2SR_F}$$

R_F= n-C_6F_{13}

Detection of $R_FS(CH_2)_2SS(CH_2)_2SR_F$ is in agreement with the *in situ* formation of disulfides, as described as follows.

$$2\ RS^- + R_FI \longrightarrow RSSR + R_F^-$$

$$RSSR + R_FI + \dot{S}O_2^- \longrightarrow R_FSR + SO_2 + I^-$$

$$R_F^- + SO_2 \longrightarrow R_fSO_2^-$$

1.5. Conclusions

Organic compounds that contain fluorine have a wide range of applications and so methodology for the introduction of fluorine and perfluoroalkyl groups into organic systems is of great interest. C-H bond of a wide variety of substrates can be functionalised by radical additions to various fluoroalkenes giving rise to new 'fluorinated building blocks'. Perfluoalkyl iodides also constitute 'building blocks' for the synthesis of organic compounds that contain fluorine.

RESULTS AND DISCUSSION

2. Free radical additions to fluoroalkenes

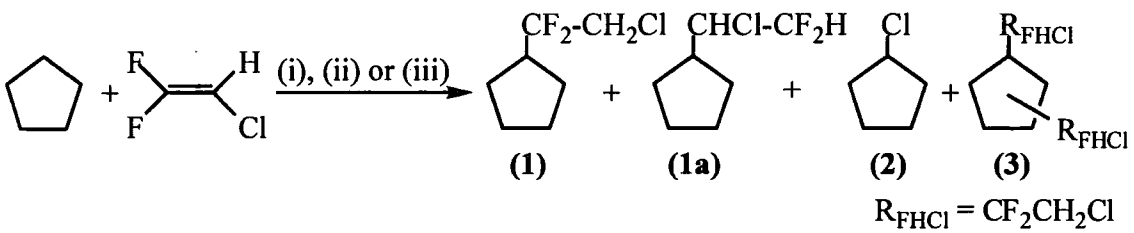
The first part of this work was concerned with the functionalisation of carbon-hydrogen bonds by free radical additions of carbon centred radicals to several fluoroalkenes to give some fluoroalkylated derivatives, precursors for subsequent syntheses. Thus, this chapter describes radical additions of carbon centred radicals to two chlorofluoroethenes (1-chloro-2,2-difluoroethene and 1,1-dichloro-2,2-difluoroethene) and to hexafluoro-propene.

2.1. Addition of cyclopentane to chlorofluoroethenes

Free radical addition reactions between carbon-centred radicals generated from alcohols,[38] aldehydes,[39] ethers[40] and dialkyl phosphonates[41] and chlorodifluoroalkenes have been described in the literature (see part 1.3.1). However, no examples of reactions between radicals generated from hydrocarbons and chlorodifluoroalkenes have been reported. Therefore we decided to study the reactivity of cyclopentane with 1-chloro-2,2-difluoroethylene and 1,1-dichloro-2,2-difluoroethylene.

2.1.1. Addition of cyclopentane to 1-chloro-2,2-difluoroethene

Cyclopentane was added to 1-chloro-2,2-difluoroethene using both γ-ray and DTBP initiation to give 2-chloro-1-cyclopentyl-1,1-difluoroethane (**1**) as the major product. The reverse-addition product, 1-chloro-1-cyclopentyl-2,2-difluoroethane (**1a**) was observed by GLC/MS and ^{1}H NMR. Chlorocyclopentane (**2**) and various di-adducts (**3**) were also observed by GLC/MS.



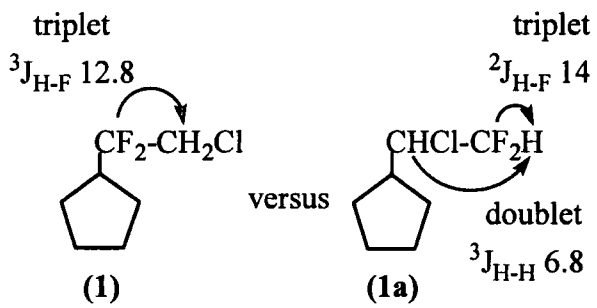
$R_{FHCl} = CF_2CH_2Cl$

Initiator and conditions	Ratio C_5H_{10} : CF_2=CHCl	Product ratio (1) : (1a) : (2) : (3)	Yield (%) (1)
(i) γ-rays, r.t., 4 weeks	1 : 2	2 : / : / : 1	0 (Dec)
(ii) γ-rays, r.t., 4 weeks	1 : 1	3 : / : / : 1	0 (Dec)
(iii) DTBP, 140°C, 24 hrs	5 : 1	49 : 1 : 3 : 4	24

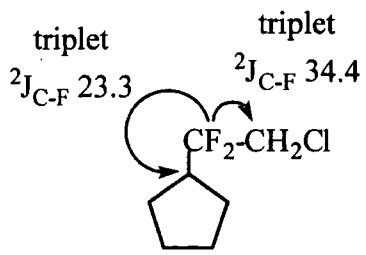
Fluorine NMR showed the presence of unreacted 1-chloro-2,2-difluoroethene in the recovered cyclopentane, and therefore a conversion of the fluoroalkene based on the quantity of volatiles recovered would not have been accurate here. The products arising from the γ-ray initiated reactions decomposed during distillation, most probably due to the loss of hydrogen chloride from the reverse-addition compound (**1a**). For the DTBP initiated reaction, an excess of cyclopentane was used to give the mono-adduct (**1**) as the major product. However, its isolated yield was relatively low due again to decomposition during distillation.

* *Structure elucidation of compound (1)*

Structure of compound (**1**) was elucidated from NMR data. The ^{1}H NMR spectrum confirmed the mode of addition for compound (**1**) because a triplet ($^3J_{H\text{-}F}$ 12.8) accounting for two protons was observed at 3.7 ppm. It was assigned to the CH_2Cl hydrogens atoms, showing the cyclopentyl ring to be directly attached to the CF_2 carbon atom. For the minor reverse-addition compound (**1a**), the triplet ($^2J_{H\text{-}F}$ 14) of doublet ($^3J_{H\text{-}H}$ 6.8) at 2.3 ppm was assigned to the CF_2H hydrogen atom.

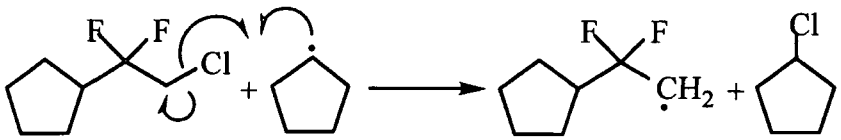


The ^{13}C NMR spectrum confirmed the structure of compound (1) as two triplets with characteristic two-bond coupling constants occurred at 44.4 ppm ($^2J_{C-F}$ 34.4) and at 42.6 ppm ($^2J_{C-F}$ 23.3).



* *Chlorocyclopentane (2)*

The formation of chlorocyclopentane (2) probably resulted from chlorine abstraction by a cyclopentyl radical from adduct (1) as shown as follows.

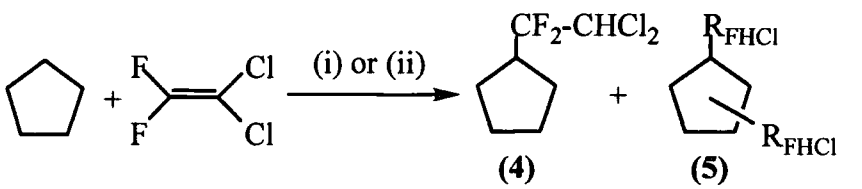


* *Orientation of the addition*

Radical attack occurred predominantly at the CF_2 position as it is the most electrophilic site due to the fluorine substituents and the least sterically hindered site bearing only small fluorine atoms rather than larger chlorine atoms.

2.1.2. Addition of cyclopentane to 1,1-dichloro-2,2-difluoroethene

Cyclopentane was added to 1,1-dichloro-2,2-difluoroethene to give 2,2-dichloro-1-cyclopentyl-1,1-difluoroethane (4) and an isomer of di-adduct (5).

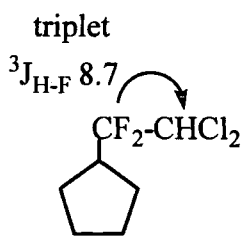


$R_{FHCl} = CF_2CHCl_2$

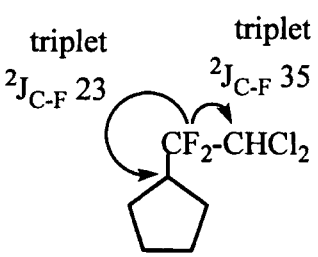
Initiator and conditions	Ratio C_5H_{10} : CF_2=CCl_2	Product ratio (4) : (5)	Yield (%) (4)
(i) γ-rays, r.t., 3 weeks	1.5 : 1	no reaction	0
(ii) DTBP, 140°C, 24 hrs	4 : 1	11.5 : 1	48

No reaction occurred using γ-ray initiation but, using DTBP initiation, the difluorodichloro adduct (**4**) was prepared in average isolated yield (48%) with only minor impurities. Thus, GLC/MS showed the presence of an isomer of di-adduct (**5**) ($[M]^+$ at m/z 336). Compound (**4**) appeared to be more stable upon distillation than compound (**1**) probably because there was no trace of the reverse-addition compound which could readily lose hydrogen chloride.

The mode of addition for compound (**4**) was determined by NMR data. The ^1H NMR spectrum contained a triplet at 5.7 ppm with a characteristic three-bond coupling constant to fluorine ($^3J_{H\text{-}F}$ 8.7) which was assigned to the $CHCl_2$ hydrogen atom.



^{13}C NMR confirmed the structure as two triplets with a two-bond coupling constant to fluorine were observed at 42.1 ppm ($^2J_{C\text{-}F}$ 22.3) and at 70.1 ppm ($^2J_{C\text{-}F}$ 35.1). They were assigned to the CH ring carbon atom and to the $CHCl_2$ carbon atom respectively.



If the reverse mode of addition had occurred, only one carbon atom would have shown a two-bond coupling constant to fluorine, as the fluorine atoms would be at the end of the side chain.

* *Orientation of addition*

As previously, radical attack occurred at the CF_2 position because it is the most electrophilic and the least hindered site. No trace of attack at the CCl_2 position was observed, most probably because of the large steric requirement of two chlorine atoms.

2.1.3. Conclusions for additions to chlorofluoroethenes

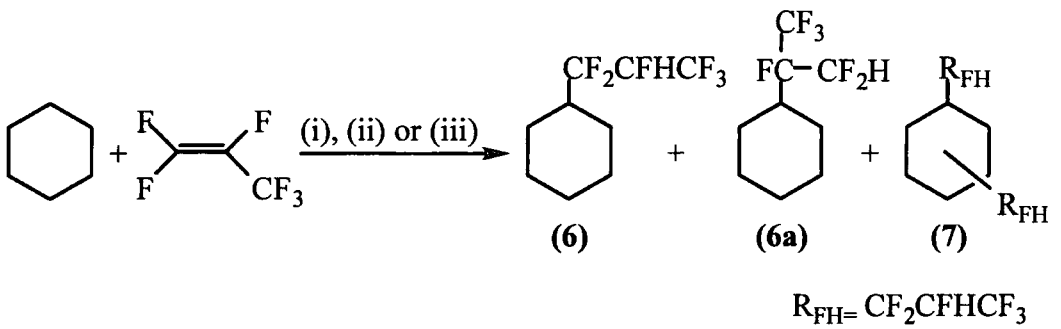
1 : 1 Adducts (**1**) and (**4**) derived from chlorofluoroethenes and cyclopentane can be prepared in useful quantitative scale despite low reactivity as shown by the presence of unreacted alkene in the recovered cyclopentane and the low isolated yields. The regioselectivity of the addition step was good with attack occurring predominantly at the CF_2 position (the most electrophilic and the least hindered position). In the reaction with 1,1-dichloro-2,2-difluoroethene, attack at the CCl_2 position was completely prohibited because of the steric bulk of two chlorine atoms. These regioselectivities were consistent with free-radical additions to various chlorofluoropropenes reported by Paleta.[28]

2.2. Additions to hexafluoropropene (HFP)

Some polyfluoroalkylated derivatives were prepared by radical additions to hexafluoropropene (HFP) following previous work (The references will be quoted at the beginning of each of the following sections). HFP was used in this project because it does not homopolymerise and therefore provides a convenient route to polyfluoroalkylated compounds, which can be further functionalised as described in subsequent chapters.

2.2.1. Addition of cyclohexane to HFP[50]

Cyclohexane was added to HFP using both γ-ray and DTBP initiation to give (1,1,2,3,3,3-hexafluoropropyl)cyclohexane (**6**) and several isomers of the di-adduct 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (x=2-4) (**7**). A trace (less than 6% by GLC/MS) of the reverse-addition product 2-cyclohexyl-1,1,1,2,3,3-hexafluropropane (**6a**), which has not been reported previously, was also observed by GLC/MS and ^{1}H NMR.



R_{FH}= CF_2CFHCF_3

Initiator and conditions	Ratio C_6H_{12} : HFP	Conversion (%) (based on C_6H_{12})	Yield (%) (6)	(7)
(i) γ-rays, r.t., 14 days	1 : 1.5	90	85	6
(ii) DTBP, 140°C, 24 hrs	1 : 1.3	99	70	25
(iii) DTBP, 140°C, 24 hrs	1 : 3	99	28	66

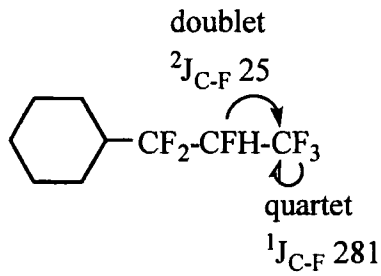
The ratio of mono- to di-addition products depended on the ratio of HFP to cyclohexane and fractional distillation separated (1,1,2,3,3,3-hexafluoropropyl)cyclohexane (**6**) from the di-adducts isomers (**7**).

i) Structure elucidation of compound (6)

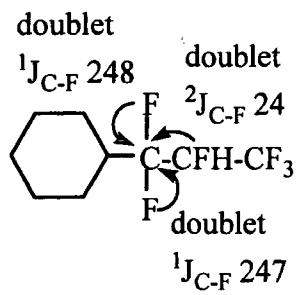
Although NMR data of compound (**6**) have been reported in the literature[50] and explained by Cooper[35] and Spink,[7] they will be again described in details here as compound (**6**) is an important precursor in this project and therefore its characterisation assists with the characterisation of subsequent compounds.

* *^{13}C NMR*

On the ^{13}C NMR spectrum of compound (**6**) three signals appeared at very low field and were assigned to the hexafluoropropyl carbon atoms according to their coupling constants to fluorine. The *C*F_3 carbon atom resonance occurred at 120.9 ppm as a quartet ($^1J_{C\text{-}F}$ 281) of a doublet ($^2J_{C\text{-}F}$ 25).

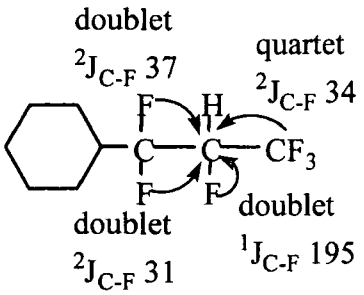


The *C*F_2 carbon atom resonance occurred at 119.7 ppm as a doublet ($^1J_{C\text{-}F}$ *ca.* 248) of a doublet ($^1J_{C\text{-}F}$ *ca.* 247) due to two-non equivalent fluorine atoms. These doublets were splitted again into doublets with a two-bond coupling constant ($^2J_{C\text{-}F}$ *ca.* 24).

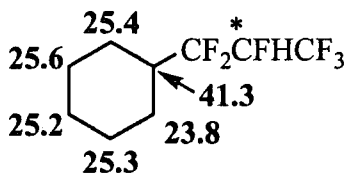


The *C*FH carbon atom resonance occurred at 84.6 ppm as a doublet of a doublet of a quartet of a doublet. This splitting was explained by one relatively large one-bond coupling constant ($^1J_{C\text{-}F}$ *ca.* 195) and three smaller two-bond coupling constants ($^2J_{C\text{-}F}$ *ca.* 37, $^2J_{C\text{-}F}$ *ca.*

34 and $^2J_{C\text{-}F}$ *ca.* 31) (the two fluorine atoms of the difluoromethylene group being magnetically inequivalent).

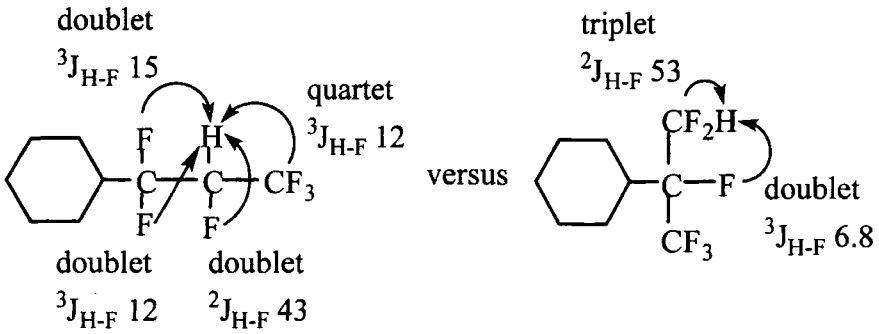


At low frequency, six more resonances corresponded to the cyclohexyl ring carbon atoms. Despite their chemical equivalency, the ring carbon atoms are magnetically inequivalent because the cyclohexyl ring bears a chiral substituent.[88] Therefore, each ring carbon atom has a different chemical shift leading to six distinct resonances. A triplet at 41.3 ppm was assigned to the methyne carbon atom on account of a two-bond coupling constant to fluorine ($^2J_{C\text{-}F}$ 21.3). A multiplet at 25.4 ppm and a triplet at 23.8 ppm ($^3J_{C\text{-}F}$ 4.5) were assigned to the two carbon atoms next to the methyne group because of a three-bond coupling constant to fluorine. The three other methylene carbons gave three singlets at 25.2, 25.3 and 25.6 ppm with the methylene carbon furthest away from the electron-withdrawing fluoroalkyl chain being assigned to the signal at highest field.



* *^{1}H NMR*

^{1}H NMR confirmed that compound **(6)** was formed by the addition at the difluoromethylene group as a doublet ($^2J_{H\text{-}F}$ 43) of a doublet ($^3J_{H\text{-}F}$ 15) of a quartet ($^3J_{H\text{-}F}$ 12) of a doublet ($^3J_{H\text{-}F}$ 12) occurred at 4.8 ppm and was attributed to the CF*H* proton. For the minor reverse-addition product **(6a)**, the CF_2H proton resonance consisted of a triplet ($^2J_{H\text{-}F}$ 53) of a doublet ($^3J_{H\text{-}F}$ 6.8) at 5.9 ppm.



(6) **(6a)**

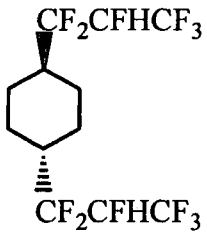
* *^{19}F NMR*

Structure of compound (**6**) was also confirmed by the ^{19}F NMR spectrum. The resonances were assigned by their relative integration. The C*F*$_3$ fluorine atoms gave a multiplet at –74.5 ppm characteristic for a CF_3 group. The C*F*H fluorine atom gave a doublet ($^2J_{F-H}$ 44) of a quartet ($^3J_{F-F}$ 10) at –212 ppm. The CF_2 fluorine atoms appeared as an AB system at –119.1 and –118.3 ppm as the fluorine atoms are diastereotopic. If the reverse-mode of addition was the major pathway, the tertiary fluorine atom and the difluoromethyl group in R-CF(CF_3)CF_2H would give resonances between –140 and –190 ppm on the ^{19}F NMR spectrum.

ii) Di-adduct mixture (7)

The mixture of di-adducts (**7**) consisted of seven isomers in a ratio of 1 : 4.6 : 0.7 : 10 : 6 : 7.4 : 2.9 by GLC/MS. A white solid crystallised out from the di-adduct mixture on standing in the fridge overnight. In its ^{13}C NMR spectrum, only three resonances were observed for the ring carbon atoms, which ruled out the possibility that the solid di-adduct was the 1,3-bis-adduct. The triplet ($^2J_{C-F}$ 22) at 40.7 ppm was assigned to the methyne ring carbon atoms. Two other triplets ($^3J_{C-F}$ 4.6 and $^3J_{C-F}$ 3.1) at 22.9 and 24.3 corresponded to the methylene ring carbons.

Previously in this laboratory a single crystal X-ray structure conclusively identified the solid di-adduct (**7a**) as the 2*R*,2'*S*-*trans*-1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane diastereoisomer.[7]

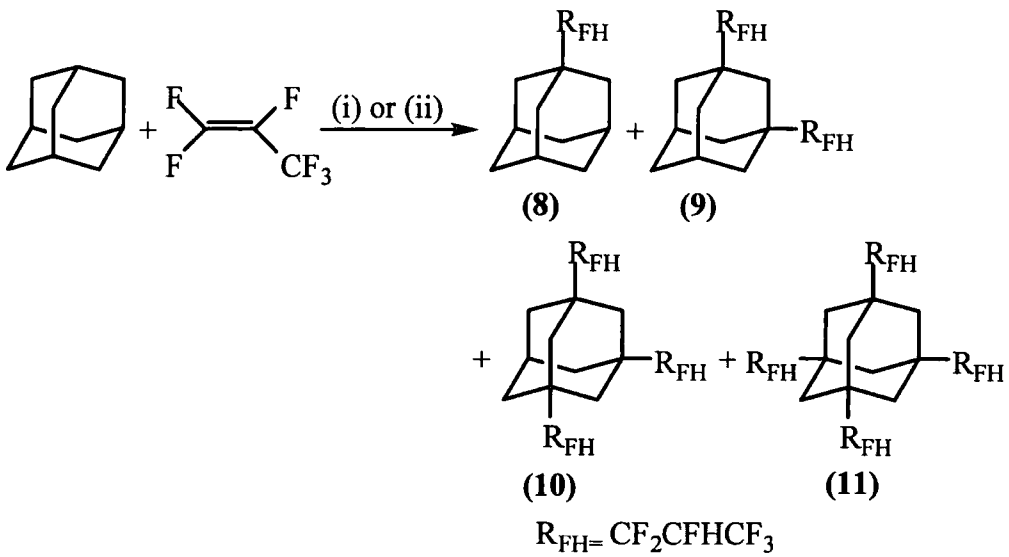


(7a)

This compound is a highly symmetric molecule dominated by a centre of inversion.

2.2.2. Addition of adamantane to HFP[50]

1-(1,1,1,2,3,3-Hexafluoropropyl)adamantane (**8**), 1,3-bis(1,1,1,2,3,3-hexafluoropropyl)adamantane (**9**), 1,3,5-tris(1,1,1,2,3,3-hexafluoropropyl)adamantane (**10**) and 1,3,5,7-tetrakis(1,1,1,2,3,3-hexafluoropropyl)adamantane (**11**) were prepared by radical addition of adamantane to HFP using DTBP initiation.



R_{FH}= CF_2CFHCF_3

Initiator and conditions	Ratio $C_{10}H_{16}$: HFP	Conversion (%) (based on $C_{10}H_{16}$)	Yield (%) (8)	(9)	(10)	(11)
(i) DTBP, 140°C, 24 hrs	1 : 1.2	94	55	28	/	/
(ii) DTBP, 140°C, 24 hrs	1 : 7	100	/	/	40	13

The product distribution depended on the molar ratios of the reactants. With a slight excess of HFP, the mono-adduct (**8**) and the di-adduct (**9**) were obtained as the major

products and they were separated by distillation after sublimation of the remaining adamantane. With a large excess of HFP, the tri-adduct (**10**) and the tetra-adduct (**11**) were obtained and easily separated because the tetra-adduct crystallised out from the waxy product mixture when mixed with chloroform.

The ^{19}F, ^{13}C, ^{1}H and EI^{+} mass spectra of each adduct were in agreement with the literature.[50]

* *Orientation of addition*

As for addition of cyclohexane to HFP, the presence of doublets of doublets of quartets of doublets in the region 4-6 ppm on the ^{1}H NMR spectrum showed that radical addition of adamantane occurred at the CF_2 site of HFP.

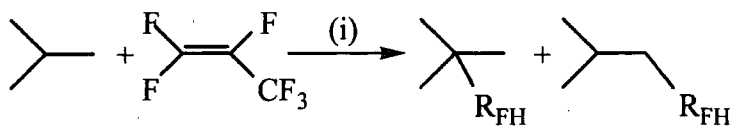
* *Sites of substitution in adamantane*

In the ^{1}H NMR spectrum of the mono-adduct (**8**) only three signals were observed showing that the product is symmetric and that the fluoroalkyl chain was attached to a bridghead position. For the tetra-adduct (**11**) no C*H* proton was observed on the ^{1}H NMR spectrum confirming that all the fluoroalkylations occurred at the bridghead positions.

Hydrogen abstraction occurred at the bridghead carbons in adamantane in preference to the methylene carbons. Although the bridghead radical of adamantane is pyramidal and cannot invert, it is unstrained and therefore still favourable to hydrogen abstraction.

2.2.3. Addition of 2-methylpropane to HFP[50]

2-Methylpropane was added to HFP using DTBP initiation to give 4,4-dimethyl-1,1,1,2,3,3-hexafluoropentane (**12**) in good yield (75%) and a minor product (1% by GLC/MS) identified as 1,1,1,2,3,3-hexafluoro-5-methylhexane (**13**) by comparison to the literature.[50]



(12) (75%) **(13)** (trace)

$R_{FH=}$ CF_2CFHCF_3

Initiator and conditions	Ratio C_4H_{10} : HFP	Yield (%) (12)
(i) DTBP, 140°C, 24 hrs	1 : 1.2	75

* *Structure elucidation of compound (12)*

^1H, ^{19}F NMR and EI^+ mass spectra of compound **(12)** were in agreement with the literature.[50]

Radical addition to HFP occurred preferentially *via* the methyne carbon, as confirmed by the ^1H NMR spectrum. Two resonances (in a ratio of 9 to 1) were observed at chemical shifts consistent with CH_3 hydrogen atoms (1.1 ppm) and with CFH hydrogen atoms (4.9 ppm).

The ^{13}C NMR spectrum, which was not reported in previous work, also confirmed the site of addition : only five signals were observed. Two signals appeared at low frequency : a singlet at 23.8 ppm was assigned to the CH_3 carbon atoms and a triplet at 38.7 ppm ($^2J_{C\text{-}F}$ 21.5) corresponded to the carbon atom attached to the fluoroalkyl chain. At low field, three more resonances were attributed to the hexafluoropropyl carbon atoms according to their coupling constants to the fluorine atoms (see paragraph 2.2.1). If addition had occurred *via* the methyl carbons, six resonances would have been observed in the ^{13}C NMR spectrum.

* *Compound (13)*

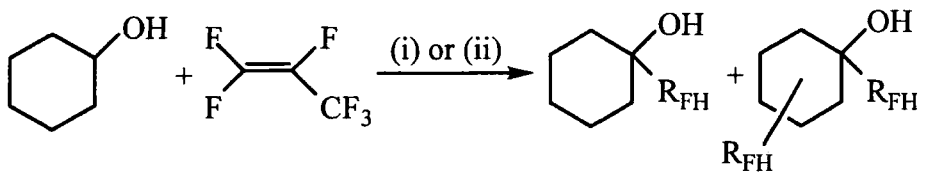
The minor compound **(13)** was identified by comparison to the literature. No characterisation by NMR was obtained here but the EI^+ mass spectrum displayed a base peak at m/z 43 corresponding to the loss of $[CH_2CF_2CFHCF_3]^+$ fragment which suggested that addition had occurred at a methyl carbon.

* *Discussion of the results for addition of 2-methylpropane to HFP*

Addition occurred *via* the methyne group preferentially rather than *via* the methyl groups because of the increased stability of tertiary radicals over primary radicals (due to hyperconjugation in the tertiary carbon radical) and also because the H-abstraction is facilitated at the tertiary site (due to polar effects).

2.2.4. Addition of cyclohexanol to HFP[44]

Cyclohexanol was added to HFP using DTBP initiation to give 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexanol (**14**) in average yield (41-55%) after distillation.



(14) **(15)**

$R_{FH=}$ CF_2CFHCF_3

Initiator and conditions	Ratio ROH : HFP	Conversion (%) (based on ROH)	GC Yield(%)[isolated] **(14)**	**(15)**
i) DTBP, 140°C, 24 hrs	1 : 1.1	85	52 [41]	26
ii) DTBP, 120°C, 24 hrs	1 : 1.1	94	58 [55]	25

R= C_6H_5

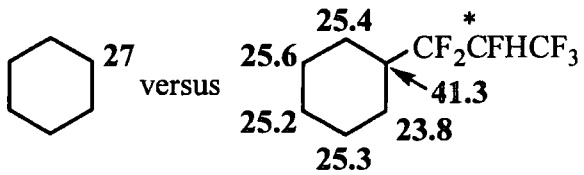
GLC/MS of the crude mixture showed the presence of large amounts of di-addition products (25% by GLC/MS) as opposed to previous work which reported that only trace amount of di-adducts (less than 5% by GLC/MS) were formed.[44] Formation of the di-addition products did not decrease by lowering the temperature and their structure were not determined due to the complexity of their NMR spectra.

On the EI^+ mass spectrum of compound (**14**), no molecular ion was observed but a strong $[M\text{-}R_{FH}]^+$ fragment occurred at m/z 99.

* *^{13}C NMR*

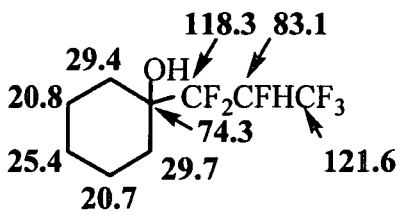
The ^{13}C NMR spectrum of compound (**14**) determined the site of substitution in cyclohexanol. ^{13}C NMR chemical shifts for the CH_2 carbon atoms in cyclohexanol occur in the region 20-40 ppm, while the resonance for the site attached to the hydroxy group occurs in the region 60-80 ppm.[89] Changes in chemical shift induced by the introduction of the

hexafluoropropyl chain are much smaller than this difference (less than 15 ppm) as illustrated by the ^{13}C NMR chemical shifts for the ring carbon atoms of (**6**).



(**6**)

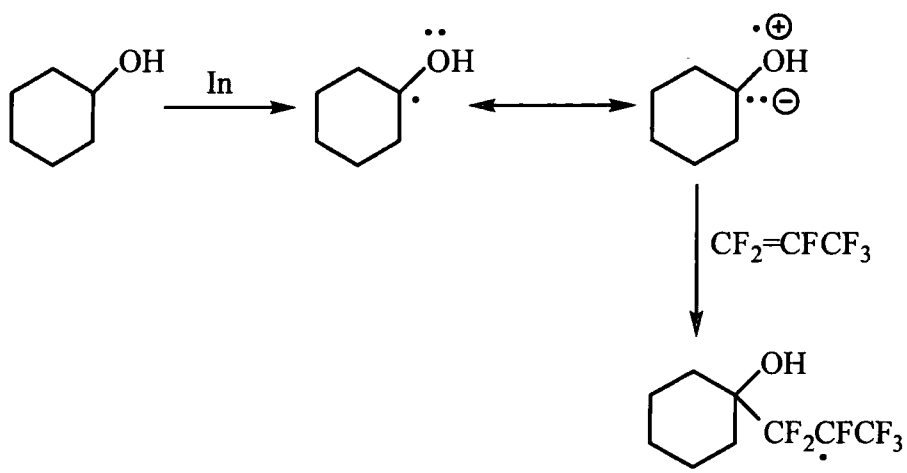
Therefore the triplet ($^2J_{C\text{-}F}$ 24.2) at 74.3 ppm was assigned to the hydroxyl carbon atom. Five other resonances were observed at low frequency and accounted for the magnetically inequivalent ring carbon atoms (see paragraph 2.2.1). At low field, the three resonances were assigned to the hexafluoropropyl carbon atoms, as described previously (see paragraph 2.2.1).



(**14**)

* *Discussion of the results for addition of cyclohexanol to HFP*

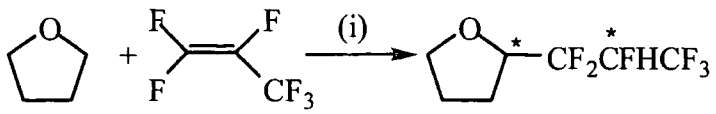
The radical addition occurred selectively at the carbon atom directly attached to the hydroxy group, because of the effects the oxygen atom. It promotes the addition step by conjugative stabilisation.



But, the inductively electron-withdrawing oxygen atom also reduces the reactivity towards radical attack at positions where the conjugative stabilisation does not apply.

2.2.5. Addition of tetrahydrofuran (THF) to HFP[52]

THF was added to HFP using DTBP initiation to give two diastereoisomers of 2-(1,1,2,3,3,3-hexafluoropropyl)oxolane **(16)** in a ratio of 1 : 1.1 by GLC/MS.



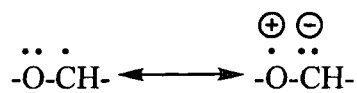
(16)
1 : 1.1 (82%)

Initiator and conditions	Ratio THF : HFP	Conversion (based on HFP)	GC yield (%) [isolated] **(16)**
(i) DTBP, 140°C, 18 hrs	2.5 : 1	100	93 [82]

Structure of compound **(16)** was elucidated from NMR and mass spectra. In the EI^+ mass spectra of each diastereoisomer of compound **(16)** the molecular ions gave weak peaks at m/z 222. As explained earlier (see paragraph 2.2.1) the radical attack occurred at the CF_2 site. The site of substitution in THF was determined by ^{13}C NMR. The CH_2O carbon atoms in THF occurred at 67.9 ppm, whereas the CH_2 carbon atoms furthest away from the oxygen occurred at 25.8 ppm.[89] Introduction of the hexafluoropropyl chain should give a shift of less than 15 ppm (see paragraph 2.2.4). Thus, the two resonances (due to two diastereoisomers) at 77.1 and 75.6 ppm were assigned to one of the carbon atoms adjacent to oxygen. These resonances appeared as doublets of doublets because of a two-bond coupling constant to two non-equivalent fluorine atoms.

* *Discussion of the results for addition of THF to HFP*

The radical addition occurred selectively at one of the carbon atoms adjacent to oxygen because of the stabilising interaction of the electron-pair on the oxygen with the orbital containing the odd electron, analogous to alcohols.

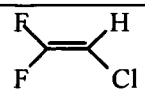
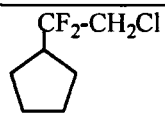
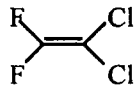
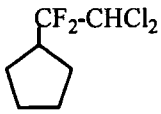
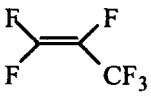
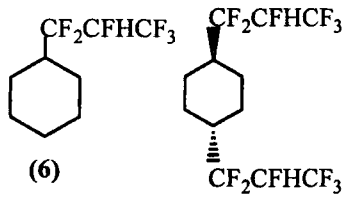
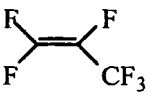
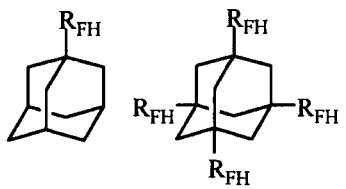
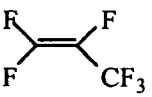
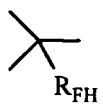
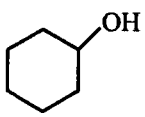
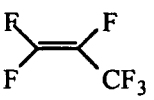
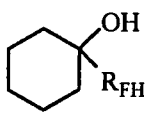
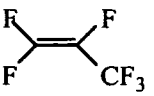
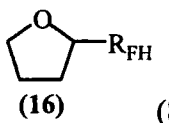


2.3. Conclusions

Radical additions of various substrates (several saturated hydrocarbons, cyclohexanol and ether) to fluoroalkenes (1-chloro-2,2-difluoroethylene, 1,1-dichloro-2,2-difluoroethylene and hexafluoropropene) gave a range of fluoroalkylated derivates (reported in the following table) with a wide potential for further functionalisation.

Radical additions to chlorodifluoroethenes and hexafluoropropene occurred predominantly at the CF_2 site, because this is the most electrophilic and the least hindered site. The favoured sites of substitution on the substrates depended on the radical stabilities and on the H-abstraction step.

The next chapter will describe the further functionalisation (mainly by dehydrofluorination) of the fluoroalkylated derivates.

Substrate	Fluoroalkene	Major products (used in subsequent reactions) and isolated yields (%)
		 **(1)** (24%)
		 **(4)** (48%)
		 **(6)** **(7a)** (yields depended on ratio of reactants)
		 **(8)** **(11)** (yields depended on ratio of reactants)
		 **(12)** (75%)
		 **(14)** (55%)
		 **(16)** (82%)

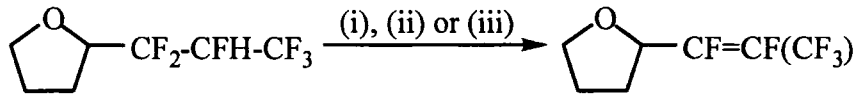
R_{FH}= CF_2CFHCF_3

3. Dehydrofluorinations and other functionalisations of fluoroalkylated derivatives

3.1. Introduction

An obvious way of further functionalisation of the fluoroalkylated derivatives described in chapter 2 was the elimination of hydrogen fluoride to give several fluoroalkenes. Dehydrofluorinations have been reviewed in the literature[90, 91] and so only examples directly related to this project will be presented here.

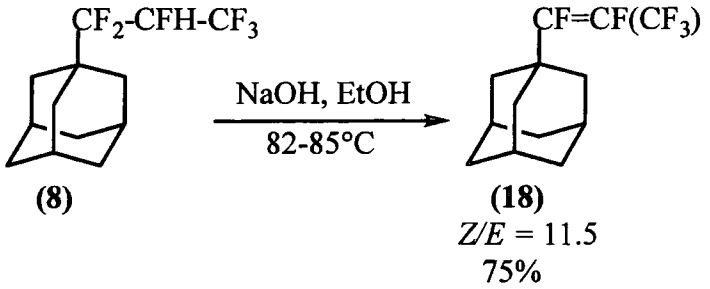
Dehydrofluorination of ether-HFP adducts have been performed in various conditions. In general, the reactions were performed using alkoxide bases with or without solvent to give isomeric mixtures of *Z*- and *E*-alkenes which could not be separated.



(16) **(17)** *Z/E*

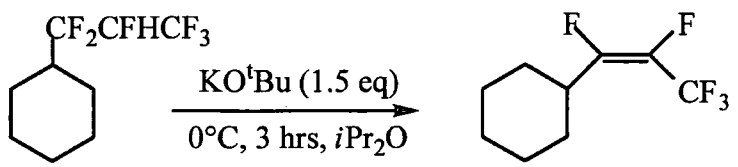
Conditions	Ratio *Z* : *E*	Yield (%) **(17)**	Reference
i) KOH powder, 150°C	1.15 : 1	47	[52]
	1.9 : 1	75	[92]
ii) KOH powder, diglyme, 120°C	1.9 : 1	75	[93]
	not reported	36	[92]
iii) NaO^{t}Bu, ^{t}BuOH, 25°C	1.15 : 1	71	[93]

Similarly, dehydrofluorination of the mono-adduct **(8)** of adamantane was achieved using alcoholic sodium hydroxide to give some isomeric mixtures of *Z*- and *E*-alkenes which could not be separated.[94]



(8) **(18)**
Z/E = 11.5
75%

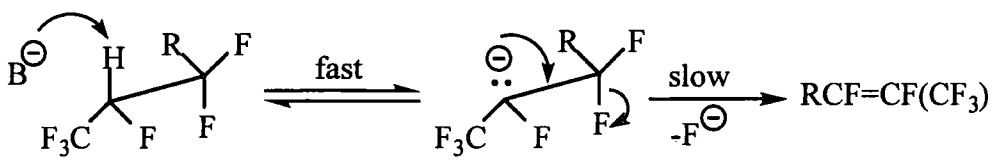
More recently, Chambers[50] showed that, under favourable reaction conditions, only one isomer was formed by dehydrofluorination. Thus, elimination of hydrogen fluoride at low temperatures gave only the *Z*-isomer in many cases and reasons for that will be explained in paragraph 3.3.7.



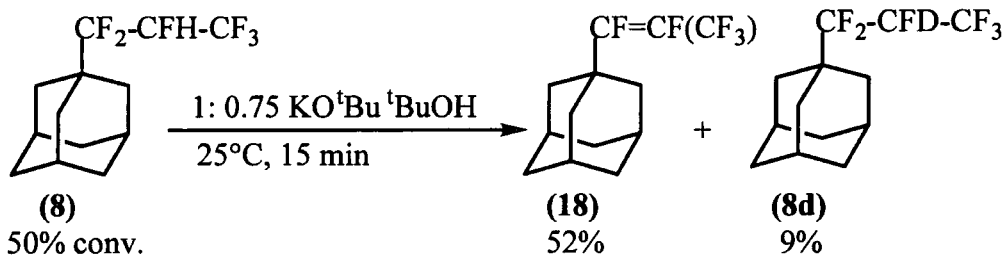
(6) **(19)**
Z-only
(92%)

* *Mechanism*

For compounds in which hydrogen is sufficiently acidified by several β-fluorine atoms, the dehydrofluorination mechanism is likely to be E1cB or E2 (concerted) with an 'E1cB-like' transition state. In the E1cB mechanism, represented below, the C-H bond stretching occurs before the C-F bond stretching and so the reaction proceeds *via* a carbanion intermediate.



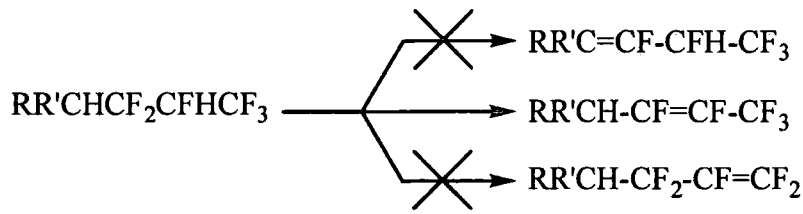
Deuterium exchange reactions carried out previously in this laboratory,[7] using a deuterated solvent, confirmed the E1cB mechanism, because some deuterium was found to be incorporated into the starting material.



(8) 50% conv. **(18)** 52% **(8d)** 9%

* *Regiochemistry of the double bond*

In all cases reported,[50] the double bond is formed at the two-position in the fluoroalkyl side chain, although theoretically three isomers could be formed.



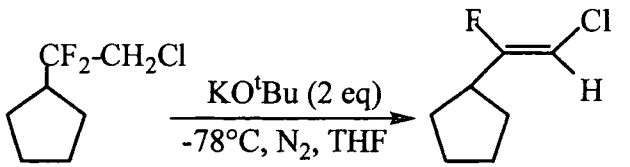
This regiochemistry is explained by the high acidity of the proton removed and the strength of the C-F bond being broken. First, if hydrogen fluoride can be eliminated in two different ways, it is always the more acidic hydrogen atom that leaves preferentially. The CF*H* hydrogen atom is more acidic than the *CH*CF_2 hydrogen atom because fluorine atoms in β-positions stabilise the carbanion intermediate. Then, the fluoride ion which is eliminated preferentially comes from the difluoromethyl rather than the trifluoromethyl group as this results in a smaller number of vinylic fluorine atoms whose lone pairs have unfavourable interactions with the π-electrons of the double bond.

3.2. Dehydrofluorinations of the chlorofluoro-adducts

This section describes dehydrofluorination of the difluorinated adducts (**1**) and (**2**) to give two novel fluoroalkenes of general formula R-CF=CXY (X, Y= H, Cl).

3.2.1. 2-Chloro-1-cyclopentyl-1,1-difluoroethane

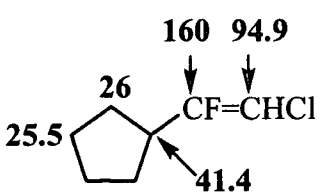
Dehydrofluorination of 2-chloro-1-cyclopentyl-1,1-difluoroethane (**1**) gave (*Z*)-2-chloro-1-cyclopentyl-1-fluoroethene (**20**) in good isolated yield (62%).



(**1**) (**20**)
Z-only (62%)

Two equivalents of potassium *tert*-butoxide (a sterically hindered base which promotes elimination with little competing nucleophilic attack) were used to achieve complete conversion. The structure of compound (**20**) was elucidated from MS and NMR data. In the EI^+ mass spectrum, strong $[M]^+$ ion peaks occurred at m/z 150 and 148 (in relative intensities of 1 to 3). Weak $[C_2FHCl]^+$ fragments also occurred at m/z 79 and 81, suggesting the regiochemistry of the double bond.

In the ^{13}C NMR spectrum, a doublet ($^1J_{C\text{-}F}$ 262) at 160 ppm was assigned to the *C*F carbon atom on account of a one-bond coupling constant to fluorine. A doublet ($^2J_{C\text{-}F}$ 19.4) at 94.9 ppm and a doublet ($^2J_{C\text{-}F}$ 23.6) at 41.4 ppm were assigned to the *C*HCl and to the *C*H ring carbon atom respectively. The methylene carbons gave singlets, with the methylene carbons furthest away from the electron-withdrawing fluoroalkyl group being assigned to the signal at highest field.

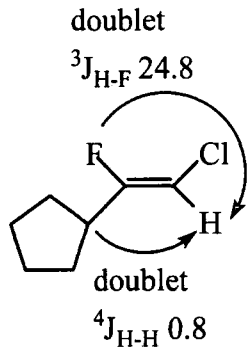


* *Stereochemistry*

The stereochemistry of the alkene (**20**) was deduced by consideration of the H-F coupling constant. In the ^{19}F NMR spectrum, a doublet at –109.8 ppm showed a characteristic *trans* H-F coupling constant ($^3J_{trans\ H\text{-}F}$ 24.8) according to $^3J_{H\text{-}F}$ values (10.8 and 24.2 Hz) reported by Reilly for *cis*- and *trans*-1-chloro-2-fluoroprop-1-ene respectively.[95] Therefore the alkene was assigned as the *Z*-isomer. If the *E*-isomer was formed, the coupling constant would be expected to be smaller ($^3J_{cis\ H\text{-}F}$ *ca* 1-15 Hz).[96]

* *Regiochemistry*

The ^1H NMR spectrum confirmed the regiochemistry of the double bond as a doublet ($^3J_{trans\ H\text{-}F}$ 24.8) of a doublet ($^4J_{H\text{-}H}$ 0.8) at 5.31 ppm was assigned to the C*H*Cl proton and a multiplet at 2.6 ppm was attributed to the methyne proton.

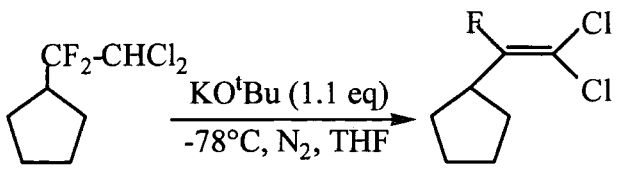


* *Discussion of the results*

The only product obtained at –78°C was the isomer with the cyclopentyl ring and the chlorine atom *trans* to one another. This was expected as the *Z*-isomer is thermodynamically stable because the sterically bulky cyclopentyl ring and the chlorine atom are on opposite sides of the double bond.

3.2.2. 2,2-Dichloro-1-cyclopentyl-1,1-difluoroethane

Dehydrofluorination of 2,2-dichloro-1-cyclopentyl-1,1-difluoroethane **(2)** gave 2,2-dichloro-1-cyclopentyl-1-fluororoethene **(21)** in good isolated yield (63%).



(2) **(21)** (63%)

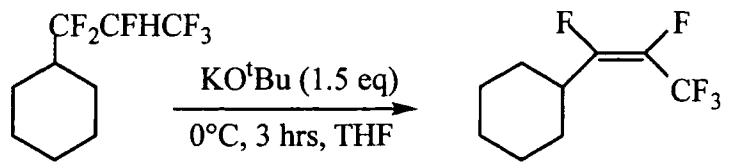
The reaction was conveniently monitored by ^{19}F NMR because the doublet ($^3J_{F\text{-}H}$ 14.7) of doublets ($^3J_{F\text{-}H}$ 8.6) at −113.8 ppm was gradually replaced by a doublet ($^3J_{F\text{-}H}$ 30) at −113.4 ppm. The structure of compound **(21)** was elucidated from MS and NMR data. In the EI^+ mass spectrum, weak $[M]^+$ ion peaks occurred at m/z 182, 184 and 186. $[C_2FCl_2]^+$ fragments were also observed at m/z 113, 115 and 117 suggesting the regiochemistry of the double bond. In the ^1H NMR spectrum, a doublet ($^3J_{H\text{-}F}$ 30.4) of a pentet ($^3J_{H\text{-}H}$ 8.4), assigned to the methyne proton, confirmed the regiochemistry of the double bond. A DEPT spectrum also confirmed the regiochemistry of the double bond as a *C*H carbon atom resonance occurred at 38.8 ppm as a doublet ($^2J_{C\text{-}F}$ 23.6) and was assigned to the methyne ring carbon atom.

3.3. Dehydrofluorinations of the HFP-derivatives

This section describes the dehydrofluorination of some HFP-derivatives reported in chapter 2 to give several fluoroalkenes of general formula R-CF=CF(CF_3).

3.3.1. (1,1,2,3,3-Hexafluoropropyl)cyclohexane

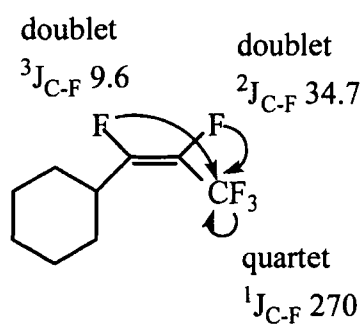
Dehydrofluorination of (1,1,2,3,3-hexafluoropropyl)cyclohexane (**6**) gave (1*Z*)-1-cyclohexyl-1,2,3,3,3-pentafluoropropene (**19**) in good isolated yield (70%) in agreement with previous work.[50]



(6) **(19)** *Z*-only (70%)

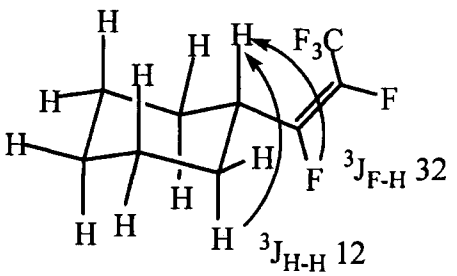
The structure of alkene (**19**) was elucidated from MS and NMR data, which were in agreement with the literature data.[50] The EI^+ mass spectrum gave a weak $[M]^+$ peak at m/z 214. The stereochemistry of the alkene (**19**) was suggested by the ^{19}F NMR spectrum. The $^3J_{F\text{-}F}$ coupling constant between the two vinylic fluorine atoms was small and caused the resonances to appear as unresolved multiplets. If the vinylic fluorine atoms were in the *trans* configuration, their coupling constant to one another would be much larger (about 130 Hz).[50] Therefore the fluorine atoms in compound (**19**) are *cis* and the stereochemistry of the double bond is *cis*.

The ^{13}C NMR spectrum confirmed the *Z*-conformation about the double bond. The CF_3 carbon atom resonance occurred at 120.2 ppm as a quartet ($^1J_{C\text{-}F}$ 270) of a doublet ($^2J_{C\text{-}F}$ 34.7) of a doublet ($^3J_{C\text{-}F}$ 9.6).



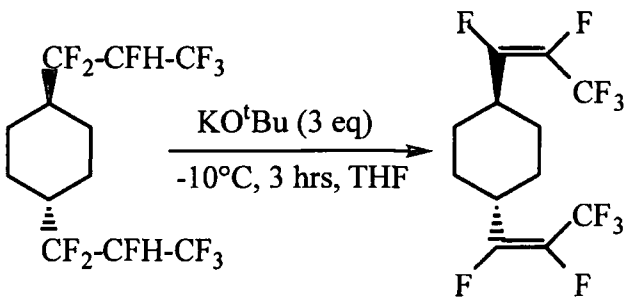
The magnitude of the third-order coupling constant ($^3J_{C\text{-}F}$ 9.6) was consistent with a *trans* coupling constant. The stereochemistry of compound (**19**) was surprising as the cyclohexyl ring and the trifluoromethyl group would be expected to be *trans* to one another for steric reasons.

On the ^{1}H NMR spectrum, a doublet ($^3J_{H\text{-}F}$ 32.8) of a triplet ($^3J_{H\text{-}H}$ 12) at 2.49 ppm was assigned to the C*H* ring proton, which confirmed the regiochemistry of the double bond. Moreover, the magnitude of the third order H-H coupling constant ($^3J_{H\text{-}H}$ 12) was consistent with an antiperiplanar vicinal coupling.[96] Therefore, the fluoroalkenyl group was in equatorial position about the cyclohexyl ring in compound (**19**).



3.3.2. 2*R*,2'*S*-*Trans*-1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane

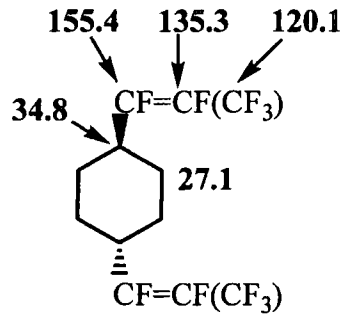
Dehydrofluorination of 2*R*,2'*S*-*trans*-1,4-bis (1,1,2,3,3,3-hexafluoropropyl) cyclohexane (**7a**) gave *trans*-1,4-bis[(1*Z*)-pentafluoroprop-1-enyl]-cyclohexane (**22**) in good isolated yield (61%) in agreement with previous work.[50]



(7a) **(22)** (61%)

A three-fold excess of potassium *tert*-butoxide was used to achieve complete conversion of the starting material (**7a**). Compond (**22**) precipitated out of the organic layer when cooling down.

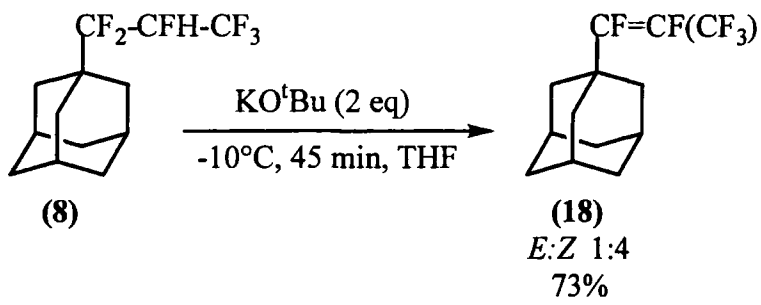
Structure of compound (**22**) was elucidated by comparison to the literature data.[50] On the EI^+ mass spectrum, a strong $[M]^+$ peak occurred at m/z 344. The high symmetry of compound (**22**) was confirmed by ^{13}C NMR, as only five signals were observed : three at low field were assigned to the fluoroalkenyl chain and two at high field corresponded to the methylene and the methyne ring carbons.



The stereochemistry of both equivalent double bonds was suggested by ^{19}F NMR as *cis*. Previously in this laboratory,[7] as single crystal X-ray structure confirmed unambiguously compound (**22**) to be *trans*-1,4-bis[(1*Z*)-pentafluoroprop-1-enyl]-cyclohexane.

3.3.3. 1-(1,1,2,3,3,3-Hexafluoropropyl)adamantane

Dehydrofluorination of 1-(1,1,2,3,3,3-hexafluoropropyl)adamantane (**8**) gave an isomeric mixture of 1-[pentafluoroprop-1-enyl]adamantane (**18**) in good isolated yield (73%), according to previous work.[50]



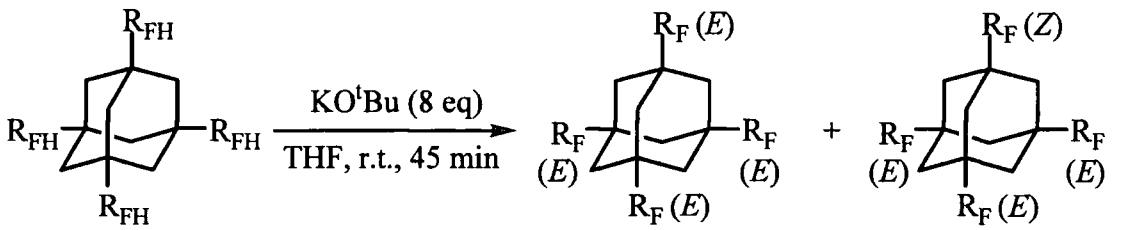
(**8**) (**18**) *E*:*Z* 1:4 73%

On the EI^+ mass spectrum of both isomers of compound (**18**) strong $[M]^+$ ion peaks occurred at m/z 266. By comparison to data in the literature,[50] the major isomer was

assigned to the *Z*-isomer, as the *cis* F-F coupling between the two vinylic fluorine atoms could not be observed on the ^{19}F NMR spectrum. The minor isomer was clearly identified as the *E*-isomer on account of a large *trans* coupling constant between the two vinylic fluorine atoms : a doublet ($^3J_{trans\ F\text{-}F}$ 131.7) of a quartet ($^4J_{F\text{-}F}$ 22.6) at –149.3 ppm and a doublet ($^3J_{trans\ F\text{-}F}$ 131.4) of a quartet ($^3J_{F\text{-}F}$ 9.4) at –175.6 ppm were assigned to the C*F* and the C*F*CF_3 fluorine atoms respectively.

3.3.4. 1,3,5,7-Tetrakis(1,1,2,3,3,3-hexafluoropropyl)adamantane

Dehydrofluorination of 1,3,5,7-tetrakis(1,1,2,3,3,3-hexafluoropropyl) adamantane (**11**) gave an isomeric mixture of 1,3,5,7-tetrakis(pentafluoroprop-1-enyl)adamantane (**23a**) and (**23b**), in agreement with previous work.[50]



(11) **(23a)** **(23b)**

5 : 1

54%

R_{FH}= CF_2-CFH-CF_3

R_F= CF=CF(CF_3)

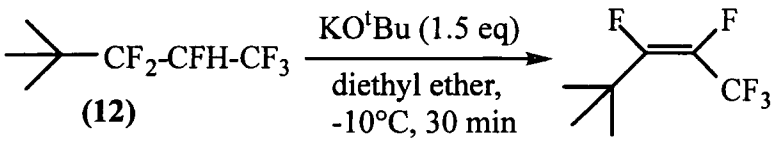
Complete conversion of the tetra-adduct (**11**) was achieved by using an excess of potassium *tert*-butoxide and performing the reaction at room temperature. Distillation under reduced pressure gave an isomeric mixture of (**23a**) and (**23b**) in a ratio of 5 :1 by ^{19}F NMR, from which compound (**23a**) crystallised out when mixing with chloroform and cooling down at –50°C.

NMR spectra of compounds (**23a**) and (**23b**) were in agreement with the literature.[50] On the ^{19}F NMR spectrum of compound (**23a**) only three signals were observed confirming the high symmetry of the molecule. The two vinylic fluorine atoms resonances occurred as doublets at –150.1 ppm ($^3J_{trans\ F\text{-}F}$ 134.3) and –170.8 ppm ($^3J_{trans\ F\text{-}F}$ 133.6) confirming the *E*-conformation about the four equivalent double bonds. A doublet ($^3J_{F\text{-}F}$ 22.9) of a doublet ($^4J_{F\text{-}F}$ 10.2) at –68.1 ppm was assigned to the CF_3 fluorine atoms. On the ^{19}F NMR spectrum of compound (**23b**), six signals were observed. Two resonances at –60.3 and –67.9 ppm in

a ratio of 1 to 3 were attributed to the CF_3 fluorine atoms of the *Z*- and *E*-double bond respectively. Four vinylic resonances were also observed. Two broad singlets at –126.5 and –150 corresponded to the two *cis*-fluorine atoms. Two large doublets ($^3J_{trans\ F\text{-}F}$ 132.8 and 132.5) were assigned to the six *trans*-fluorine atoms.

3.3.5. 4,4-Dimethyl-1,1,1,2,3,3-hexafluoropentane

Dehydrofluorination of 4,4-dimethyl-1,1,1,2,3,3-hexafluoropentane (**12**) gave (2*Z*)-1,1,1,2,3-pentafluoro-4,4-dimethylpent-2-ene (**24**).



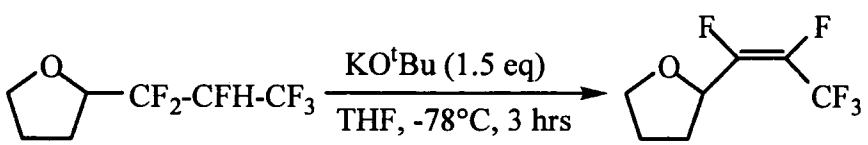
(12) **(24)**
Z only
no yield recorded

When the dehydrofluorination of compound (**12**) was carried out in THF, no product was recovered after work-up due to the volatility of the product which probably evaporated with the solvent during distillation. However, when the reaction was attempted using KOH pellets without solvent, it resulted only in decomposition products. Therefore the dehydrofluorination of compound (**12**) was performed in diethyl ether and careful evaporation of the solvent gave (**24**) only on an NMR scale. Thus, no yield was recorded.

Structure of compound (**24**) was elucidated from NMR data and ^{13}C NMR confirmed the *Z*-conformation about the double bond, as previously.

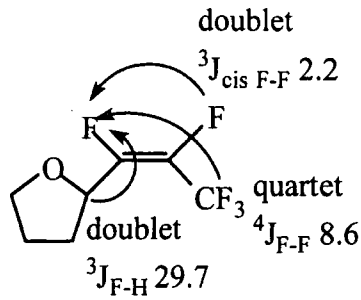
3.3.6. 2-(1,1,2,3,3,3-Hexafluoropropyl)oxolane

Dehydrofluorination of 2-(1,1,2,3,3,3-hexafluoropropyl)oxolane (**16**) gave only 2-[(1*Z*)-1,2,3,3,3-(pentafluoroprop-1-enyl)]oxolane (**17**) in good isolated yield (64%).



(16) **(17)**
Z-only
64%

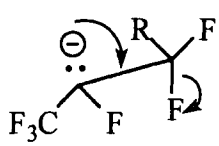
Structure of compound (**17**) was elucidated from MS and NMR data. On the EI^+ mass spectrum a strong $[M]^+$ peak occurred at m/z 202. In the ^1H NMR spectrum, a doublet ($^3J_{H\text{-}F}$ 29.2) of multiplet at 4.78 ppm assigned to the C*H*-CF proton (on account of a three-bond coupling to fluorine) confirmed the regiochemistry of the double bond. The ^{19}F NMR spectrum was in agreement with the literature[52] and confirmed the *Z*-conformation about the double bond, as a small *cis* F-F coupling constant between the two vinylic fluorine atoms was observed. Thus, at –140.3 ppm the doublet ($^3J_{F\text{-}H}$ 29.7) of a quartet ($^4J_{F\text{-}F}$ 8.6) of a doublet ($^3J_{cis\ F\text{-}F}$ 2.2) was assigned to the C*F* fluorine atom.



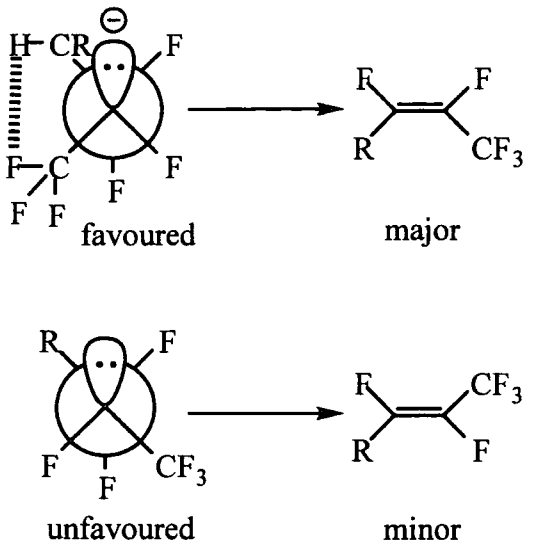
3.3.7. Discussion of the results for dehydrofluorination of HFP-derivatives

The *Z*-isomers (i.e. the isomers with the fluorine atoms *cis* to each other) were formed preferentially at low temperatures (from –78°C to 0°C). This was surprising as the *Z*-isomers are the less thermodynamically stable alkenes due to steric interactions between the alkyl and the trifluoromethyl groups. Obviously kinetic control led to the *Z*-isomers.

It is probable that the dehydrofluorination occurs by an E1cB mechanism and in such a mechanism the rate determining step is the loss of fluoride ion from the intermediate anion.



Thus, for the less thermodynamically stable isomer to be formed preferentially, there must be some energy-lowering interaction between R and the trifluoromethyl groups, such as hydrogen bonding in the carbanion-like transition state. This situation has been supported by calculations performed by other workers.[97]

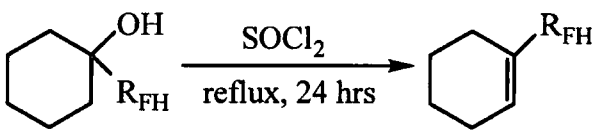


3.4. Synthesis of diene (26)

1-(1,2,3,3,3-Pentafluoro-*Z*-prop-1-enyl-cyclohexene (**26**) was prepared from 1-(1,1,2,3,3,3-hexafluoropropyl)cyclohexanol (**14**) by a two-step synthesis following some previous work.[51]

3.4.1. Dehydration

The first step of the di-ene synthesis was the dehydration of 1-(1,1,2,3,3,3-hexafluoropropyl)cyclohexanol (**14**) using thionyl chloride to give 1-(1,1,2,3,3,3-hexafluoropropyl)cyclohexene (**25**) in good isolated yield (73%).



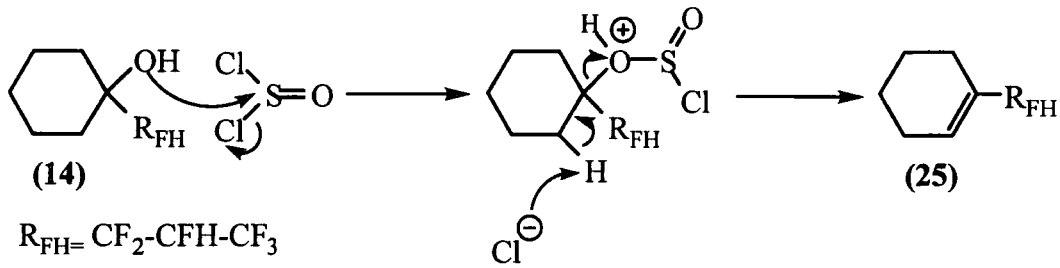
(14) **(25)**

R_{FH}= CF_2-CFH-CF_3 73%

The course of the reaction was conveniently monitored by ^{19}F NMR as the AB system at –127.7 and –128.4 ppm was gradually replaced by an AB system at –110.9 and –113.7 ppm. On the ^{1}H NMR spectrum of compound (**25**) a multiplet was observed at 6.30 ppm, which is characteristic of a vinylic proton. ^{13}C NMR confirmed the formation of a ring double bond as a triplet ($^{3}J_{C\text{-}F}$ 9.2) at 130.3 ppm and a triplet ($^{2}J_{C\text{-}F}$ 21.7) at 130.1 ppm were

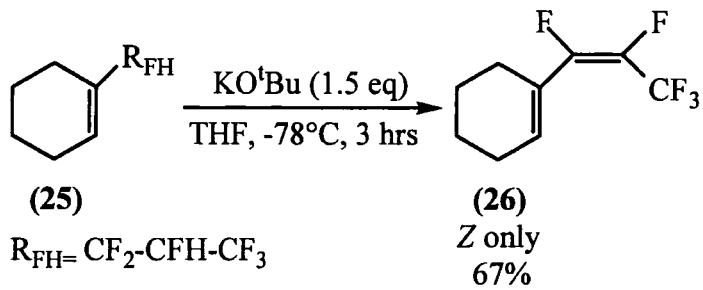
attributable to the unsaturated carbon atoms. Three other resonances occurred at low field and corresponded to the hexafluoropropyl carbon atoms.

A possible mechanism for the dehydration suggested by Chambers[44] involves a nucleophilic displacement of chloride ion which can subsequently act as a base to promote the elimination process.



3.4.2. Dehydrofluorination

Dehydrofluorination of 1-(1,1,2,3,3,3-hexafluoropropyl)cyclohexene (**25**) gave (1,2,3,3,3-pentafluoro-*Z*-prop-1-enyl-cyclohexene (**26**) in good yield (67%) after fractional distillation.



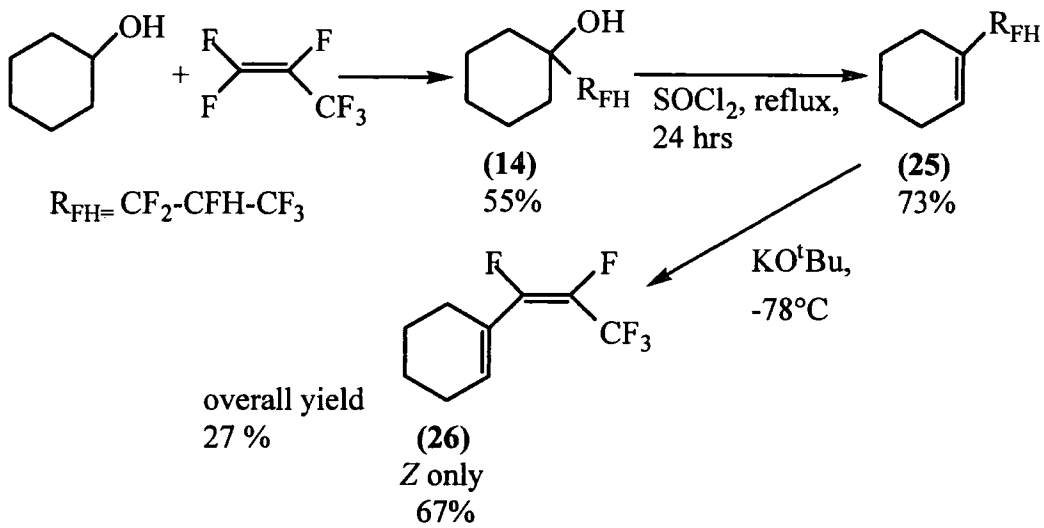
The course of the reaction was conveniently monitored by fluorine NMR. On the ^{19}F NMR spectrum of compound (**26**), three signals were observed in a ratio of 3 : 1 : 1. A doublet ($^3J_{F\text{-}F}$ 12.4) of a doublet ($^4J_{F\text{-}F}$ 8.6) at –65.9 ppm was attributed to the CF_3 fluorines. An unresolved multiplet (due to a small *cis* F-F coupling) occurred at –117.6 ppm and corresponded to the C-C*F* fluorine atom. A pentet ($^3J_{F\text{-}F}$ 12.4) was assigned to the C*F*-CF_3 fluorine atom.

The structure of compound (**26**) was further elucidated from MS, ^{13}C NMR and ^1H NMR spectra. On the EI^+ mass spectrum, a strong $[M]^+$ ion peak occurred at m/z 212. On the ^{13}C NMR spectrum, five resonances were observed at low field : three corresponded to

the carbon atoms in the fluoroalkenyl chain and two to the ring double bond carbon atoms. These five resonances were attributed in accordance with F-C coupling contants. The CF_3 carbon atom resonance occurred at 120.1 ppm as a quartet ($^1J_{C\text{-}F}$ 269.9) of a doublet ($^2J_{C\text{-}F}$ 34.9) of a doublet ($^3J_{C\text{-}F}$ 8.7). The magnitude of the third order coupling constant confirmed, as previously (see paragraph 3.1.1), the *Z*-conformation about the fluorinated double bond.

3.4.3. Summary

Diene (**26**) was prepared from cyclohexanol and HFP in a three step synthesis (first radical addition of cyclohexanol to HFP followed by dehydration of alcohol and dehydrofluorination of the fluoroalkyl chain) in a overall isolated yield of 27%.

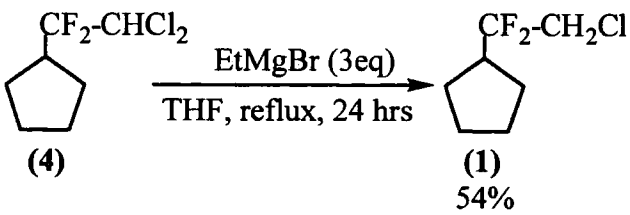


The reactivity of diene (**26**) toward electrophiles was studied and will be presented in chapter 4.

3.5. Miscellaneous

3.5.1. Reduction of 2,2-dichloro-1-cyclopentyl-1,1-difluoroethane

Reduction of 2,2-dichloro-1-cyclopentyl-1,1-difluoroethane (**4**) to the chlorodifluoro system (**1**) was accomplished by reaction with a Grignard reagent.



Compound (**1**) was obtained in good isolated yield (54%) with the spectral data described earlier (see paragraph 2.1.1.). The synthesis adapted from methodology described by Okuhara[98] was envisaged to proceed by an SET (Single Electron Transfert) mechanism as shown below.

$$EtMgBr \xrightarrow{heat} Et^{\bullet} + {}^{\bullet}MgBr$$

$$RCF_2CHCl_2 + {}^{\bullet}MgBr \longrightarrow RCF_2\dot{C}HCl + MgBrCl$$

$$RCF_2\dot{C}HCl \xrightarrow{THF} RCF_2CH_2Cl$$

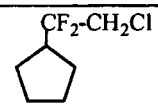
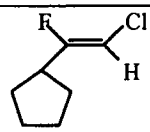
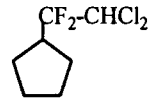
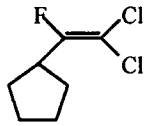
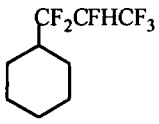
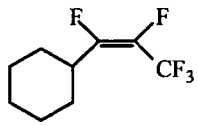
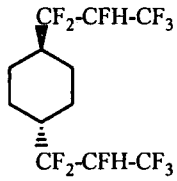
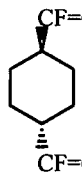
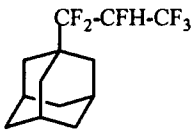
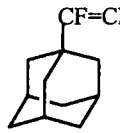
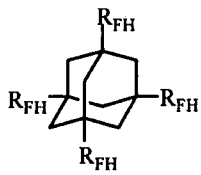
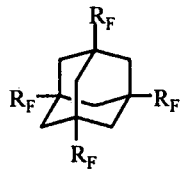
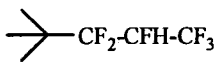
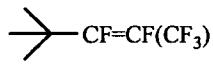
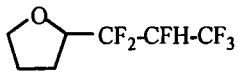
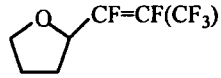
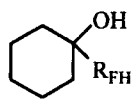
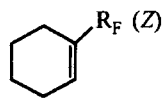
R= 

3.5.2. Attempted replacement of Cl by F using SbF_5

Antimony pentafluoride can replace halogens located at unactivated sites by fluorine atoms.[99] But, in the present work 2,2-dichloro-1-cyclopentyl-1,1-difluoroethane (**4**) and antimony pentafluoride at 0°C for 2 hours gave no reaction.

3.6. Conclusions

The fluoroalkylated derivatives described in chapter 2 were further functionalised mainly by dehydrofluorination to give various fluoroalkenes reported in the following table. By performing the dehydrofluorinations at low temperature and by using a bulky base such as potassium *tert*-butoxide, the *Z*-isomers were formed preferentially for the HFP-derivatives. These fluoroalkenes can be further functionalised and this will be described in the next chapter.

Starting material	Conditions	Products and yields (%)
 (1)	KO^{t}Bu, -78°C	 (20) *Z*-only, 62%
 (2)	KO^{t}Bu, -78°C	 (21) 63%
 (6)	KO^{t}Bu, 0°C	 (19) Z-only, 70%
 (7a)	KO^{t}Bu, -10°C	 (22) *Z*-only, 61%
 (8)	KO^{t}Bu, -10°C	 (18) *Z*/*E* = 4, 73%
 (11)	KO^{t}Bu, -10°C	 (23a) (23b) 54%
 (12)	KO^{t}Bu, -10°C	 (24) *Z*-only, NMR scale
 (16)	KO^{t}Bu, -78°C	 (17) *Z*-only, 64%
 (14)	$SOCl_2$, reflux then KO^{t}Bu, -78°C	 (26) *Z*-only

R_f= CF_2-CFH-CF_3, R_F= CF=CF(CF_3)

4. Reactions of fluoroalkenes with electrophiles

4.1. Introduction

Fluoroalkenes exhibit a high reactivity toward nucleophilic reagents, because of the strong electron-acceptor influence of fluorine atoms and perfluoroalkyl groups. But, because the electron density on the double bond is reduced, fluorinated alkenes are often quite resistant to electrophilic attack. However, some reactions of fluoroalkenes with electrophiles have been reported.[100, 101] For example, Naae[102] added bromine to some fluorinated phenyl substituted alkenes.

$$RC_6H_4CF{=}CFX \xrightarrow[HOAc,\ dark]{Br_2} RC_6H_4CFBr\text{-}CFXBr$$

R=CO_2H, Br, CH_3, OCH_3
X= Cl, CF_3

4.1.1. Mechanism : radical or electrophilic ?

Reaction of fluoroalkenes with electrophilic reagents can occur by a radical or an ionic process, depending on the reaction conditions.[100, 101]

i. Radical process

Addition of halogens to the double bond of fluoroalkenes can occur by a radical mechanism as a result of a photochemical process or thermally. For example, Ameduri[103] has recently reported the addition of iodine monochloride to 1,1-difluoroethylene under radical conditions (thermal, photochemical, presence of radical initiators or redox catalysts) to give a mixture of two isomers :

$$ICl + F_2C{=}CH_2 \longrightarrow ClCF_2CH_2I + ICF_2CH_2Cl$$

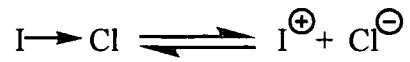
Ameduri[104] also reported the thermally and photochemically initiated addition of iodine monobromide to chlorotrifluoroethylene to give mixtures of four isomers :

$$IBr + F_2C{=}CFCl \longrightarrow BrCF_2CFClI + ICF_2CFClBr + BrCF_2CFClBr + ICF_2CFClI$$

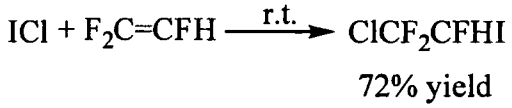
ii. Electrophilic process

However, some additions of halogens to fluoroalkenes under ionic conditions (low temperature, darkness, Lewis-acid catalysts...) have been reported in the literature. For example, bromination of fluorinated phenyl substituted alkenes performed by Naae[102] were carried out in acetic acid in the dark.

Additions of mixed halogens (IF, ICl, IBr and BrF) are also most likely to occur by an ionic process as these compounds are very polar.[100]

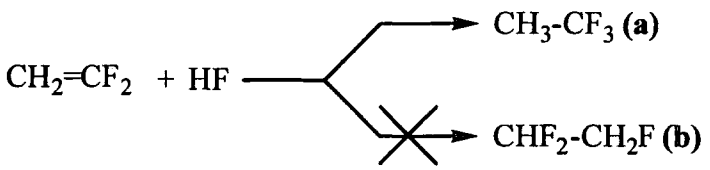


For example, iodine monochloride added readily to 1,1,2-trifluoroethylene at room temperature.[105]



4.1.2. Orientation of electrophilic addition to fluoroalkenes

Electrophilic additions across the double bond of fluoroalkenes are usually regiospecific. For example, reaction of difluoroethylene with HF gave only one regioisomer **(a)**.[106]



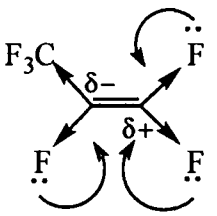
Thus, it is of interest to understand the factors affecting the orientation of electrophilic additions across the double bond of fluoroalkenes. They can be divided into two main effects : the initial state effects and the transition state effects (i.e. the stabilitity of the carbocation intermediate).

i. The initial state effects

The initial state effects are related to the polarisation of the fluorinated double bond, which depends on two factors : the electron-withdrawing effect of fluoroalkyl groups

(σ-inductive effect through the σ-bonded system) and the resonance effects of fluorine atoms attached directly to the double bond. Interaction between the unshared p-electron pairs of the fluorine atoms and the π-electrons of the double bond leads to the shift of the π-electrons (p-π repulsions) and polarisation of the double bond.

The overlaping inductive and resonance effects of substituents in hexafluoropropene result in directing the attack of electrophiles to the central carbon atom.

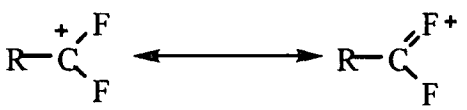


The double bond in this system is also relatively 'electron rich', which favours attack by electrophiles.

ii. The transition state effects

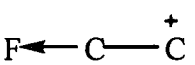
As carbocations are important intermediates in electrophilic additions, carbocation stabilities (which are influenced by α- and β- fluorine substituents) can predict the orientation of electrophilic attack.

A fluorine atom directly attached to a carbocation center is stabilising by 'back-donation'.



+π (stabilising)

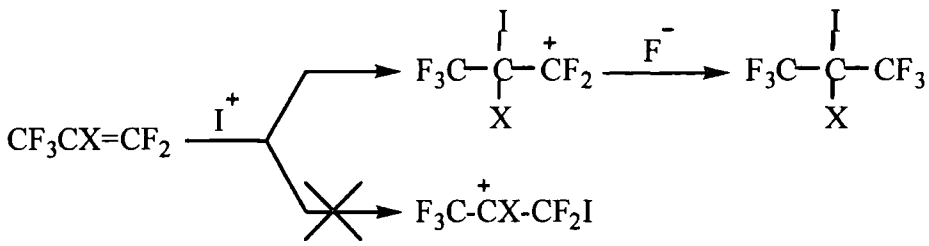
However, fluorine in β-positions are strongly destabilising as a result of the strong σ-inductive effect.



-σ (destabilising)

iii. Examples

As it has just been described, electrophilic additions to fluoroalkenes are usually regiospecific. For example, iodofluorinations of CF_2=CX-CF_3 starts with the attack of 'I^+' on the central carbon atom of the alkene, according to polarisation.[107]



However, mixtures of isomers are sometimes formed. For example, the addition of iodine monochloride to trifluorochloroethylene gave two isomers, their relative amounts depending on reaction conditions (temperature, reaction vessel, solvent...).[108]

$$CF_2{=}CFCl \longrightarrow \underset{\textbf{(a)}}{CF_2ClCFClI} + \underset{\textbf{(b)}}{CFCl_2CF_2I}$$

Conditions	Isomeric composition (%)	
	a	**b**
i) 0°C, glass reactor, CH_2Cl_2	97	3
ii) 50°C, glass reactor, no solvent	45	55
iii) 40°C, iron reactor, no solvent	38	62

Although the dual orientation is consistent with a radical mechanism, the reason for such duality in liquid phase processes could arise from steric factors.[58]

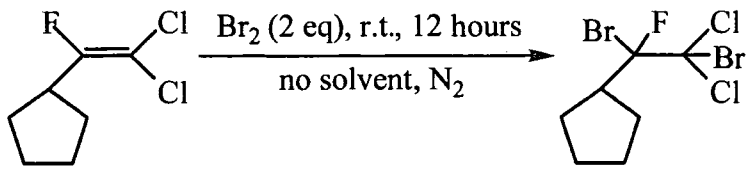
4.2. Reactions of fluoroalkenes with electrophiles

In this project, a variety of fluoroalkenes of general formula R-CF=CXY (X, Y = Cl, F, CF_3) were prepared and described in chapter 3. The reactivity of these systems towards electrophiles (Br_2, IBr, ICl and IF) was then explored and we focussed upon the reactions with iodine monofluoride to give some novel fluorine and iodine containing organic compounds. Thus, this chapter describes the reactions of 2,2-dichloro-1-cyclopentyl-1-fluoroethene (**21**) and 1-(1,2,3,3,3-pentafluoro-*Z*-prop-1-enyl)-cyclohexene (**26**) with various electrophiles as well as additions of iodine monofluoride to various fluoroalkenes.

4.2.1. Reactions of 2,2-dichloro-1-cyclopentyl-1-fluoroethene with electrophiles

i. Bromine

Bromination of 2,2-dichloro-1-cyclopentyl-1-fluoroethene (**21**) with elemental bromine proceeded readily at room temperature to give 1,2-dibromo-2,2-dichloro-1-cyclopentyl-1-fluoroethane (**27**).



(21) **(27)**

88% (GC yield)
50% (isolated yield)

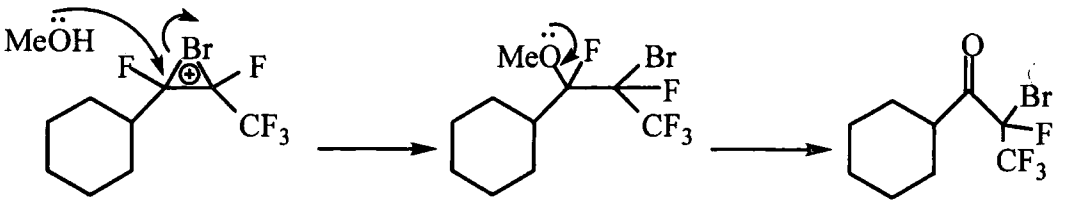
Elemental analysis, MS and carbon NMR data confirmed that addition of bromine across the double bond had occurred. In its EI^+ mass spectrum, compound (**27**) showed peaks at m/z 161/163/165/167 corresponding to $[CCl_2Br]^+$ ion and peaks at m/z 110/112 corresponding to $[CFBr]^+$ ion.

In the carbon NMR spectrum, the carbons bearing the bromine atoms were shifted toward lower frequency by at least 20 ppm compared to compound (**21**). A doublet ($^2J_{C\text{-}F}$ 35) occurred at 85.7 ppm and was assigned to the *C*Cl_2Br carbon atom. The *C*FBr carbon atom resonance occurred as a doublet with a characteristic one-bond coupling constant to

fluorine ($^1J_{C\text{-}F}$ 268) at 119.8 ppm. As the cyclopentyl ring contained a chiral substituent, each CH_2 ring carbon atom gave a distinct resonance, so there were five resonances in the low frequency region of the spectrum, instead of only three as in compound (**21**).

* *Mechanism*

In this laboratory, it was confirmed that bromination of fluoroalkenes could proceed through an electrophilic rather than a radical process.[35] Bromination of (1*Z*)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**19**) was carried out in the presence of a stoichiometric quantity of methanol, so that the bromonium ion (if formed) would be trapped. The ketone 2-bromo-1-cyclohexyl-2,3,3,3-tetrafluoropropan-1-one (**28**) was formed, as illustrated below, supporting the fact that a bromonium ion is the intermediate.

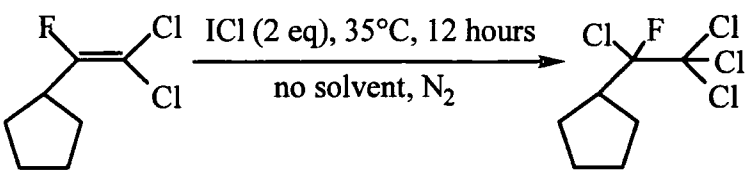


(**28**)

According to these previous results and as formation of 1,2-dibromo-2,2-dichloro-1-cyclopentyl-1-fluoroethene (**27**) was not inhibited in the dark, bromination of compound (**21**) is postulated to occur by an electrophilic process.

ii. Iodine monochloride

Reaction of 2,2-dichloro-1-cyclopentyl-1-fluoroethene (**21**) with iodine monochloride at 35°C gave only 1,2,2,2-tetrachloro-1-cyclopentyl-1-fluoroethane (**29**) in good yield (88%).



(**21**) (**29**)

88% (isolated yield)

The reaction was carried out at 35°C in order to melt the iodine monochloride to achieve better mixing, as no solvent was used. GLC/MS of the crude gave no evidence of addition of both iodine and chlorine across the double bond, but showed that the product arises from addition of two chlorine atoms across the double bond. Thus, on the mass spectrum of compound (**29**), weak peaks occurred at m/z 183/185/187/189/191 corresponding to $[CFClCCl_3]^+$ ion fragment. Elemental analysis confirmed the compound as arising from addition of two chlorine atoms.

The carbon NMR spectrum gave a doublet ($^1J_{C\text{-}F}$ 259) at 120.2 ppm, assigned to the *C*FCl carbon atom on account to a one-bond coupling constant to fluorine. The *C*Cl_3 carbon atom resonance occurred as a doublet ($^2J_{C\text{-}F}$ 35) at 101.8 ppm.

* *Mechanism*

The reaction occurred readily in the dark at 0°C, which confirmed an ionic process. The formation of compound (**29**) could result from decomposition of iodine monochloride into elemental iodine and chlorine.

$$2\,ICl \rightleftharpoons I_2 + Cl_2$$

This would enable chlorine to add across the double bond, whereas iodine would not because of steric hindrance. A mechanism involving electrophilic addition of iodine monochloride followed by displacement of the iodine atom by a chlorine atom was excluded as no trace of the iodo compound was observed.

iii. Iodine monobromide and iodine monofluoride

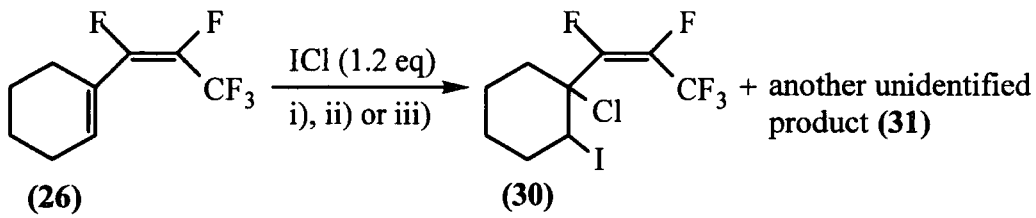
Additions of iodine monobromide and iodine monofluoride to 2,2-dichloro-1-cyclopentyl-1-fluoroethene (**21**) were attempted, but extensive decomposition occurred, probably due to steric effects, which inhibited addition and allowed other reactions to compete.

4.2.2. Reactions of 1-(1,2,3,3,3-pentafluoro-Z-prop-1-enyl)-cyclohexene

1-(1,2,3,3,3-Pentafluoro-Z-prop-1-enyl)-cyclohexene (**26**) was reacted with electrophiles in order to compare the reactivity of the ring double bond and the fluorinated double bond.

i. Iodine monochloride

Addition of iodine monochloride to 1-(1,2,3,3,3-pentafluoro-Z-prop-1-enyl)-cyclohexene (**26**) was performed under various conditions.



(26) **(30)**

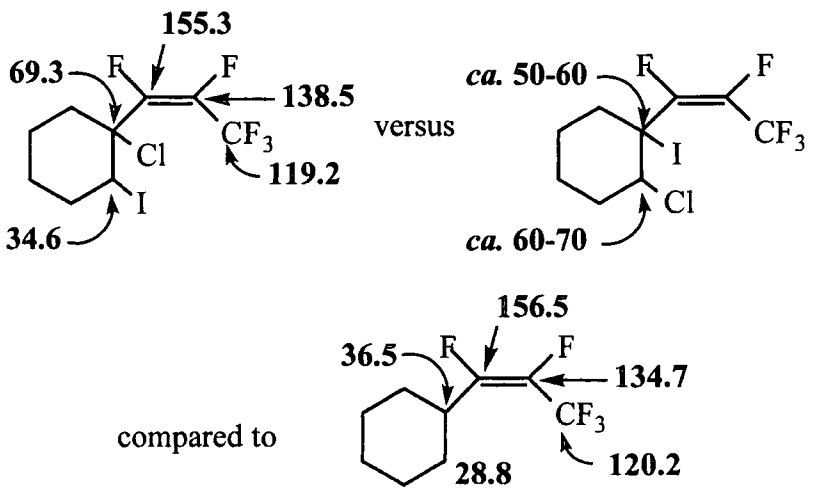
Conditions	Diene conversion (%)	Products yield (GC %) [isolated]	
		(30)	**(31)**
i) no solvent, N_2, 35°C, 12 hrs	89	0	20
ii) DCM, N_2, 0°C, 3 hrs	93	32	8
iii) DCM, N_2, -78°C, 30 mins	87	61 [56]	6

At –78°C, (1Z)-1-(1-chloro-2-iodocyclohexyl)-1,2,3,3,3-pentafluoroprop-1-ene (**30**) was obtained in average isolated yield (56%). At higher temperature, another unidentified compound (**31**) was formed. It could not be isolated (attempted column chromatography and distillation failed) and MS data did not give any information on fragmentations but presumably the product could arise from a 1,4-addition mode, as expected for electrophilic addition to a conjugated diene at high temperature. But this has not been proved.

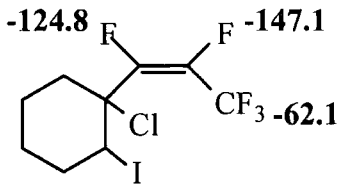
MS data could not confirm the structure of compound (**30**), as no molecular ion was observed and only weak $[M\text{-}I]^+$ fragments occurred at m/z 247 and 249. However, elemental analysis showed compound (**30**) to arise from a single addition of iodine monochloride.

NMR data proved that addition had occurred across the ring double bond. Thus, on the proton NMR spectrum, the doublet at 6.14 ppm arising from the vinylic hydrogen atom in the diene **(26)** was replaced by a resonance at 4.93 ppm characteristic of a C*H*I hydrogen atom. A DEPT spectrum confirmed that the ring double bond had reacted as no C*H* was observed at high frequency. Furthermore, in the carbon NMR spectrum, resonances arising from the fluoroalkyl chain were identical to those of the diene **(26)**, which eliminated the possibility of a 1,4-addition mode.

The orientation of addition of iodine monochloride to the ring double bond was elucidated from the ^{13}C NMR and DEPT spectra. By comparison to the literature,[89] the changes in chemical shifts induced by introduction of chlorine and iodine were consistent with addition of iodine at the least substituted end of the double bond. The *C*Cl carbon atom resonance occurred as a doublet ($^2J_{C\text{-}F}$ 21.7) and was shifted by at least 30 ppm toward higher frequency compared to fluoroalkene **(19)**. The *C*HI carbon atom resonance occurred as a multiplet at 34.6 ppm and was shifted by less than 6 ppm toward higher frequency. If the reverse addition had occurred, the *C*HCl carbon atom resonance would be shifted to much higher frequency (*ca.* 30-40 ppm) compared to fluoroalkene **(19)**, according to the literature.[89]

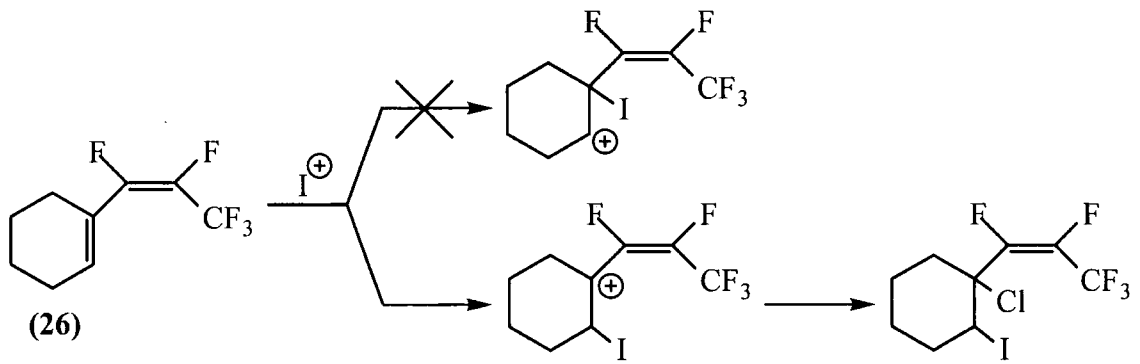


In the fluorine NMR spectrum, the three resonances were assigned by comparison to compound **(26)** as no significant change for the chemical shifts occurred. However, line broadening (probably due to the steric bulk of the iodine and chlorine atoms) caused the signals to appear as singlets.



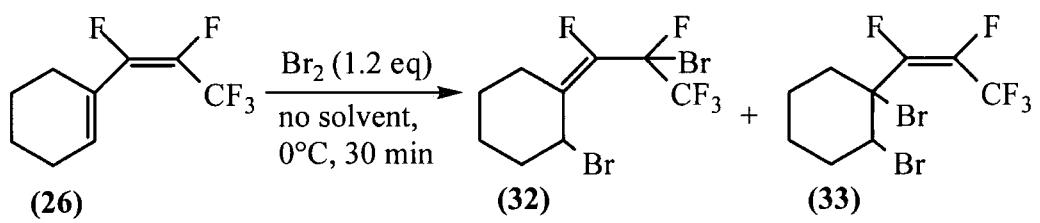
* *Mechanism*

Iodine monochloride added preferentially across the ring double bond rather than across the electron-deficient fluoroalkene double bond. Although two diastereoisomers were expected to be formed by addition across the ring double bond, only one was observed. The fluoroalkyl group should direct the formation of the iodonium bridged and the subsequent nucleophilic attack by chloride ion. Formation of compound **(30)** occurred *via* the most stable carbocation (tertiary rather than secondary and stabilised by resonance).



ii. Bromine

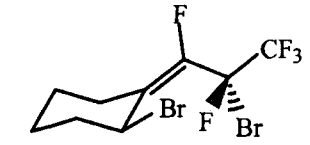
Bromination of 1-(1,2,3,3,3-pentafluoro-*Z*-prop-1-enyl)-cyclohexene **(26)** occurred very rapidly to give a complex mixture of isomers in a ratio of 1.8 : 3.4 : 1.4 : 1.0 : 3.2 by fluorine NMR.



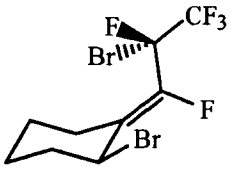
mixture yield 71%

1.8 : 3.4 : 1.4 : 1.0 : 3.2

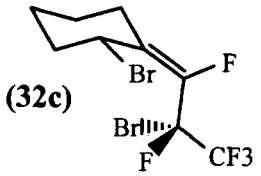
In the mass spectra, no molecular ions were observed but $[M-Br]^+$ fragments occurred at m/z 291 and 294. Elemental analysis indicated that only two bromine atoms had added. A DEPT spectrum confirmed that the ring double bond had reacted as no *C*H carbon atoms were observed at high frequency. In the proton NMR spectrum, disappearance of the multiplet at 6.14 ppm arising from the vinylic proton was observed. Due to the complexity of the spectra, every signal could not be attributed with certainty. However, the mixture was assumed to contain four isomers of **(32)** represented below.



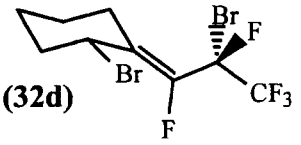
(32a)



(32b)



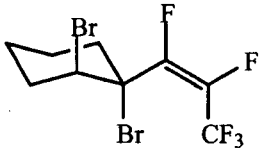
(32c)



(32d)

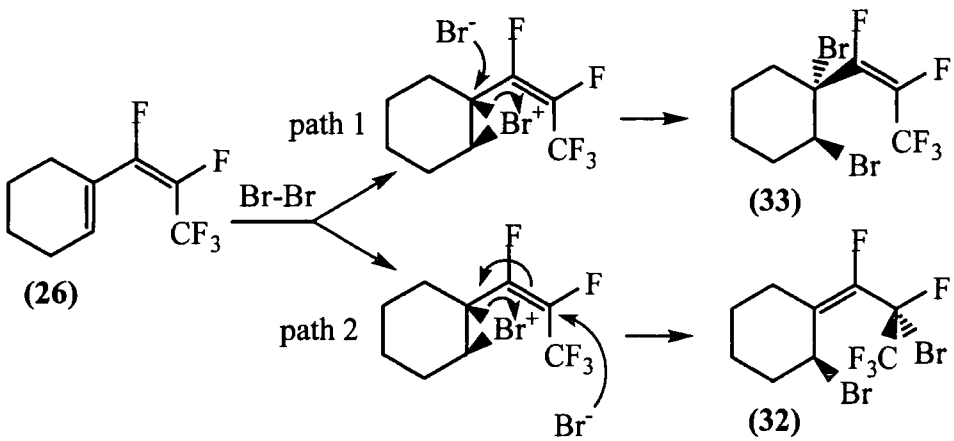
As a matter of fact, in the fluorine NMR, four doublets ($^3J_{F-F}$ around 25) of quartets ($^3J_{F-F}$ around 10) were observed at –127.5, -128.7, -129.7 and –129.9 and could arise from C*F*Br fluorine atoms. Another proof of addition of bromine at the *C*F-CF_3 carbon atom came from the carbon NMR : a doublet ($^1J_{C-F}$ 263.9) of doublet ($^2J_{C-F}$ 43.8) of quartet ($^2J_{C-F}$ 38.6) at 94.2 ppm could arise from *C*FBr.

The fifth isomer in the mixture could be attributed to compound **(33)** as on the carbon NMR spectrum, three resonances attributed to the fluoroalkyl chain were identical to those of the diene **(26)**.



* *Mechanism*

Bromination of compound (**26**) proceeded rapidly in the dark at 0°C so that light could not have initiated a possible radical mechanism. Bromination also occurred readily in acetic acid, which is consistent with an electrophilic process. However, formation of the 1,4-adduct (**32**) was really surprising as a bromonium ion would be formed at the ring double bond (the most electron rich) followed by attack of Br^- at the *C*F-CF_3 position (path 2) rather than directly at the ring carbon atom (path 1). Path 2 involves the opening of the reactive bromonium ions intermediates (only one is represented below) and resulted in a mixture of four diastereoisomers (**32**).



We have been unable to trap the bromonium ion by carrying out the reaction in methanol. Thus, the mechanism for the bromination of diene (**26**) is still unclear.

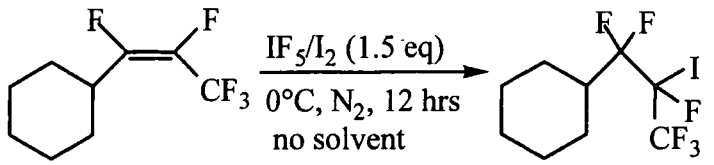
iii. Iodine monobromide and iodine monofluoride

Addition of iodine monofluoride and iodine monobromide to 1-(1,2,3,3,3-pentafluoro-*Z*-prop-1-enyl)-cyclohexene (**26**) resulted in extensive decomposition.

4.3. Addition of iodine monofluoride to fluoroalkenes

4.3.1. (1Z)-1-cyclohexyl-1,1,2,3,3,3-pentafluoropropene

Reaction of (1*Z*)-1-cyclohexyl-1,1,2,3,3,3-pentafluoropropene (**19**) with iodine and iodine pentafluoride gave 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) in high isolated yield (88%).

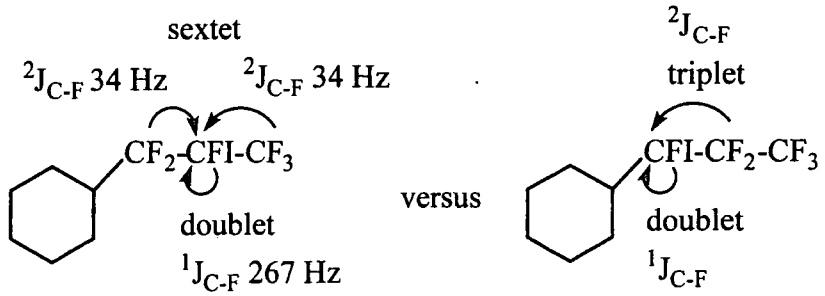


(19) **(34)**

93% (GC yield)
88% (isolated yield)

The reaction proceeded rapidly without requiring a catalyst, which suggested that the fluoroalkene (**19**) is relatively electron-rich. Although the use of solvent was not necessary to give good conversion and good yield, use of freon FC113 or chloroform made the work-up easier.

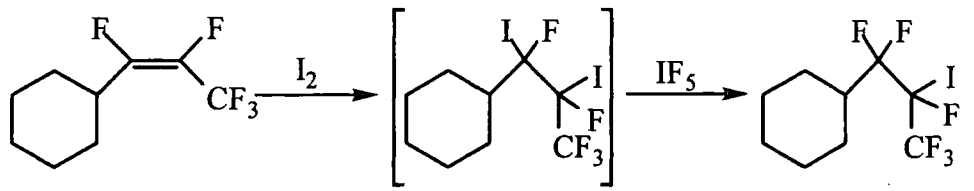
Structure of compound (**34**) was elucidated from MS and NMR data. In the mass spectrum, a weak $[M]^+$ ion peak occurred at m/z 360. A strong peak corresponding to the $[M\text{-}I]^+$ fragment was also observed at m/z 233. The carbon NMR spectrum confirmed the structure of compound (**34**) as the *C*FI carbon atom occurred as a doublet ($^1J_{C\text{-}F}$ 267) of sextets ($^2J_{C\text{-}F}$ 34) at 81.3 ppm, characteristic for a CFI functionality.[96] If the reverse mode of addition had occurred, a doublet ($^1J_{C\text{-}F}$) of a triplet ($^2J_{C\text{-}F}$) would have been observed instead.



In the fluorine NMR spectrum, a sextet ($^3J_{F\text{-}F}$ 14) at 140.1 ppm corresponded to the C*F*I fluorine atoms and an AB system (J_{AB} 267) at −107.4 and −108.1 ppm was attributed to the CF_2 fluorine atoms.

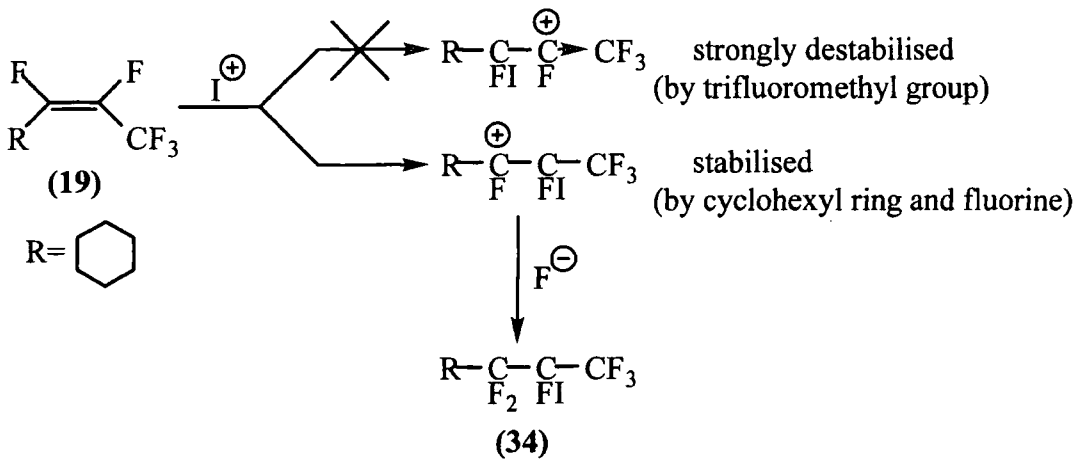
* *Mechanism*

'The mechanism of iodine monofluoride addition is of interest'[109] as the process is regiospecific to the limits of detection by NMR. Addition of iodine monofluoride to fluoroalkene **(19)** could proceed by two possible routes. Addition of iodine followed by selective replacement of the iodine atom next to the cyclohexyl ring by fluorine could occur as represented as follows.



(19) **(34)**

But, addition of iodine to fluoroalkene **(19)** failed, probably because of steric hindrance. Moreover, previously in this laboratory, Cooper[35] showed that additions of iodine monochloride and iodine monobromide to compound **(19)** were regiospecific. Thus, the regioselectivity is more consistent with an electrophilic process (*via* the most stable carbocation) as represented as follows.



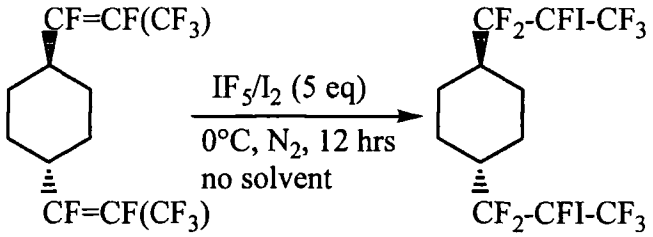
(19)

R=

(34)

4.3.2. *Trans*-1,4-bis(Z-pentafluoroprop-2-enyl)cyclohexane

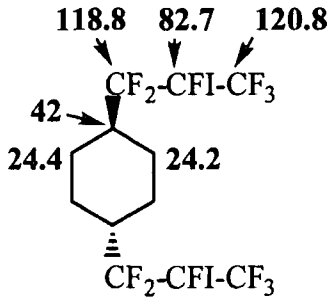
Reaction of *trans*-1,4-bis(Z-pentafluoroprop-2-enyl)cyclohexane (**22**) with iodine and iodine pentafluoride gave 1,1,2,3,3,3-hexafluoro-1-[4-(1,1,2,3,3,3-hexafluoro-2-iodopropyl)cylohexyl]-2-iodopropane (**35**) in good yield (66%).



(22) **(35)**

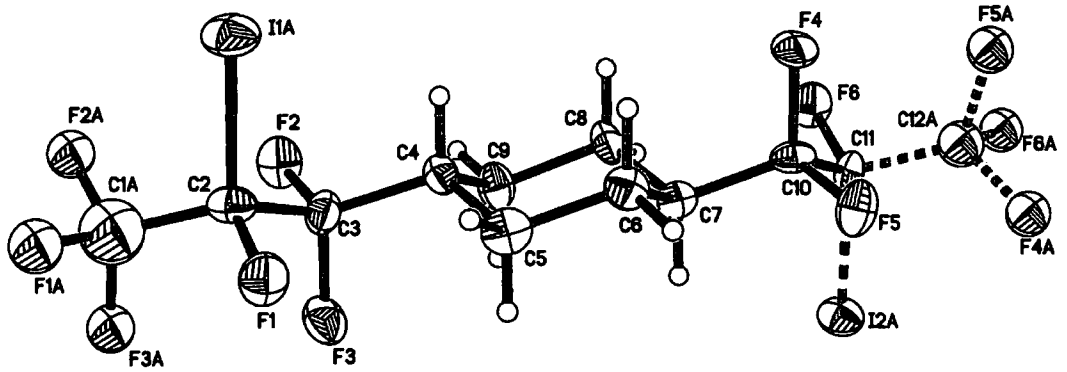
66% (isolated yield)

Compound (**35**) crystallised out from the organic layer as a white solid when cooling down. Structure of compound (**35**) was elucidated from MS and NMR data. In its mass spectrum, a weak $[M]^+$ ion peak occurred at m/z 636 and a strong $[M\text{-}CF_3CFI]^+$ fragment was observed at m/z 409. The high symmetry of compound (**4.11**) was confirmed by the simplicity of the carbon NMR spectrum. Only three resonances attributed to the cyclohexane ring occurred at low frequency. At high frequency, only three signals corresponding to the fluoroalkyl chain were observed, shown as follows.



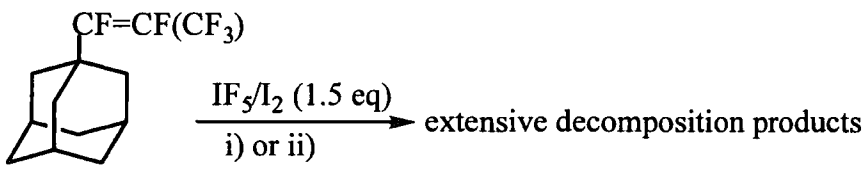
A single crystal X-ray structure was obtained and confirmed unambiguously compound (**35**) as 1,1,2,3,3,3-hexafluoro-1-[4-(1,1,2,3,3,3-hexafluoro-2-iodopropyl)-cylohexyl]-2-iodopropane. Molecule (**35**) is a highly symmetric molecule as it is possesses a crystallographic inversion center. Therefore, it is a *meso*-isomer with two asymmetric

carbon atoms C2 and C11. The cyclohexane adopts a chair conformation with its R_{FI} substituents in equatorial position.



4.3.3. 1[(1Z)-pentafluoroprop-1-enyl]adamantane

As additions of 'IF' to the fluoroalkenes **(19)** and **(22)** were succesful, addition of 'IF' to 1[(1Z)-pentafluoroprop-1-enyl]adamantane **(18)** was attempted. Unfortunately, only extensive decomposition occurred.



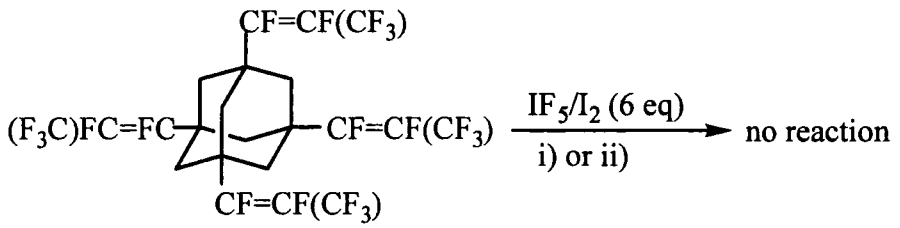
(18)

Conditions	Fluoroalkene conversion (%)	Products
i) no solvent, N_2, 0°C, 12 hrs	100	extensive decomposition products
ii) freon 113, N_2, -10°C, 10 hrs	23	extensive decomposition products

Lowering the temperature did not avoid decomposition but just drastically decreased the conversion. The degradation products could probably arise from some carbocationic rearrangement.

4.3.4. 1,3,5,7-tetrakis(pentafluoroprop-1-enyl)-adamantane

Addition of IF to 1,3,5,7-tetrakis(pentafluoroprop-1-enyl)-adamantane (**23**) was attempted as it could give rise to a fluorocarbon tetra-iodide. No reaction was observed even at 60°C after12 hours.



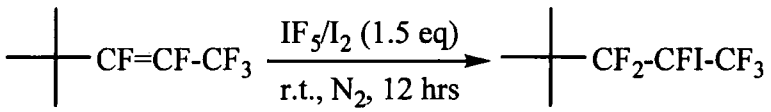
(23a) (23b)

Conditions	Results
i) chloroform, N_2, r.t., 10 days	only starting material
ii) chloroform, N_2, 60°C, 12 hrs	only starting material

Compound (**23**) seems to be deactivated toward electrophilic attack due to the presence of several electron-withdrawing fluoroalkyl groups.

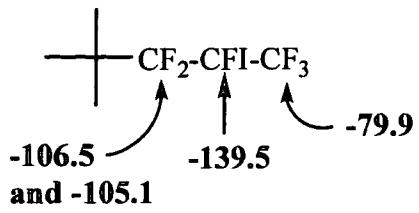
4.3.5. (2*E*)-1,1,1,2,3-pentafluoro-4,4-dimethylpent-2-ene

In order to understand if in the case of addition to the adamantane derivative (**18**) the extensive decomposition could arise from some carbocationic rearrangement, reaction of (**24**) with iodine and iodine pentafluoride was carried out to give only 1,1,1,2,3,3-hexafluoro-2-iodo-4,4-dimethylpentane (**36 a**).

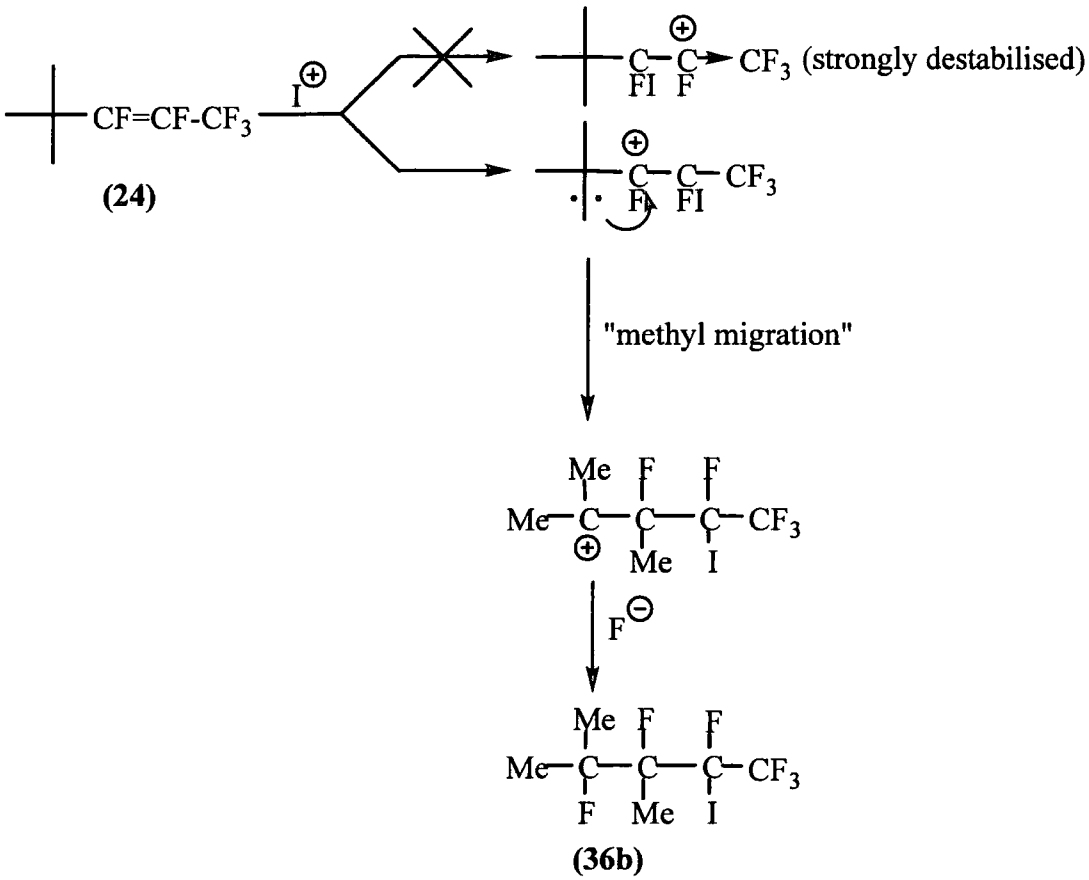


(24) **(36a)** NMR scale

GLC/MS of the crude showed that only one 'IF-adduct' was formed, with a weak $[M]^+$ ion peak at m/z 334, which on basis of the fluorine NMR spectrum was elucidated as (**36a**), as shown as follows.



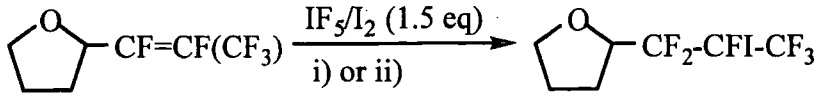
If there was carbocationic rearrangement, compound (**36b**) would have been formed as represented as follows.



However, there was no evidence for formation of compound (**36b**).

4.3.6. 2-(1,2,3,3,3-pentafluoroprop-1-enyl)oxolane

Reaction of 2-(1,2,3,3,3-pentafluoroprop-1-enyl)oxolane (**17**) with iodine and iodine pentafluoride was carried out to give 2-(1,1,2,3,3,3-hexafluoro-2-iodopropyl)oxolane (**37**) but this derivative could not be isolated.



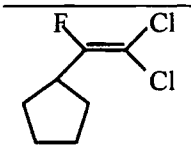
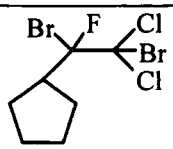
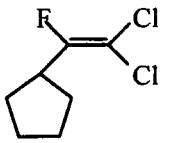
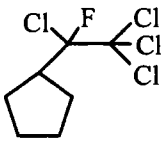
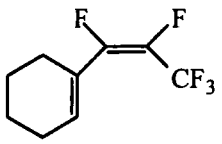
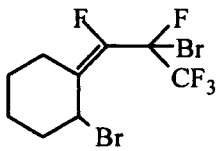
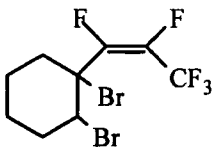
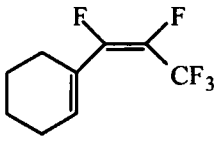
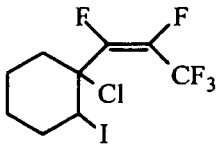
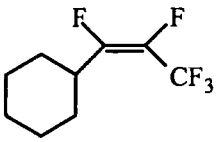
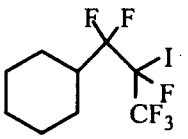
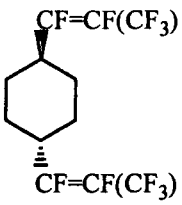
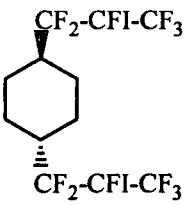
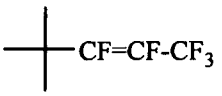
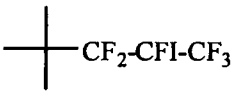
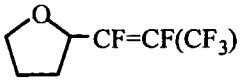
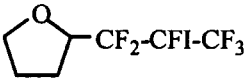
(17) **(37)**

Conditions	Conversion (%)	GC yield (%) **(37)**
i) no solvent, N_2, 0°C to r.t., 12 hrs	41	60
ii) freon 113, N_2, r.t., 5 days	100	65

Compound (**37**) was observed by GC/MS with a $[M]^+$ ion peak at m/z 348. It could not be isolated as it decomposed on silica gel and during attempted distillation.

4.4. Conclusions

Various fluoroalkenes and a diene were functionalised by reaction with electrophiles to give some novel fluorinated derivatives reported in the following table.

Reactant	Conditions	Products and isolated yield (%)
 (21)	(i) Br_2, r.t. (ii) Br_2, 0°C, dark	 (27) 50%
 (21)	(i) ICl, 35°C (ii) ICl, 0°C, dark	 (29) 88%
 (26)	Br_2, 0°C	 (32)  (33) 71%
 (26)	ICl, -78°C	 (30) 28%
 (19)	IF, 0°C	 (34) 88%
 (22)	IF, 0°C	 (35) 66%
 (24)	IF, r.t.	 (36a) (NMR scale)
 (17)	IF, r.t.	 (37) (not isolated)

Addition of iodine monofluoride to (1*Z*)-1-cyclohexyl-1,2,3,3,3-pentafluoroprop-1-ene (**19**) was especially interesting as it gave readily 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) in high yield. This novel fluorocarbon iodide can be further functionalised and this is described in the next chapter.

5. Reactivity of 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (34)

Reactions involving fluorocarbon iodides were reviewed in chapter 1 and in this project the potential of using 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) for further synthesis of fluorinated derivatives was explored. Thus, this chapter describes the reactivity of this novel fluorocarbon iodide.

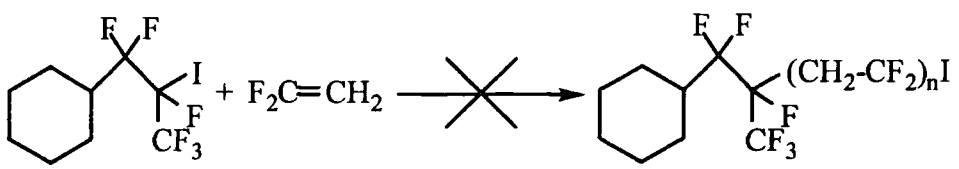
5.1. Reaction with unsaturated compounds

The relative weakness of the carbon-iodine bond (238 kJ mol^{-1}) explains why perfluorocarbon iodides readily undergo homolytic dissociation to give fluoroalkyl radicals. These radicals can react with various unsaturated substrates (see introduction part 4) and this paragraph will describe the radical addition of 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) to some unsaturated compounds.

5.1.1. Attempted telomerisation of (34)

Iodoperfluoroalkanes can give telomers by radical addition to alkenes (see introduction part 4.1.) and those telomers can form fluorocarbon surfaces (oil repellant, chemically inert and good resistance toward heat).

In the present work, 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) was reacted with an excess of 1,1-difluoroethylene using γ-rays and peroxide initiation with a view of producing a fluorocarbon telomer with a hydrocarbon end.



(34)

Unfortunately, with γ-rays, no reaction was observed and with peroxide initiation, black tar was mainly obtained and a trace amount (less than 5% by GC) of mono-adduct 2-(cyclohexyldifluoromethyl)-1,1,1,2,4,4-hexafluoro-4-iodobutane (**38**) was observed by

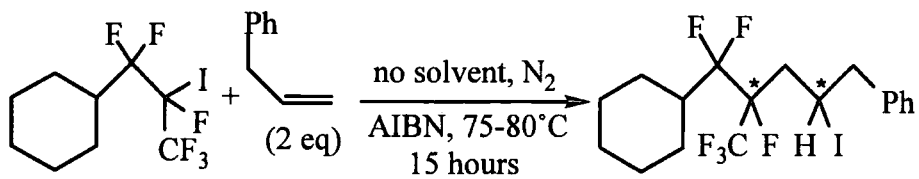
GLC/MS (M^+ 424). The lack of reactivity of compound (**34**) compared to CF_3I may be explain by steric effects : the steric bulk of the cyclohexyl group probably prevented the radical addition to 1,1-difluoroethene. Thus, no further investigation on telomerisation was performed and instead reactions using AIBN initiation were investigated.

5.1.2. Reaction with unsaturated compounds using AIBN initiation

1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) was reacted efficiently with some unsaturated compounds using AIBN as an initiator and this is described in the following paragraphs.

i. Allylbenzene

Addition of 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) to allyl benzene using AIBN as initiator gave a pair of diastereoisomers of [4-cyclohexyl-difluoromethyl-4,5,5,5-tetrafluoro-2-iodopentyl]benzene (**39**) in a ratio of 1.2:1 by ^{19}F NMR.



(34) **(39)**
85%
2 diastereoisomers 1.2:1 ratio

The progress of the reaction was conveniently monitored by ^{19}F NMR, as the C*F*I fluorine atom occurred as a sextet at –140.1 ppm ($^3J_{F\text{-}F}$ 14), whereas the C*F*CH_2 fluorine atoms of the two diastereoisomers of (**39**) occurred at –180.3 and –181.0 ppm.

The orientation of addition was proved by proton NMR and by DEPT. The proton NMR spectrum displayed a signal at 4.5 ppm characteristic of a C*H*I hydrogen atom. Furthermore, DEPT allowed us to identify the *C*HI carbon atom resonance at 25.7 ppm.

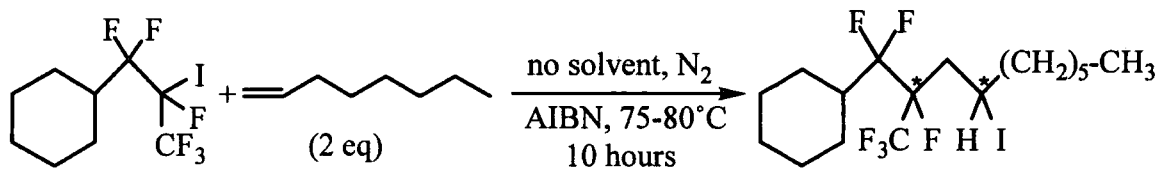
The structure of compound (**39**) was confirmed by MS and NMR data. The mass spectrum of (**39**) displayed a very weak $[M]^+$ ion at m/z 478 and contained a strong peak at m/z 351 corresponding to the loss of iodine. The carbon NMR spectrum of compound (**39**) gave two resonances for almost all carbon atoms as a result of the pair of diastereoisomers.

Characteristics resonances of aromatic ring carbon atoms were observed between 127 and 140 ppm. Two hexafluoropropyl groups were also identified. The 119-122 ppm region of the spectrum was complex with two overlapping doublets of doublets (two $^1J_{C-F}$) at 120.4 and 119.9 ppm, assigned to the two difluoromethylene groups, and these signals overlapped with two overlapping quartets of doublets of doublets ($^1J_{C-F}$, $^2J_{C-F}$ and $^3J_{C-F}$) at 122.3 and 121.8 ppm, attributed to the two trifluoromethyl groups. The *C*F carbon atoms appear as doublets of multiplets around 96 ppm, and because of extensive signal overlap they could not be clearly assigned. The carbon atoms adjacent to the benzyl ring occurred as doublets at 48.1 and 47.9 ppm with small $^4J_{C-F}$ coupling constants (3.2 and 2.4).

As discussed earlier, when a cyclohexyl ring bears a chiral substituent, the ring carbon atoms are magnetically inequivalent and therefore each ring carbon atom has a different chemical shift on the proton-decoupled carbon NMR spectrum. Moreover almost each CH_2 ring carbon atom for each diastereoisomers of compound (**39**) gave a resonance leading to almost twelve more resonances in the low frequency region of the spectrum. By comparison to compound (**39**), triplets at 42.6 and 42.5 ($^2J_{C-F}$ 14.6 and 21.8 respectively) were assigned to the methyne ring carbon atoms.

ii. 1-Octene

Addition of 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) to 1-octene using AIBN as initiator gave a pair of diastereoisomers of 2-(cyclohexyldifluoromethyl)-1,1,1,2-tetrafluoro-4-iododecane (**40**) in the ratio of 1.2:1 by GLC and ^{19}F NMR.



(34) **(40)**
87%
2 diastereoisomers 1.2 : 1 ratio

Compound (**40**) was identified by MS, fluorine and carbon NMR datas. Its EI^+ mass spectrum displayed a weak $[M]^+$ ion at m/z 472 and a strong peak at m/z 345 corresponding to the fragment $[M-I]^+$.

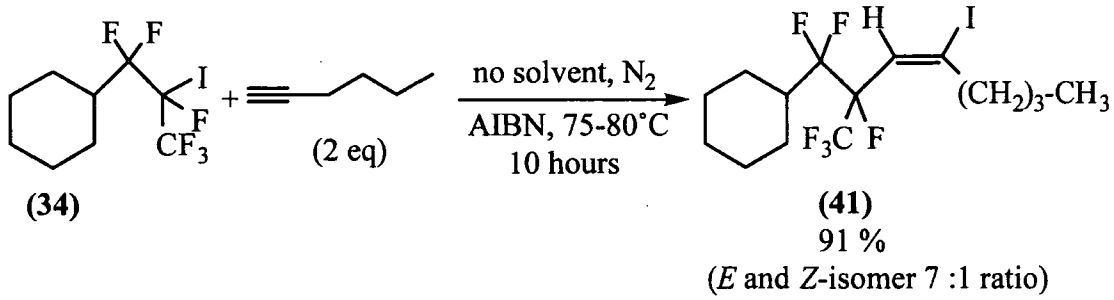
As previously, the orientation of addition across the double bond was proved by a DEPT and proton NMR. A characteristic signal assigned to the C*H*I hydrogen atom occurred at 4.4 ppm on the proton NMR spectrum. Moreover, DEPT spectrum showed the *C*HI carbon atom resonances for the two diastereoisomers to occur at 26.6 and 26.8 ppm.

The proton-decoupled carbon NMR spectrum confirmed the structure of compound (**40**). Two resonances were again observed for almost every carbon atoms because of the pair of diastereoisomers. At very low field, the CF_3, CF_2 and CF carbon atoms gave again overlapping signals (see compound (**39**)). The cyclohexyl ring carbon atoms resonances were attributed by comparison to compound (**34**). The CH_2 carbon atoms of the alkyl side chain gave singlets between 41.6 and 22.9 ppm with the signal at highest field being assigned to the methylene carbon furthest away fom the iodine atom.

iii. 1-Hexyne

As reaction of compound (**34**) with alkenes occurred readily, addition to an alkyne was carried out and is described in the following paragraph.

Addition of 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) to 1-hexyne gave (3*E*) and (3*Z*)-2-(cylohexyldifluoromethyl)-1,1,1,2-tetrafluoro-4-iodooct-3-ene (**34**) in a ratio of 7.2 : 1 as determined by GLC/MS.



(34)

(41)
91 %
(*E* and *Z*-isomer 7 :1 ratio)

In the mass spectrum of compound (**41**), a weak $[M]^+$ ion peak occurred at m/z 442. The major isomer of compound (**41**) was isolated in good yield (75%) by column chromatography over silica gel using hexane as eluant and it was presumed to be the *trans*-isomer as would be expected in a radical addition because of steric effects, but no definitive structural proof could be found. Allylic $^4J_{H\text{-}H}$ coupling constants are generally the same for *cis*- and *trans*-isomers ($^4J_{H\text{-}H}$ between 0.5 and 3 Hz) and so were not of any use here. ^{13}C NMR spectrum was used to attempt to identify the major isomer of compound (**41**), without giving information on the double bond configuration. At very low field, three resonances

similar to those of previous compounds were attributed to the carbon atoms in the hexafluoropropyl side chain. Two more resonances were attributed to the alkenic carbon atoms. The *C*H alkenic carbon atom gave a doublet ($^2J_{C\text{-}F}$ 14.2) at 126.3 ppm, and the *C*I carbon atom gave a singlet at 117.9 ppm, as the iodine shifted the resonance upfield. The CH_2 carbon atom next to the *C*I carbon atom gave a doublet ($^4J_{C\text{-}F}$ 9.6) at 41.1, as the coupling was facilitated through the double bond.

iv. Conclusions

As expected for radical addition of R_FI to mono-substituted 1-alkenes,[54] regioselective addition of 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) to allyl benzene and 1-octene occurred to give the adducts (**39**) and (**40**) with the R_F group attached to the least substituted end of the double bond due to steric effects. Radical additions occurred in high yields. Addition of compound (**34**) to 1-hexyne gave two geometric isomers of an alkene (**41**) in high yield. The *trans* isomer was assumed to be the major isomer (due to steric effects) but no structural proof could be found.

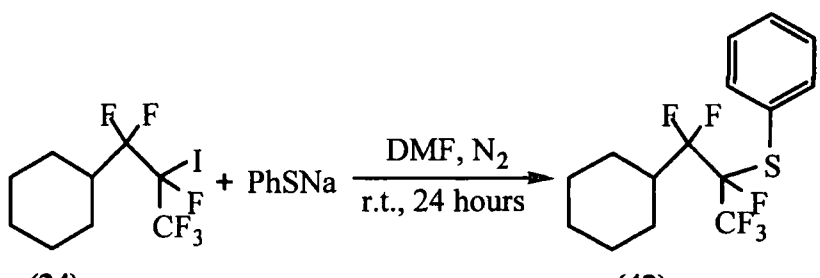
5.2. Reactions with thiols

This section describes mostly the reactions of 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) with thiols and di-thiols via an $S_{RN}1$ process (see introduction part 4). Reactions of some fluorocarbon diiodides with thiols is also covered.

5.2.1. Reactions of fluorocarbon iodide (5.01) with thiols and dithiols

i. Benzenethiol

The condensation of benzenethiolate with 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) gave 1-(cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoro-1-phenylthioethane (**42**) in high yield (73%).

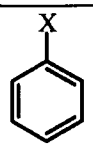


(34) **(42)**

73% (isolated yield)

^{19}F NMR was used to monitor the course of the reaction, as a sextet at -140.1 ppm ($^3J_{F\text{-}F}$ 14) corresponding to the *CF*I fluorine atom was gradually replaced by a sextet at -152.9 ppm ($^3J_{F\text{-}F}$ 10.5) assigned to *CF*S fluorine atom.

GLC/MS analysis of the crude reaction mixture showed the presence of disulfides $(PhS)_2$ (13% GC yield) as expected in an $S_{RN}1$ process. Compound (**42**) was identified from MS, carbon and fluorine NMR data. A strong [M^+] ion peak occurred at m/z 342 on its EI^+ mass spectrum.The CF_2 fluorine atom resonances appeared as an AB system at –111.6 and –112.3 ppm (J_{AB} 269). The structure was also confirmed by the carbon NMR spectrum. The *C*FS carbon atom resonance occurred at 101.8 ppm. The aromatic ring carbon atoms signals were assigned by comparison to reported chemicals shifts of some substituted benzenes, as shown in the following table.[89]



$\delta C = 128.5 + \Delta\delta C$

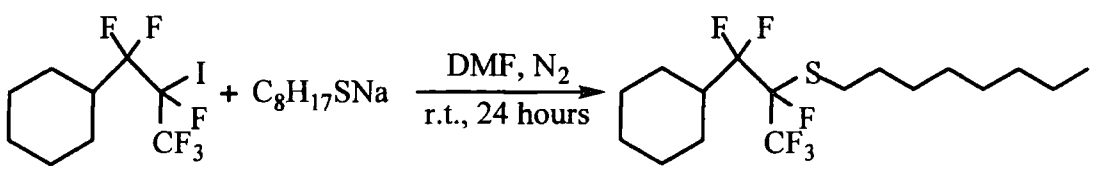
$\Delta\delta C$

X	C-X	C-ortho	C-meta	C-para
SH	2.1	0.7	0.3	-3.2
SCH_3	10.0	-1.9	0.2	-3.6

Thus, resonances for the aromatic ring carbon atoms were observed at 125 ppm (C_{para}), 129 ppm (C_{ortho}), 130.5 ppm (C_{meta}) and 137.3 ppm (CS). As discussed earlier, in the low frequency region of the spectrum, six resonances were observed for the magnetically inequivalent cyclohexyl ring carbon atoms.

ii. Octanethiol

The reaction of octanethiolate with 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) gave 1-(cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoro-1-octylthioethane (**43**) in good yield (70%).



(34) **(43)**

70% (isolated yield)

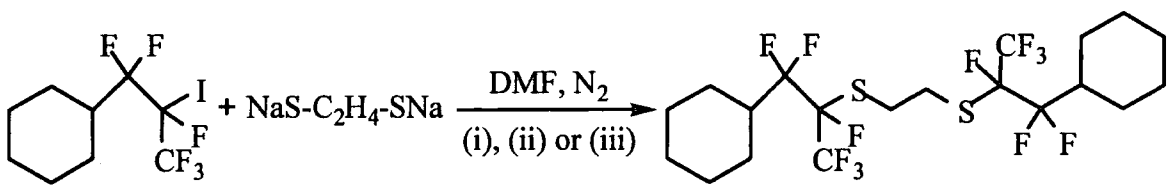
As for the condensation of benzenethiolate, the reaction could be conveniently monitored by ^{19}F NMR, with replacement of the resonance at –140.1 ppm (C*F*I fluorine atom) by a resonance at –158.4 ppm corresponding to the C*F*S fluorine atom.

GLC/MS of the crude reaction mixture showed the presence of disulfides $(RS)_2$ (M^+ 290, 11% GC yield). The EI^+ mass spectrum of compound (**43**) contained only a very weak $[M^+]$ ion peak at m/z 378 but it showed a strong $[CH_3(CH_2)_7S]^+$ ion at m/z 145. Compound (**43**) was identified by fluorine and carbon NMR data. The fluorine NMR spectrum displayed an AB system at –112.1 and –112.8 ppm (J_{AB} 269.1), which corresponded to the CF_2 fluorine atoms. The proton decoupled carbon NMR spectrum also confirmed the structure, as it contained a resonance at 101.5 ppm assigned to the *C*FS carbon atom. The low frequency region of the spectrum also displayed six resonances for the ring carbon atom (as discussed earlier) and eight resonances for the alkyl chain, with especially a resonance at 31.7 ppm characteristic of a CH_2S carbon atom.[89]

As condensation of thiolates (octanethiolate and benzenethiolate) to the fluorocarbon iodide (**34**) were successful, condensation of dithiolates were attempted and this is described next.

iii. 1,2-Ethanedithiol

With a view of coupling two molecules of fluorocarbon iodide, 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) was reacted with 1,2-ethanedithiolate, to give 1-(cyclohexyldifluoromethyl)-1-{2—[1-(cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoro-ethylthio]ethylthio}-1,2,2,2-tetrafluoroethane (**44**).



(34) **(44)**

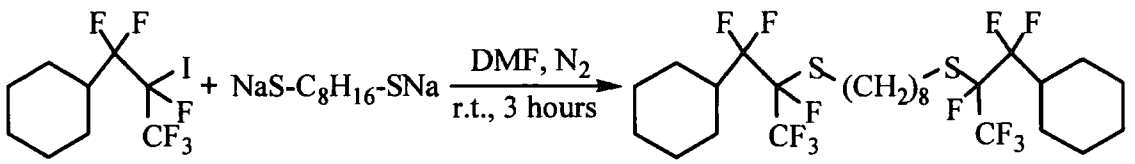
Conditions	Conversion of (**34**)	GC yield of (**44**) [isolated yield]
(i) r.t., 24 hours	0%	0%
(ii) 45°C, 3 days	65%	25% [20%]
(iii) 80°C, 24 hours	complete	70%

No reaction occurred at room temperature (as judged by ^{19}F NMR). After the reaction mixture was heated at 40-50°C for 3 days, conversion based on fluorocarbon iodide was 47% by GC. GLC/MS of the crude showed the presence of cyclic disulfides (35% by GC) which accounted for the low isolated yield. By increasing the temperature to 80°C, yield of compound (**44**) was significantly improved to 70% by GC.

The structure of compound (**44**) was again established by ^{19}F and ^{13}C NMR data. The fluorine NMR spectrum displayed an AB system at –111.4 ppm and -112.1 ppm (J_{AB} 270.2) corresponding to the *gem*-CF_2 group and the multiplet at –158.5 ppm was assigned to the C*F*S fluorine atom. The simplicity of the carbon NMR spectrum confirmed the symmetry of the molecule. There were only seven resonances at low frequency : six were assigned to the magnetically inequivalent ring carbon atoms and one to the CH_2S carbon atom (at 35.6 ppm). Only three resonances were observed at very low field and were attributed to the carbon atoms of the fluorocarbon alkyl chain.

iv. 1,8-Octanedithiol

Reaction of 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) with 1,8-octanedithiolate gave 1-(cyclohexyldifluoromethyl)-1-{8-[1-(cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoroethylthio}-1,2,2,2-tetrafluoroethane (**45**) in modest isolated yield (25%).



(34)

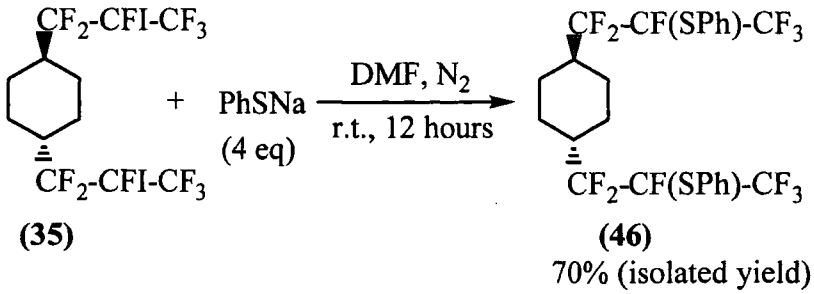
(45)
88% (GC yield)
25% (isolated yield)

Cyclic disulfides were not observed by GLC/MS of the crude material, and so disulfide formation did not account for the low isolated yield. The low yield was actually due to purification problems : compound (**45**) decomposed during distillation and because of its really low polarity column chromatography was not of any use. The mass spectrum of compound (**45**) displayed only a very weak [M^+] ion peak at m/z 642 but contained a strong peak at m/z 409 corresponding to the loss of one fluorocarbon moiety. As previously, the relatively simple carbon NMR spectrum confirmed the symmetry of the structure.

5.2.2. Reactions of some fluorocarbon diiodides with thiols

i. Diiodo HFP-diadduct derivative and benzenethiol

As 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) reacted successfully with thiols and di-thiols, 1,1,2,3,3,3-hexafluoro-1-[4-(1,1,2,3,3,3-hexafluoro-2-iodopropyl) cyclohexyl]-2-iodopropane (**35**) was reacted with benzenethiol to give 1-{ difluoro[4-(1,1,2,3,3,3-hexafluoro-2-phenylthiopropyl)cyclohexyl]methyl}1,2,2,2-tetrafluoro-1-phenylthioethane (**46**) in high yield (70%).

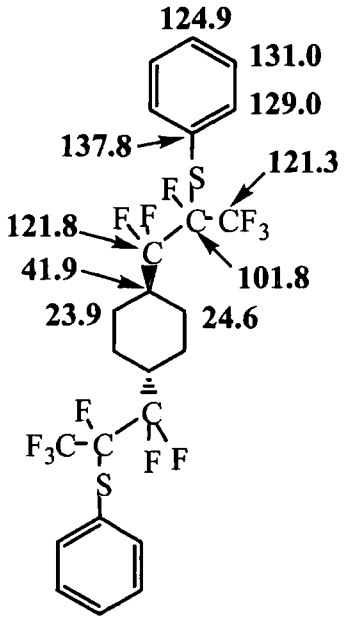


(35) **(46)**

70% (isolated yield)

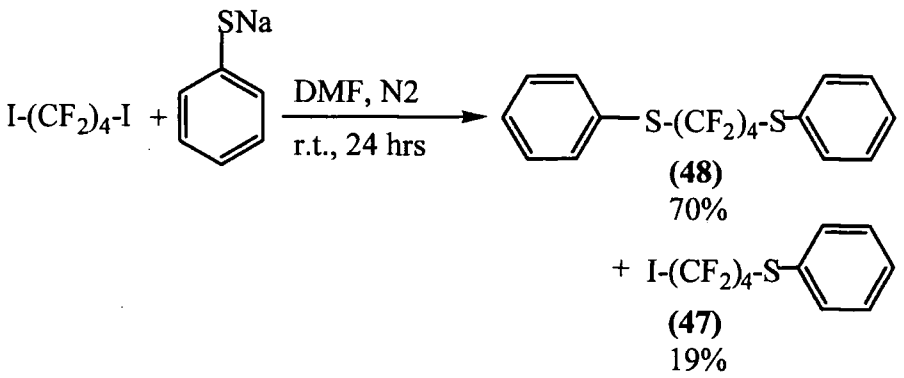
Compound (**46**) precipitated out from the organic layer as a white solid, but attempts to grow crystals suitable for X-ray analysis were unsuccessful. However, the structure of compound (**46**) was expected to be *trans* as 'IF' addition and iodine substitution should not affect the stereogenic centers of *trans*-1,4-bis(Z-pentafluoroprop-2-enyl)cyclohexane.

Structure of compound (**46**) was established by MS and NMR data. It displayed a weak $[M]^+$ ion peak at m/z 600 in its EI^+ mass spectrum. The symmetry of the molecule was clearly confirmed by the carbon NMR spectrum. Only three resonances corresponding to the cyclohexane ring carbon atoms were observed at low frequency. At high frequency, four signals corresponded to the aromatic ring carbon atoms and three more signals accounted for the fluoroalkyl chain, as shown as follows.



ii. 1,4-Diiodooctafluorobutane and benzenethiol

1,4-Diiodooctafluorobutane was reacted with benzethiolate to give 1,1,2,2,3,3,4,4-octafluoro-4-iodo-1-phenylthiobutane (**47**) and 1,1,2,2,3,3,4,4-octafluoro-1,4-diphenylthiobutane (**48**).



Compounds (**47**) and (**48**) were separable by silica gel column chromatography and were identified from EI^+ and NMR data. In the mass spectrum, compound (**47**) showed a weak $[M]^+$ ion peak at m/z 436 and a strong $[CF_2\text{-}S\text{-}C_6H_5]^+$ fragment at m/z 159. Compound (**48**) gave also a weak $[M]^+$ ion peak at m/z 418 and a strong $[CF_2\text{-}S\text{-}C_6H_5]^+$ ion peak at m/z 159.

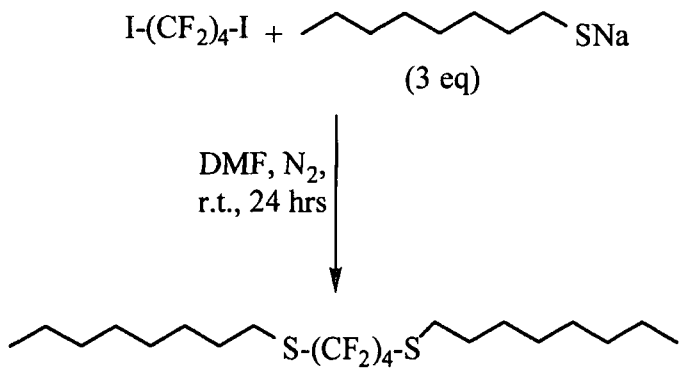
The symmetry of compound (**48**) was confirmed by ^{19}F and ^{13}C NMR spectra. In the ^{19}F NMR spectrum, two signals were observed : a triplet at –87.1 ppm was attributed to the CF_2S fluorine atoms and the other resonance was observed at –118.9 ppm. The ^{13}C

NMR spectrum displayed only six resonances : four singlets between 123.3 and 137.6 ppm were attributed to the benzylic carbon atoms, as earlier. Two more resonances accounted for the fluoroalkyl chain : a triplet of a quintet ($^1J_{C-F}$ 268.9 and $^2J_{C-F}$ 32.9) was attributed to the 'inner' carbon atoms, and a triplet of triplet ($^1J_{C-F}$ 288.4 and $^2J_{C-F}$ 32.4) was attributed to the CF_2S carbon atoms.

The ^{19}F NMR spectrum of compound **(47)** displayed four multiplets including a signal at –58.8 ppm corresponding to the CF_2I fluorine atom and another one at –87.2 ppm corresponding to the CF_2S fluorine atom by comparison to compound **(48)**. ^{13}C NMR also confirmed the structure, as 4 four signals could be attributed to the fluoroalkyl chain. A triplet of triplet ($^1J_{C-F}$ 321.5 and $^2J_{C-F}$ 42.2) occurred at 94.5 and corresponded to the CF_2I carbon atoms. Another triplet of triplet ($^1J_{C-F}$ 291.7 and $^2J_{C-F}$ 34.3) at 123.2 ppm was attributed to the CF_2S carbon atom by comparison again to compound **(48)**.

iii. 1,4-diiodooctafluorobutane and octanethiol

1,4-Diiodooctafluorobutane was reacted with a large excess of octanethiolate to give 1,1,2,2,3,3,4,4-octafluoro-1,4-dioctylthiobutane **(49)**.



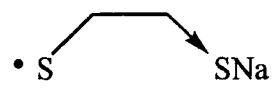
(49)
84% (GC yield)
72% (isolated yield)

Compound **(49)** was identified from MS and NMR data. In its EI^+ mass spectrum, a very weak $[M]^+$ ion peak occurred at m/z 490 and a strong $[CH_3(CH_2)_7S]^+$ fragment at m/z 145. ^{19}F NMR spectrum of compound **(49)** was similar to the one of compound **(48)** with a triplet at –87.8 ppm attributed to the CF_2S fluorine atoms. The carbon NMR spectrum of

compound (**49**) contained eight singlets in the low frequency region, which corresponded to the alkyl chains. At high frequency, a triplet of a quintet at 111.3 ppm was attributed to the 'inner' carbon atoms and a triplet of a triplet at 125.1 ppm corresponded to the CF_2S carbon atoms.

5.2.3. Discussion of the results

Perfluoroalkylation of various thiols using 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) were easily performed. However, the reactivities of the various thiolates used in this project toward this fluorocarbon iodide were different. The condensations of benzenethiol and octanethiol occurred readily at room temperature, whereas the condensation of 1,2-ethanedithiol required higher temperature and longer reaction time to occur. This may be explained by the inductively electron-withdrawing sulfur atom which causes the nucleophilic radical to be less nucleophilic and thus less reactive toward iodine substitution.

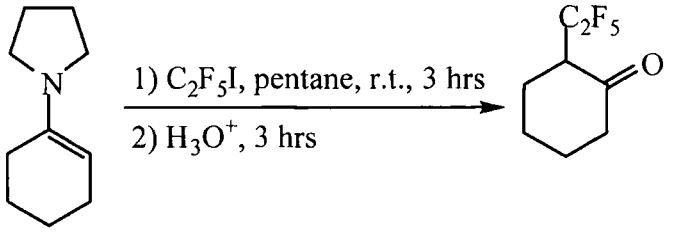


Moreover the amount of disulfides formed in that case was important as disulfide formation competed succesfully with a too slow chain reaction. By increasing the alkyl chain length between the two sulfur atoms (i.e. by using 1,8-octanethiol) the reaction occurred more readily.

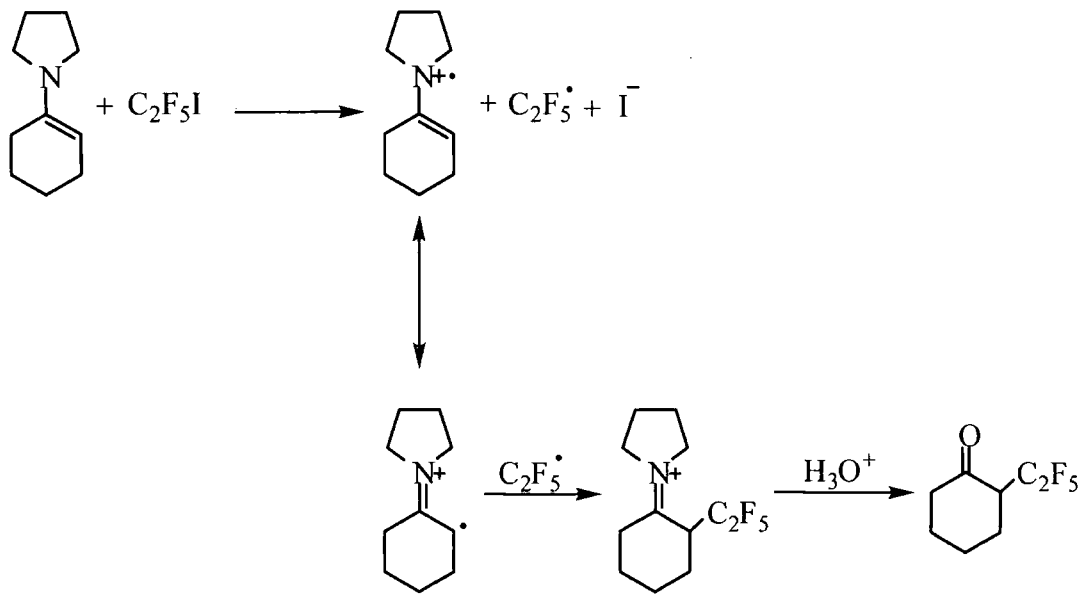
The fluorocarbon di-iodide (**35**) reacted efficiently with thiols (e.g. with benzenethiol) and this could allow the formation of telomers if dithiols were used.

5.2.4. Reaction of fluorocarbon iodide (34) with pyrrolidine-derivative

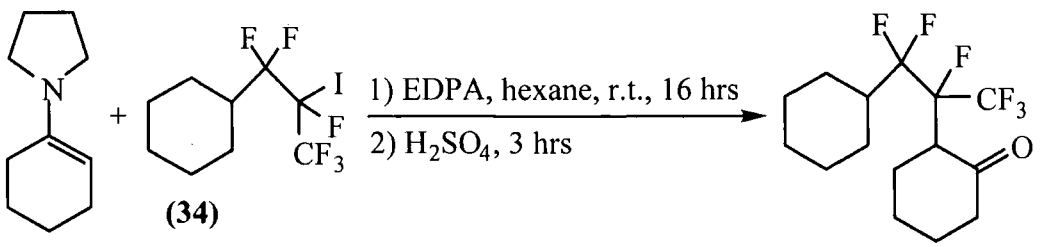
Fluorocarbon iodides react with thiolates via a $S_{RN}1$ mechanism. They can also react with other electron donor nucleophiles, such as enamines, and Wakselman[110] described the rapid condensation at room temperature without initiator of some enamines with primary perfluoroalkyl iodides to yield α-perfluoroalkyl ketones as reported in the following example.



Although an ionic mechanism cannot be excluded, Wakselman[110] suggested a radical mechanism for such reaction as follows :



Thus, in this project 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) was reacted with pyrrolidine-derivative. Additional ethyl di-isopropylamine was used to trap HI, if formed.



(34)

(50)
less than 5% by GLC

Unfortunately, only low conversion was achieved and a trace amount (less than 5% by GLC) of compound (**50**) was formed as observed from GC/MS ($[M]^+$ ion peak at

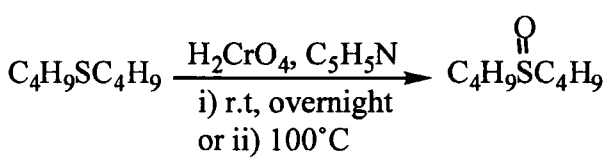
m/z 330). The radical process could not have been inhibited by traces of oxygen as the solvent was carefully degassed and the reactants distilled prior use. Thus, the low reactivity may be explained by steric factors and it is worth noting that no reaction of secondary fluorocarbon iodides with enamines have been reported in the literature.

5.3. Oxidation of some thioethers to sulfones

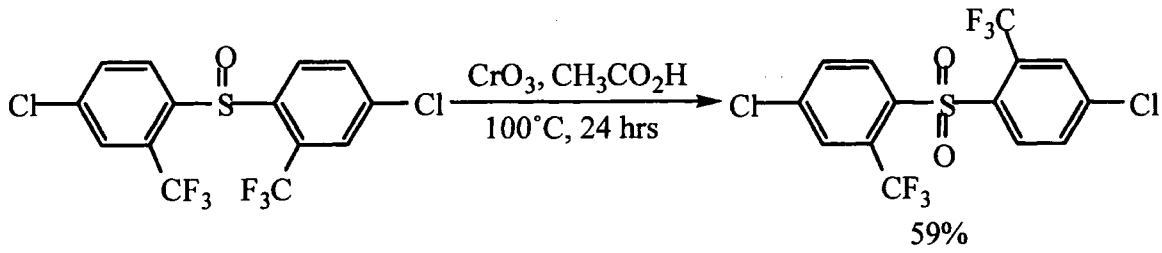
Thioethers (**42**) and (**43**), whose formation have been described in paragraphs 5.2, have been oxidised to sulfones as reported here.

Oxidation of thioethers to sulfoxides and sulfones can be brought about by many oxidizing reagents, including 30% hydrogen peroxide, peroxy acids, periodates and chromic acid. The state of oxidation achieved depends largely on reaction conditions (i.e. if enough oxidizing agent is present, thioethers can be directly converted to sulfones without isolation of the sulfoxides).[111]

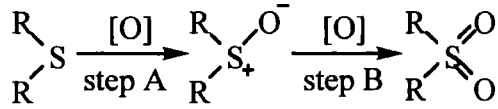
Chromium trioxide has been used in this project as it is 'one of the most powerful and universal oxidants'. Although chromium trioxide is essentially used to oxidize primary alcohols into aldehydes and secondary alcohols into ketones, some examples of conversion of sulfides into sulfoxides and sulfones are reported in the literature. According to Edwards,[112] chromic acid is specific for oxidation of sulfide to sulfoxide. For example, dibutyl sulfide with chromic acid gave only dibutyl sulfoxide, even when a large excess of oxidant was used at 100°C.



However, Clark[113] reported more recently the conversion of 4,4'-dichloro-2,2'-bis(trifluoromethyl)diphenyl sulfoxide into 4,4'-dichloro-2,2'-bis(trifluoromethyl)diphenyl sulfone using chromium trioxide.

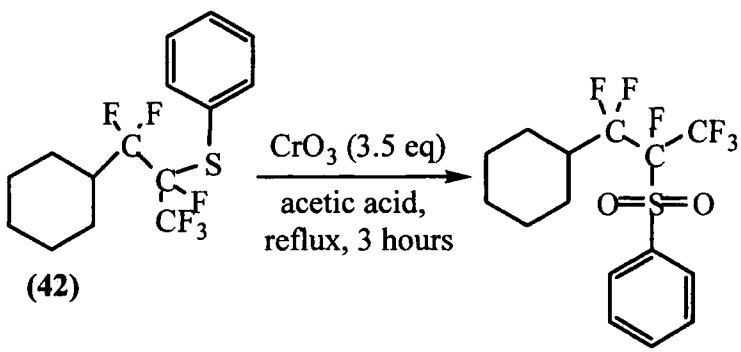


These different reactivities may be rationalised by electronic effects : the oxygen-transfer to the sulfur of thioethers to give sulphones occurs in two steps, as shown as follows.



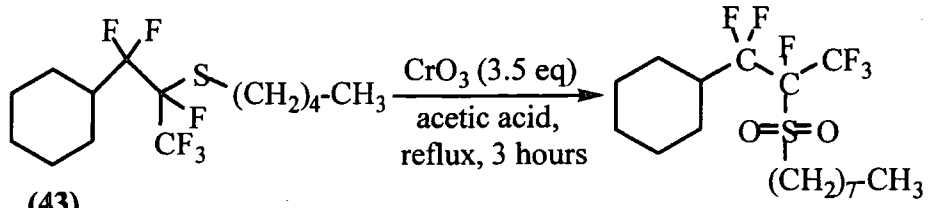
Rates of step A compared to those of step B are faster with electrophilic oxidising agents ; inversely rates of step B compared with those of step A are faster with nucleophilic oxidising agents. The electron-withdrawing or electron-donating character of the substituents attached to the sulfur atom also influences the electronic properties of the thioethers and thus the rates of steps A and B.

In the current project, 1-(cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoro-1-phenylthioethane (**42**) and 1-(cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoro-1-octylthioethane (**43**) were oxidised to the corresponding sulfones (**51**) and (**52**) in high yield using an excess of chromium trioxide in acetic acid at reflux temperature for only 3 hours.



(42)

(51)
95% (GC yield),
74% (isolated yield)



(43)

(52)

78% (isolated yield)

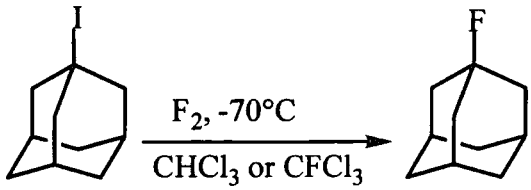
The EI^+ mass spectrum of compound (**51**) displayed no molecular ion and fragmentation was dominated by rupture of the sulfone linkage leading to the base peak at m/z 141 corresponding to $[SO_2Ph]^+$ ion. Thus, ammonia CI^+ mass spectra were used to identify the sulfones (**51**) and (**52**). Compound (**51**) displayed a strong $[M+NH_4]^+$ ion peak at m/z 392 and compound (**52**) also showed a strong $[M+NH_4]^+$ ion peak at m/z 428.

Infra-red is also a useful tool to distinguish between sulfoxide and sulfone as for a sulfoxide, one band should be observed at 1060-1040 cm^{-1}, whereas for a sulfone, two bands should be observed at 1360-1310 cm^{-1} and 1160-1120 cm^{-1}.[114] Infra-red spectra of compounds (**51**) and (**52**) showed bands at 1361 and 1362 cm^{-1} respectively, confirming that sulfones were formed.

To conclude on oxidation performed in this project, it seems that the electron-donating groups (cyclohexyl ring and alkyl chain) and the electron-withdrawing fluoroalkyl chain in thioethers (**42**) and (**43**) constitute a 'good electronic balance' allowing the sulfones to be obtained in less than 3 hours.

5.4. Attempted deiodinative fluorinations.

Substitution of the iodine atom in 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) by a fluorine atom was attempted, as this would amount to the addition of a perfluoroalkyl group to a simple organic molecule in two steps. Several methods for replacing halogens by fluorine have been described in the literature.[90] These methods include use of metal fluorides (such as silver fluoride, mercurous fluoride, or potassium fluoride), hydrogen fluoride (especially in the presence of catalysts such as antimony halides), antimony fluorides[115, 117] and elemental fluorine[116] and some examples are reported as follows.



90% [ref. 116]

$$CHF_2CF_2CF_2CClF_2 \xrightarrow[175°C,\ 3\ hours]{SbF_5} CHF_2CF_2CF_2CF_3$$ 50% [ref. 115]

$$CCl_3C(CF_3)_2OH \xrightarrow[35\text{-}40°C]{SbF_5} (CF_3)_3COH$$ 92% [ref. 117]

Xenon difluoride has also been used to replace iodine by fluorine in organic compounds.[118-120] This type of fluorination is believed to proceed *via* organic iodine difluorides that decompose to give fluorinated compounds.

Unfortunately, in the current project, every attempts to replace the iodine atom by a fluorine atom in 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) failed. Reaction of the fluorocarbon iodide with antimony pentafluoride at temperatures ranging from 0°C to 50°C, using perfluorodecalin or CFC solvent gave no reaction at all or degradation at high temperature. Reaction of the fluoroiodide with elemental fluorine in acetonitrile or CFC was not succesful either and decomposition also occurred when excess of fluorine was used. Lastly, reaction of the polyfluoroiodoalkane (**34**) with xenon difluoride gave no reaction at all.

The iodine atom in 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) resisted displacement by several fluorinating reagents (SbF_5, F_2, XeF_2) because in the case when antimony pentafluoride was used, iodide abstraction would have formed a carbocation next to a electron-withdrawing (i.e. destabilising) trifluoromethyl group.

$$R\text{-}CF_2\text{-}CFI\text{-}CF_3 + SbF_5 \not\longrightarrow R\text{-}CF_2\text{-}\overset{+}{C}F\text{-}CF_3 + SbF_5I^-$$

destabilised

↓ "F-transfer"

$$R\text{-}CF_2\text{-}CF_2\text{-}CF_3$$

The lack of reactivity was no more surprising when elemental fluorine or xenon difluoride were used, as even if iodine difluorides could be expected to be easily formed, the reaction mechanisms also involved carbocations.

5.5. Conclusions

Deiodinative fluorinations of the new fluorocarbon iodide (**34**) synthesised in this project failed. However, the synthetic utility of this system was clearly demonstrated in reactions with unsaturated compounds and thiols.

6. Conclusion

In this thesis, we described mainly a general, efficient approach for the synthesis of fluorocarbon iodides and di-iodides from the commercially available hexafluoropropene (HFP). The synthesis consists of three steps:

1) Efficient free radical addition to HFP (quantitative scale in autoclave)

2) Stereospecific elimination of hydrogen fluoride to give a fluoroalkene

3) Electrophilic addition of iodine monofluoride (formed *in situ* by using a mixture of IF_5/I_2) to the fluoroalkene

Using this approach, a novel fluorocarbon iodide (**34**) was efficiently prepared and its synthetic utility was clearly demonstrated. Thus, compound (**34**) reacted with thiols and di-thiols, most likely *via* an $S_{RN}1$ mechanism, giving thioethers (**42**)-(**45**), mostly in good yields and the thioethers were oxidized to the corresponding sulfones using chromium trioxide. Compound (**34**) also reacted efficiently with unsaturated compounds using AIBN as initiator. A novel fluorocarbon di-iodide (**35**) was also efficiently synthesised and reacted with benzenethiol to give a novel di-thioether (**46**), which opens up the possibility of forming some telomers if compound (**46**) was coupled with di-thiols.

Therefore, these novel fluorocarbon iodides could constitute some 'unusual building blocks' for synthesis of a variety of new fluorine containing systems. For example, radical additions of (**34**) to unsaturated compounds could allow the introduction of other functional groups (e.g. by using alkynyl alcohols).

In this thesis, we also demonstrated that addition of carbon-centred radicals to chlorodifluoroethenes was possible. Thus, useful quantitative amounts of adducts (**1**) and (**4**) can be isolated and these adducts can be used as 'building blocks' for the incorporation of fluorine atoms into organic molecule. For example, elimination of hydrogen fluoride gave two fluoroalkenes (**20**) and (**21**), which reacted efficiently with electrophiles.

EXPERIMENTAL

7. Experimental

7.1. Supplementary materials : Accompanying Compact Disc

Full infra-red spectra, mass spectrometry spectra and X-ray crystal structure data, where relevant, are supplied on the CD.

7.2. Instrumentation

Reagents and solvents

Unless otherwise stated, all chemicals were used as received from suppliers (Aldrich, Apollo, Fluorochem, ABCR). All solvents were dried by literature procedures and stored over molecular sieves (4 Å).

Distillation

Fractional distillations of product mixtures (up to 150°C at atmospheric pressure) were carried out using standard distillation equipment. Higher boiling materials were distilled using a Büchi Kugelrohr GKR-51 apparatus.

Column chromatography

Column chromatography was performed on silica gel (Merck no. 1-09385) and TLC analysis was performed on silica gel TLC plates (Merck).

NMR spectra

NMR spectra were recorded on a Varian VXR400S NMR spectrometer with tetramethylisilane (TMS) and/or trichlorofluoromethane ($CFCl_3$) as standards and deuteriochloroform as solvent, unless otherwise stated. In ^{19}F NMR spectra, upfield shifts are quoted as negative. Coupling constants are given in Hertz.

Gas liquid chromatography analysis

Gas liquid chromatography (GLC) analysis were performed on a Hewlett Packard 5890 Series II gas liquid chromatograph equipped with a 25m cross-linked methyl silicone

capillary column. Preparative scale GLC was performed on a Varian Aerograph Model 920 gas chromatograph (catharometer detector) fitted with a 3m 10% SE 30 packed column.

Mass spectra

Mass spectra were recorded on either a VG 7070 E spectrometer or a Fisons VG Trio 1000 spectrometer coupled with a Hewlett Packard 5890 series II gas chromatograph. Accurate mass determinations were performed on a Micromass Autospec Mass spectrometer.

Elemental analysis

Carbon and hydrogen elemental analyses were obtained using a Perkin-Elmer 240 Elemental Analyser or a Carlo Erba 1100 Elemental analyser.

IR spectra

Infra-red spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer using KBr discs (solid samples) or thin films between two KBr plates (liquid samples).

Melting and boiling points

Melting and boiling point were recorded at atmospheric pressure, using a Gallenkamp apparatus and are uncorrected. Some boiling points were also recorded directly during distillation.

7.3. Experimental to chapter 2

General procedure for γ-ray initiated reactions

Any liquid or solid reagents were introduced into a Pyrex Carius tube (volume *ca.* 50 ml). The tube was then degassed three times by freeze-thawing. Any gaseous reagents were also degassed separately and then transferred into the Carius tube cooled with liquid nitrogen using standard vacuum line techniques. The tube was sealed *in vacuo* while frozen and then placed inside a metal tube. The tube was irradiated by ^{60}Co γ-ray source (500 Ci original activity) at room temperature. On termination of the reaction the tube was frozen

and opened. Any unreacted gas was collected as it returned to room temperature using a vacuum transfer. The crude product mixture was collected, purified by distillation and analysed.

General procedure for peroxide initiated reactions

The reaction were carried out in nickel autoclaves, fitted with bursting discs (maximum working pressure *ca.* 200 atm). The autoclave was charged with any liquid or solid reagents and sealed with a copper gasket which was first cleaned with methanol. The autoclave was degassed three times by freeze-thawing. Any gaseous reagents were also degassed separately and then transferred into the autoclave cooled with liquid air using standard vacuum line techniques. The autoclave was closed (valve) and then transferred while frozen to a high pressure cell where it was heated in a thermostatically controlled rocking furnace. On termination of the reaction, the autoclave was frozen and any remaining gas was collected as it returned to room temperature using a vacuum transfer. The crude product mixture was collected, purified by distillation and analysed.

Cyclopentane with 1-chloro-2,2-difluoroethylene (γ-ray initiation)

Cyclopentane (10 g, 142 mmol) and 1-chloro-2,2-difluoroethylene (7.8 g, 79 mmol) were irradiated with γ-rays for 4 weeks. 1-Chloro-2,2-difluoroethylene (1.5 g) was recovered and a brown oil obtained. GLC/MS gave indication of the presence of *2-chloro-1-cyclopentyl-1,1-difluoroethane* (**1**) (m/z (EI^+) 203 (M^+, 0.27%)) which could not be separated by distillation.

Cyclopentane with 1-chloro-2,2-difluoroethylene (DTBP initiation)

Cyclopentane (33.9 g, 484 mmol), 2-chloro-1,1-difluoroethylene (9.8 g, 97 mmol) and DTBP (1 g, 7 mmol)) were contained in a rocking autoclave at 140 °C for 24 hours. No gas was recovered. A mixture of mono-adducts and di-adducts in a ratio of 50:1:5 by GLC/MS was obtained. Distillation under reduced pressure gave *2-chloro-1-cyclopentyl-1,1-difluoroethane* (**1**) (4 g, 24%) as a colourless oil; bp 197 °C (dec) (Found: C, 49.7; H, 6.5. $C_7H_{11}ClF_2$ requires C, 49.8; H, 6.5%); ν_{max} (cm^{-1}) 2875 and 2963 (C-H); m/z (EI^+) 119 (47), 99 (78), 77 (23), 69 (100), 51 (20), 49 (12); NMR no. 1. The presence of the reverse-

addition compound *1-chloro-1-cyclopentyl-2,2-difluoroethane* (**1a**) was confirmed by ^1H NMR; δ_H 2.3 (1 H, td, $^2J_{H-F}$ 14, $^3J_{H-H}$ 6.8, CF_2H).

Cyclopentane with 1,1-dichloro-2,2-difluoroethylene (DTBP initiation)

Cyclopentane (99 g, 1.41 mol), 1,1-dichloro-2,2-difluoroethylene (46.6 g, 0.35 mol) and DTBP (1.5 g, 0.011 mol) were heated in a rocking autoclave at 140 °C for 24 hours. Distillation under reduced pressure gave *2,2-dichloro-1-cyclopentyl-1,1-difluoroethane* (**4**) (34.2 g, 48%) as a colourless liquid; bp 170-171 °C (Found: C, 41.1; H, 4.9. $C_7H_{10}Cl_2F_2$ requires C, 41.4; H, 4.9 %); ν_{max} (cm^{-1}) 2875 and 2962 (C-H); m/z (EI^+) 203 (M^+, 0.27%), 119 (67), 111 (12), 99 (100), 83 (34), 90 (16), 77 (48), 69 (44), 55 (52); NMR no. 2.

Cyclohexane with hexafluoropropene (γ–ray initiation)

Cyclohexane (8.0 g, 95 mmol) and HFP (21.6 g, 144 mmol) were irradiated with γ-rays for 14 days. HFP (2.1 g) was recovered and a colourless liquid obtained. Cyclohexane was removed by distillation and further fractional distillation gave two fractions. The first fraction was identified as *(1,1,2,3,3,3-hexafluoropropyl)cyclohexane* (**6**) (18.9 g, 85%); bp 154-155 °C (Found: C, 46.0; H, 5.1. $C_9H_{12}F_6$ requires C, 46.2; H, 5.2%); ν_{max} (cm^{-1}) 2862 and 2941 (C-H); m/z (EI^+) 234 (M^+, 1%), 195 (11), 83 (100), 55 (76); NMR no. 3. By comparison with data in the literature the second fraction was identified as an isomeric mixture of *1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane* (**7**) (x=2-4) (2.2 g, 6% yield); bp 105-106°C at 15 mmHg; m/z (EI^+) 345 (6%), 233 (100), 213 (27), 77 (25); NMR no. 5.

Cyclohexane with hexafluoropropene (DTBP Initiation)

Cyclohexane (19.5 g, 232 mmol), HFP (47.2 g, 315 mmol) and DTBP (1 g, 7 mmol) were contained in a rocking autoclave at 140 °C for 24 hours. HFP (0.2 g) was recovered and a yellow liquid obtained. Cyclohexane was removed by distillation and further fractional distillation gave two fractions. The first fraction was identified as *(1,1,2,3,3,3-hexafluoropropyl)cyclohexane* (**6**) (38 g, 70%), and the second fraction was identified as a mixture of isomers of *1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane* (x=2-4) (**7**) (22.3 g, 25%), as described above. *2R,2'S-trans-1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane* (**7a**) crystallised out on standing as a white solid; mp 80-81°C (from MeOH) (Found; C,

37.3; H, 3.0. $C_{12}H_{12}F_{12}$ requires C, 37.5; H, 3.1%); m/z (EI^+) 345 (25), 233 (100), 213 (87); NMR no. 6. The presence of the reverse-addition compound *2-cyclohexyl-1,1,1,2,3,3,3-hexafluoropropane* (**6a**) (6% by GLC/MS) was confirmed by ^1H NMR. δ_H 5.9 (td, $^2J_{H\text{-}F}$ 53, $^3J_{H\text{-}F}$ 6.8, CF_2H); m/z (EI^+) 234 (M^+, 0.52%), 83 (100), 56 (17), 55 (49), 41 (41), 39 (14), 51 (11); NMR no. 4.

Adamantane and HFP (DTBP initiation)

Adamantane (17 g, 0.12 mol), HFP (22.5 g, 0.15 mol) and DTBP (1 g, 7 mmol) were heated in a rocking autoclave at 140 °C for 24 hours. No HFP was recovered and unreacted adamantane (1.6 g) crystallised out from the liquid product. Fractional distillation under reduced pressure gave two fractions. The first fraction was identified as *1-(1,1,2,3,3,3-hexafluoropropyl)adamantane* (**8**) (19.7 g, 55%) as a colourless oil; bp 120°C at 28 mbar (Found: C, 54.3; H, 5.6. $C_{13}H_{16}F_6$ requires: C, 54.5; H, 5,6); m/z (EI^+) 286 (M^+, 4%), 247 (15), 185 (20), 165 (12), 151 (13), 135 (100), 79 (80), 69 (62), 41 (62); NMR no. 7. The second fraction was identified as *1,3-bis-(1,1,2,3,3,3-hexafluoropropyl)-adamantane* (**9**) (15.2 g, 28%) ; bp 124-125°C at 9 mmHg; m/z (EI^+) 436 (M^+, 0.25%), 397 (24), 285 (100), 243 (79), 229 (76), 55 (70); NMR no. 8. MS and NMR data are consistent with those contained in the literature.[50]

Adamantane and excess HFP (DTBP initiation)

Adamantane (4 g, 30 mmol), HFP (30 g, 200 mmol) and DTBP (0.8 g, 6 mmol) were contained in a rocking autoclave at 140 °C for 24 hours. HFP (9.3 g) was recovered. Kugelrohr distillation (11 mbar, 230 °C) of the waxy mixture removed any unvolatile impurities. The waxy liquid was then mixed with chloroform and a white solid precipitated out on standing. Filtration of the solid followed by evaporation of the solvent gave *1,3,5-tris(1,1,2,3,3,3-hexafluoropropyl)adamantane* (**10**) (7 g, 40%) as a colourless oil; bp 145-146°C at 9 mmHg; m/z (EI^+) 586 (M^+, 0.2%), 567 (12), 547 (29), 435 (100), 277 (59), 243 (49), 69 (78); NMR no. 9. The white solid was identified as *1,3,5,7-tetrakis(1,1,2,3,3,3-hexafluoropropyl)adamantane* (**11**) (3 g, 13%); mp 111-112°C (from MeOH) (Found: C, 36.0; H, 2.2. $C_{22}H_{16}F_{24}$ requires C, 35.9; H, 2.2%); m/z (EI^+) 717 (5%), 697 (6), 585 (100), 435 (52), 277 (7), 151 (7), 69 (12), 55 (10); NMR no. 10. MS and NMR data are consistent with those contained in the literature.[50]

2-Methylpropane and HFP (DTBP initiation)

2-Methylpropane (3.4 g, 58.6 mmol), HFP (10.5 g, 70.34 mmol) and DTBP (0.7 g, 4.8 mmol) were heated in a rocking autoclave at 140 °C for 24 hours. Gaseous components (6.7 g) were recovered and distillation of the remaining pale yellow liquid gave *4,4-dimethyl-1,1,1,2,3,3-hexafluoropentane* (**12**) (8.3 g, 75%) as a colourless liquid; bp 103-104°C (Found: C, 40.7, H, 4.9. $C_7H_{10}F_6$ requires C, 40.4, H, 4.8) ; ν_{max} (cm^{-1}) 2887 and 2987 (C-H); m/z (EI^+) 193 (16), 173 (30), 65 (89), 57 (100), 41 (99); NMR no. 11. A trace of *1,1,1,2,3,3-hexafluoro-5-methylhexane* (**13**) (1% by GLC) was also observed by GLC/MS ; m/z (EI^+) 173 (3), 47 (34), 43 (100), 41 (36). MS and NMR data are consistent with those contained in the literature.[50]

Cyclohexanol and HFP (DTBP initiation)

Cyclohexanol (25 g, 250 mmol), HFP (40 g, 267 mmol) and DTBP (5.9 g, 40 mmol) were contained in a rocking autoclave at 120°C for 24 hours. Fractional distillation at reduced pressure gave *1-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexanol* (**14**) (34 g, 55%) as colourless crystals ; mp 42-43 °C; bp 55°C at 6 mbar; m/z (EI^+) 231 (4), 213 (4), 207 (9), 151 (17), 99 (82), 81 (87), 69 (43), 55 (100); NMR no. 12. MS and NMR data are consistent with those contained in the literature.[44]

Tetrahydrofuran and HFP (DTBP initiation)

Tetrahydrofuran (24 g, 0.33 mol), HFP (20 g, 0.13 mol) and DTBP (1 g, 7 mmol) were contained in a rocking autoclave at 140 °C for 24 hours. Fractional distillation under reduced pressure gave two diastereoisomers of *2-(1,1,2,3,3,3-hexafluoropropyl)oxolane* (**16**) (23.7 g, 82%) in a ratio of 1 : 1.1 by GLC/MS as a colourless liquid; bp 136.5-137.5°C (Found: C, 37.9; H, 3.6. $C_7H_8F_6O$ requires C, 37.8; H, 3.6); ν_{max} (cm^{-1}) 2887 and 2989 (C-H); m/z (EI^+) 222 (M^+, 0.3%), 151 (25), 133 (35), 101 (24), 72 (81); NMR no. 13. NMR data are consistent with those contained in the literature.[52]

7.4. Experimental to chapter 3

General procedure for dehydrofluorination

Potassium *tert*-butoxide was dried under vacuum and then dry solvent was added under nitrogen with stirring. The resulting mixture was cooled to –78°C using a carbon dioxide/acetone bath unless otherwise stated. Then the polyfluoroalkyl derivative was added dropwise to the stirred solution/suspension. The reaction was then stirred for the required time. The reaction was monitored by ^{19}F NMR. On termination of the reaction, the reaction mixture was allowed to warm up to room temperature and then poured into water and neutralised with 10% hydrochloric acid. The organic layer was extracted with dichloromethane, dried over $MgSO_4$. Solvents were removed by rotary evaporation and the products purified by distillation.

2-Chloro-1,1-difluoroethycyclopentane

Addition of 2-chloro-1,1-difluoroethylcyclopentane (**1**) (4 g, 24 mmol) to potassium *tert*-butoxide (5.3 g, 47 mmol) in THF overnight gave *Z-2-chloro-1-cyclopentyl-1-fluoroethene* (**20**) (2.2 g, 62%) as a yellow oil; bp 90°C at 10 mbar (M^+, 148.045716. $C_7H_{10}ClF$ requires 148.045506); ν_{max} (cm^{-1}) 1678 (C=C), 2872 and 2962 (C-H); m/z (EI^+) 150 (M^+, 23%), 149 (19), 148 (M^+, 69%), 147 (41), 106 (83), 93 (58), 71 (59), 68 (78), 39 (100); NMR no. 14.

2,2-Dichloro-1,1-difluoroethycyclopentane

Addition of 2,2-dichloro-1,1-difluoroethylcyclopentane (**2**) (10 g, 49 mmol) to potassium *tert*-butoxide (6 g, 54 mmol) in THF overnight gave *2,2-dichloro-1-cyclopentyl-1-fluoroethene* (**21**) (5.8 g, 63 %) as a yellow liquid; bp 185-186°C (Found: C, 45.6; H, 4.9. $C_7H_9Cl_2F$ requires C, 45.9; H, 4.9%); ν_{max} (cm^{-1}) 1656 (C=C), 2873 and 2961 (C-H); m/z (EI^+) 186 (M^+, 7%), 184 (M^+, 31%), 182 (M^+, 46%), 142 (24), 141 (20), 140 (36), 105 (28); NMR no. 15.

(1,1,2,3,3,3-Hexafluoropropyl)cyclohexane

Addition of (1,1,2,3,3,3-hexafluoropropyl)cyclohexane (**6**) (5.8 g, 25 mmol) to potassium *tert*-butoxide (4.2 g, 37.5 mmol) in THF for 3 hours at 0°C gave *(1Z)-1-*

cyclohexyl-1,2,3,3,3-pentafluoropropene (**19**) (3.7 g, 70%) as a colourless oil; bp 140-141°C (Found: C, 50.3; H, 5.2. $C_9H_{11}F_5$ requires C, 50.5 ; H, 5.1 %); ν_{max} (cm^{-1}) 1723 (C=C), 2861 and 2937 (C-H); m/z (EI^+) 214 (M^+, 9%), 158 (10), 108 (14), 107 (13), 100 (29), 82 (46), 56 (89), 41 (100); NMR no. 16. MS and NMR data are consistent with those contained in the literature.[50]

Trans-1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane

Addition of *trans*-1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (**7a**) (2 g, 5.2 mmol) to potassium *tert*-butoxide (1.7 g, 15.6 mmol) in THF at -10°C for 3 hours gave *trans-1,4-bis[(1Z)-pentafluoroprop-1-enyl]-cyclohexane* (**22**) (1.1 g, 61%) as a white solid; mp 102-103°C (from MeOH) (Found: C, 41.8; H, 2.9. $C_{12}H_{10}F_{10}$ requires C, 41.9; H, 2.9%); ν_{max} (cm^{-1}) 1750 (C=C), 2853 and 2923 (C-H); m/z (EI^+) 344 (M^+, 52%), 158 (100), 108 (85), 95 (67), 54 (88); NMR no. 17. MS and NMR data are consistent with those contained in the literature.[50]

1-(1,1,2,3,3,3-Hexafluoropropyl)adamantane

Addition of 1-(1,1,2,3,3,3-hexafluoropropyl)adamantane (**8**) (5 g, 17.5 mmol) to potassium tert-butoxide (3.9 g, 34.9 mmol) in THF (40 ml) at –10°C for 45 minutes gave, after fractional distillation, an isomeric mixture of *1[(1Z)-pentafluoroprop-1-enyl]adamantane* and *1[(1E)-pentafluoroprop-1-enyl]adamantane* (**18**) (3.4 g, 73%) in a ratio of 4:1 by GLC/MS and ^{19}F NMR as a colourless oil; bp 218-220°C; ν_{max} (cm^{-1}) 1709 (C=C), 2856 and 2911 (C-H); m/z (EI^+) 266 (M^+, 38%), 94 (100), 79 (36), 41 (31); NMR no. 18 and 19. MS and NMR data are consistent with those contained in the literature.[50]

1,3,5,7-Tetrakis-(1,1,2,3,3,3 hexafluoropropyl)adamantane

Addition of 1,3,5,7-tetrakis-(1,1,2,3,3,3 hexafluoropropyl)adamantane(**11**) (3 g, 4.1 mmol) in dry THF (20 ml) to potassium *tert*-butoxide (3.6 g, 32.6 mmol) in THF (30 ml) at room temperature for 45 minutes gave an isomeric mixture of *1,3,5,7-tetrakis(1E-pentafluoroprop-1-enyl)-adamantane* (**23a**) and *1-(Z-pentafluoroprop-2-enyl)-3,5,7-tris(E-pentafluoroprop-2-enyl)adamantane* (**23b**) (1.7 g, 54%) in a ratio of 5:1 by ^{19}F NMR; bp 200°C at 9 mbar; m/z (EI^+) 656 (M^+, 34 %), 526 (100), 145 (53), 95 (41), 69 (29).

1,3,5,7-tetrakis[(1E)-pentafluoroprop-1-enyl]-adamantane (**23a**) crystallised out when mixing with chloroform and cooling in an acetone slush bath; NMR no. 20 and 21. MS and NMR data are consistent with those contained in the literature.[50]

4,4-Dimethyl-1,1,1,2,3,3-hexafluoropentane

Addition of 4,4-dimethyl-1,1,1,2,3,3-hexafluoropentane (**12**) (1 g, 4.8 mmol) to potassium *tert*-butoxide (1.1 g, 9.8 mmol) in dry diethyl ether (20 ml) at –10°c (salt-ice bath) for 30 minutes gave after vacuum transfer *(2Z)-1,1,1,2,3-pentafluoro-4,4-dimethylpent-2-ene* (**24**) on analysis by ^{19}F NMR; no yield recorded; NMR no. 22.

2-(1,1,2,3,3,3-Hexafluoropropyl)oxolane

Addition of 2-(1,1,2,3,3,3-hexafluoropropyl)oxolane (**16**) (7.5 g, 33.8 mmol) to potassium *tert*-butoxide (5.7 g, 50.7 mmol) in THF (40 ml) at –78°C for 3 hours gave, after fractional distillation under reduced pressure, *2-((1Z)-1,2,3,3,3-pentafluoroprop-1-enyl)oxolane* (**17**) (4.6 g, 64%) as a colourless liquid; bp 130.9-131.5°C (Found: C, 41.4, H, 3.5. $C_7H_7F_5$ requires C, 41.6, H, 3.5); ν_{max} (cm^{-1}) 1727 (C=C), 2883 and 2989 (C-H); m/z (EI^+) 202 (M^+, 36%), 183 (22), 133 (74), 131 (38), 69 (55), 71 (43); NMR no. 23. NMR data are consistent with those contained in the literature.[93]

Dehydration of 1-(1,1,2,3,3,3-hexafluoropropyl)cyclohexanol

A mixture consisting of 1-(1,1,2,3,3,3-hexafluoropropyl)cyclohexanol (**14**) (26.1 g, 104.5 mmol) and thionyl chloride (approximately 10 fold molar excess) was heated at reflux temperature. The emitted gases were passed through a KOH solution scrubber. The product solution was added dropwise to a cooled (ice bath) mixture of ice and DCM. The aqueous solution was extracted three times with DCM and the combined organic extracts were washed several times with water, dried ($MgSO_4$) and condensed. Fractional distillation gave *1-(1,1,2,3,3,3-hexafluoropropyl)cyclohexene* (**25**) (17.7 g, 73%) as a colourless liquid; bp 153-154°C; m/z (EI^+) 232 (M^+, 13%), 131 (17), 103 (14), 81 (100); NMR no. 24. MS and NMR data are consistent with those contained in the literature.[44]

Dehydrofluorination of 1-(1,1,2,3,3,3-hexafluoropropyl)cyclohexene

Addition of 1-(1,1,2,3,3,3-hexafluoropropyl)cyclohexene (**25**) (17.7 g, 76.3 mmol) to potassium *tert*-butoxide (12.8 g, 114.4 mmol) in THF at -78°C for 3 hours gave, after fractional distillation, *1-(1,2,3,3,3-pentafluoro-Z-prop-1-enyl)-cyclohexene* (**26**) (11.3 g, 67%) as a pale yellow liquid; bp 123-124°C (volatility of compound prevented elemental analysis); ν_{max} (cm^{-1}) 1654 and 1718 (C=C), 2866 and 2942 (C-H); m/z (EI^+) 212 (M^+, 61%), 197 (58), 177 (49), 143 (63), 115 (85), 79 (100), 69 (56), 41 (58); NMR no. 25.

Reduction of the 2,2-dichloro-1,1-difluoroethycyclopentane

2,2-Dichloro-1,1-difluoroethycyclopentane (**4**) (2.5 g, 12 mmol) was added dropwise to a cooled, stirred solution of C_2H_5MgBr (12 ml, 36 mmol) in THF. The reaction mixture was heated at reflux for 24 hours and then was poured into 10% aqueus sodium hydrogen carbonate, extracted with dichloromethane, dried ($MgSO_4$). Solvents were removed by rotary evaporation and further distillation under reduced pressure gave *2-chloro-1,1-difluoroethylcyclopentane* (**1**) (1.1 g, 54%); as described earlier.

7.5. Experimental to chapter 4

General procedure for reaction with electrophiles

The fluoroalkene was added dropwise to the electrophile under nitrogen, and the reaction mixture was stirred at the required temperature. The reaction was monitored by ^{19}F NMR and on completion of the reaction, aqueous sodium metabisulfite was added. The mixture was extracted into dichloromethane. The combined organic layers were dried ($MgSO_4$) and the solvent removed by rotary evaporation. Purification was achieved by column chromatography.

Bromine and 2,2-dichloro-1-cyclopentyl-1-fluoroethene

Elemental bromine (2.6 g, 16 mmol) and 2,2-dichloro-1-cyclopentyl-1-fluoroethane (**21**) (1.5 g, 8.2 mmol) without solvent gave, after column chromatography on silica gel (hexane), *1,2-dibromo-2,2-dichloro-1-cyclopentyl-1-fluoroethane* (**27**) (1.4 g, 50%) as a colourless liquid; bp 195-196°C (Found: C, 24.8; H, 2.7. $C_7H_9Br_2Cl_2F$ requires C, 24.5; H, 2.7%); ν_{max} (cm^{-1}) 2871 and 2961 (C-H); m/z (EI^+) 344 (M^+, 0.02%), 342 (M^+, 0.06%), 340

(M^+, 0.04%), 186 (6), 184 (19), 182 (25), 147 (25), 112 (3), 110 (11), 81 (18), 79 (27), 69 (40), 37 (14), 35 (18); NMR no. 26.

Iodine monochloride and 2,2-dichloro-1-cyclopentyl-1-fluoroethene

ICl (2.7 g, 16 mmol) and 2,2-dichloro-1-cyclopentyl-1-fluoroethene (**21**) (1.5 g, 8.2 mmol) at 35°C gave, after column chromatography on silica gel (hexane), *1,2,2,2-tetrachloro-1-cyclopentyl-1-fluoroethane* (**29**) (1.8 g, 88%) as a pink liquid; bp130-131 °C (Found: C, 33.1; H, 3.6. $C_7H_9Cl_4F$ requires C, 33.1; H, 3.5%); ν_{max} (cm^{-1}) 2873 and 2961 (C-H); m/z (EI^+) 254 (M^+, 0.7%), 252 (M^+, 0.1%), 99 (62), 77 (10), 69 (100), 68 (33), 35 (11); NMR no. 27.

1-(1,2,3,3,3-pentafluoro-Z-prop-1-enyl)-cyclohexene and electrophiles

With iodine monochloride

1-(1,2,3,3,3-Pentafluoro-Z-prop-1-enyl)-cyclohexene (**26**) (0.5 g, 2.4 mmol) with iodine monochloride (0.5 g, 3.1 mmol) in DCM at -78 °C for 30 minutes gave , after column chromatography on silica gel (hexane), *(1Z)-1-(1-chloro-2-iodocylohexyl)-1,2,3,3,3-pentafluoroprop-1-ene* (**30**) (0.5 g, 56%) as a pale pink liquid; bp 189-190°C (Dec) (Found: C, 28.6; H, 2.4. $C_9H_9ClF_5I$ requires C, 28.9; H, 2.4%); m/z (EI^+) 249 (M^+-I, 8%), 247 (M^+-I, 16%), 211 (100); NMR no. 28.

With bromine at 0°C

1-(1,2,3,3,3-Pentafluoro-Z-prop-1-enyl)-cyclohexene (**26**) (0.9 g, 4.2 mmol) with bromine (0.9 g, 5.6 mmol) at 0°C for 5 hours gave, after column chromatography on silica gel (hexane), *2-bromo-1-(2-bromocyclohexylidene)-1,2,3,3,3-pentafluoropropane* (**32**) and *(1Z)-1-(1,2-dibromocyclohexyl)-1,2,3,3,3-pentafluoroprop-1-ene* (**33**) (1.1 g, 71%) as a colourless liquid and as a complex mixture of isomers in the ratio of 3.2 : 1.8 : 3.4 : 1.4 : 1 by ^{19}F NMR; bp 188-190°C (Found : C, 29.01; H, 2.4. $C_9H_9F_5Br_2$ requires C, 29.03; H, 2.4%); ν_{max} (cm^{-1}) 2952 (C-H); m/z (EI^+) 293 (M^+-Br, 85%), 291 (M^+-Br, 85%), 211 (100); NMR no. 29 and 30.

With bromine at 0°C, in the dark

1-(1,2,3,3,3-Pentafluoro-Z-prop-1-enyl)-cyclohexene (**26**) (0.5 g, 2.3 mmol) with bromine (0.4 g, 2.5 mmol) in the dark (flask wrapped in aluminium foil) at 0°C for 30 min gave, after quenching the reaction still in the dark via a septum, *2-bromo-1-(2-bromocyclohexylidene)-1,2,3,3,3-pentafluoropropane* (**32**) and *(1Z)-1-(1,2-dibromocyclohexyl)-1,2,3,3,3-pentafluoroprop-1-ene* (**33**) as above.

With bromine in acetic acid

1-(1,2,3,3,3-Pentafluoro-Z-prop-1-enyl)-cyclohexene (**26**) (0.25 g, 1.2 mmol) with bromine (0.2 g, 1.4 mmol) at 0°C in acetic acid for 20 min at 0-5°C gave, after usual work-up followed by washing with $NaHCO_3$, *2-bromo-1-(2-bromocyclohexylidene)-1,2,3,3,3-pentafluoropropane* (**32**) and *(1Z)-1-(1,2-dibromocyclohexyl)-1,2,3,3,3-pentafluoroprop-1-ene* (**33**) as above.

With iodine monobromide

1-(1,2,3,3,3-Pentafluoro-Z-prop-1-enyl)-cyclohexene (0.5 g, 2.4 mmol) with iodine monobromide (0.6 g, 2.8 mmol) in DCM (10 ml) at -10 °C for 2 hours gave many unidentified products corresponding to IBr addition products by GLC/MS (291/293 (M^+-I)). Degradation products prevented further purification by column chromatography over silica gel (hexane).

Addition of iodine monofluoride

General procedure

IF was produced *in situ* by addition of two equivalents of iodine to iodine pentafluoride at the required temperature under inert atmosphere. After stirring for 15 minutes, the fluoroalkene was added dropwise. On termination, the reaction mixture was carefully (HF is produced) quenched with aqueous sodium metabisulfite. Extraction into DCM enabled recovery of the products.

Iodine monofluoride and (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoropropene

IF_5 (37 g, 167 mmol), iodine (32 g, 124 mmol) and (1Z)-1-cyclohexyl-1,2,3,3,3-pentafluoropropene (**19**) (12.3 g, 57.5 mmol) gave, after column chromatography on silica gel (hexane), *1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane* (**34**) (18.2 g, 88%) as a purple liquid; bp 217-218 °C (Found: C, 30.0; H, 3.1. $C_9H_{11}F_6I$ requires C, 30.0; H, 3.1%); ν_{max} (cm^{-1}) 2859 and 2939 (C-H); m/z (EI^+) 360 (M^+, 10%), 133 (67), 127 (26), 113 (57), 83 (100); NMR no. 31.

Iodine monofluoride and *trans*-1,4-bis(Z-pentafluoroprop-2-enyl)cyclohexane.

Iodine (5.6 g, 22.1 mmol), iodine pentafluoride (8 g, 36 mmol) and trans-1,4-bis(Z-pentafluoroprop-2-enyl)cyclohexane (**22**) (12.3 g, 57.5 mmol) gave *1,1,2,3,3,3-hexafluoro-1-[4-(1,1,2,3,3,3-hexafluoro-2-iodopropyl)cylohexyl]-2-iodopropane* (**35**) (0.3 g, 66%) as a white solid; m.p. 217-218 °C (from MeOH/ H_2O) (M^+, 635.869032. $C_{12}H_{10}F_{12}I_2$ requires m^+, 635.869043); ν_{max} (cm^{-1}) 2853 and 2923 (C-H); m/z (EI^+) 636 (M^+, 7%), 409 (100), 389 (77), 359 (37), 339 (27), 81 (31); NMR no. 32.

Iodine monofluoride and (2Z)-1,1,1,2,3-pentafluoro-4,4-dimethylpent-2-ene

Iodine (1 g, 3.9 mmol), iodine pentafluoride (0.4 g, 2.0 mmol) and (2Z)-1,1,1,2,3-pentafluoro-4,4-dimethylpent-2-ene (**24**) at room temperature for 12 hours gave only *1,1,1,2,3,3-hexafluoro-2-iodo-4,4-dimethylpentane* (**36a**) on analysis by ^{19}F NMR and GLC/MS; m/z (EI^+) 334 (M^+, 17), 127 (31), 107 (60), 87 (42), 65 (76), 57 (100), 47 (34), 41 (79), 29 (47). After column chromatography over silica gel (hexane), no product was recovered; NMR no. 33.

Iodine monofluoride and 2-(1,2,3,3,3-pentafluoroprop-1-enyl)oxolane

Iodine (9.4 g, 37.1 mmol), iodine pentafluoride (4.4 g, 19.8 mmol) and 2-(1,2,3,3,3-pentafluoroprop-1-enyl)oxolane (**17**) (2.5 g, 12.4 mmol) in freon 113 (30 ml) gave after one week at room temperature *2-(1,1,2,3,3,3-hexafluoro-2-iodopropyl)oxolane* (**37**) (65% by GLC) on analysis by GLC/MS but it could not be isolated as it decomposed on silica gel and during distillation; m/z (EI^+) 348 (M^+, 62), 274 (12), 227 (43), 202 (37), 127 (74), 121 (100), 101 (67), 73 (97).

7.6. Experimental to chapter 5

Addition of 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane to alkenes

1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane and 1,1-difluoroethylene

1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) (2.5 g, 6.9 mmol), 1,1-difluoroethylene (1.2 g, 18.7 mmol) and benzoyl peroxide (0.25 g, 1 mmol) were contained in a rocking autoclave at 125°C for 2 hours. No unreacted gas was recovered. Conversion based on 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane was 60% by GLC. *2-(Cyclohexyldifluoromethyl)-1,1,1,2,4,4-hexafluoro-4-iodobutane* (**38**) was observed by GLC/MS (4% by GLC); m/z (EI^+) M^+ (424, 2.3%).

1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane and allylbenzene

1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) (2.5 g, 6.9 mmol), allyl benzene (1.6 g, 13.9 mmol) and a catalytic amount of AIBN (2%) were refluxed at 75°C under N_2 for 14 hours. Kugelrhor distillation of the crude reaction mixture gave two diastereoisomers of *[4-cyclohexyldifluormethyl-4,5,5,5-tetrafluoro-2-iodopentyl]benzene* (**39**) (2.8 g, 85%) in a ratio of 1 : 1.2 by ^{19}F NMR as a colourless oil; bp 218-219°C (Found: C, 45.3; H, 4.5. $C_{18}H_{21}F_6I$ requires C, 45.2; H, 4.4%); ν_{max} (cm^{-1}) 2857 and 2937 (C-H); m/z (EI^+) 478 (M^+, 0.15 %), 351 (69), 117 (90), 115 (66), 91 (100), 77(42), 69 (30); NMR no. 35.

1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane and 1-octene

1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) (0.78 g, 2.2 mmol), 1-octene (0.56 g, 5 mmol) and a catalytic amount of AIBN (2%) were refluxed at 75°C under inert atmosphere for 7 hours. Kugelrhor distillation of the crude reaction mixture gave two diastereoisomers of *2-(cyclohexyldifluoromethyl)-1,1,1,2-tetrafluoro-4-iododecane* (**40**) (0.90 g, 87%) in a ratio of 1 : 1.2 by ^{19}F NMR as a colourless oil; bp 247-248°C (M^+-I, 345.200875. $C_{17}H_{27}F_6$ -I requires 345.201696); ν_{max} (cm^{-1}) 2857 and 2931 (C-H); m/z (EI^+) 472 (M^+, 7%), 345 (77); NMR no. 34.

1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane and 1-hexyne

1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) (1.5 g, 4.2 mmol), 1-hexyne (0.4 g, 4.6 mmol) and a catalytic amount of AIBN (2%) were refluxed at 75°C under argon for 8 hours. Kugelrohr distillation followed by column chromatography over silica (hexane) gave *(3E)-2-cyclohexyldifluoromethyl-1,1,1,2-tetrafluoro-4-iodooct-3-ene* (**41**) (1.4 g, 75%) as a colourless oil; bp 264-265°C (Found: C, 40.62; H, 4.79. $C_{15}H_{21}F_6I$ requires C, 40.74; H, 4.78%); ν_{max} (cm^{-1}) 2886 and 2934 (C-H); m/z (EI^+) 442 (M^+, 2%), 253 (12), 133 (26), 113 (100), 93 (27), 57 (63), 55 (61), 43 (99), 41 (78); NMR no. 36.

Reaction of alkyliodides and thiols.

General procedure for addition of thiols to alkyliodides

The sodium thiolate salts were prepared *in situ* by dropwise addition of the thiol to a suspension of sodium hydride in DMF. The perfluoroalkyliodide was added in one portion to the stirred mixture, under nitrogen. After stirring for the appropriate time, the solutions were diluted with ether. The ether solutions were washed with water, dried over $MgSO_4$ and concentrated. The products were purified by column chromatography or distillation under reduced pressure.

1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane and benzenethiol.

1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) (1 g, 2.8 mmol) and sodium benzenethiolate (0.37 g, 2.8 mmol) gave, after column chromatography on silica (petroleum ether 40/60), *1-(cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoro-1-phenylthio-ethane* (**42**) (0.7 g, 73 %) as a white solid; mp 48-49 °C (from hexane) (Found: C, 52.4; H, 4.7. $C_{15}H_{16}F_6S$ requires C, 52.6; H, 4.7%); ν_{max} (cm^{-1}) 1654 (C=C), 2868 and 2962 (C-H); m/z (EI^+) 342 (M^+, 76 %), 209 (18), 113 (99), 110 (100), 109 (63), 81 (31), 77 (49); NMR no. 37.

1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane and 1-octanethiol.

1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) (1.5 g, 4.16 mmol) and sodium 1-octanethiolate (6.25 mmol) gave, after Kugelrohr distillation and column chromatography on silica gel (hexane), *1-(cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoro-1-octylthioethane* (**43**) (1.1 g, 70%) as a colourless oil; bp 265 -266°C (Found: C, 53.7; H,

7.5. $C_{17}H_{28}F_6S$ requires C, 53.9; H, 7.5%); ν_{max} (cm^{-1}) 2857 and 2930 (C-H); m/z (EI^+) 145 (100%, $C_8H_{17}S$), 113 (42), 81 (10), 69 (60), 55 (51), 41 (39); NMR no. 38.

1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane and 1,2-ethanedithiol.

1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) (1 g, 2.8 mmol) and sodium 1,2-ethanethiolate (1.4 mmol) gave, after column chromatography over silica (hexane/ether 5%), *1-(cyclohexyldifluoromethyl)-1-{2—[1-(cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoroethylthio]ethylthio}-1,2,2,2-tetrafluoroethane* (**44**) (0.15 g, 20%) as a colourless oil;bp 234-235°C (M^+, 558.13. $C_{20}H_{26}F_{12}S_2$ requires m^+, 558.13); ν_{max} (cm^{-1}) 2859 and 2939 (C-H); m/z (EI^+) 558 (M^+, 2.2 %), 325 (59), 293 (100), 113 (40), 81 (29), 77 (11), 55 (42), 47 (14), 41 (55); NMR no. 39.

1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane and 1,8-octanedithiol.

1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) (1 g, 2.8 mmol) and sodium 1,8-octanedithiolate (1.4 mmol) gave, after Kugelrohr distillation, *1-(cyclohexyldifluoromethyl)-1-{8-[1-(cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoroethylthio}-1,2,2,2-tetrafluoroethane* (**45**) as a yellow oil (0.2 g, 25%); b.p. 291-292°C (Found: C, 48.7; H, 6.3. $C_{26}H_{38}F_{12}S_2$ requires C, 48.6; H, 5.9 %); ν_{max} (cm^{-1}) 2857 and 2932 (C-H); m/z (EI^+) 642 (M^+, 0.7 %),409 (41), 389 (38), 227 (65), 205 (28), 165 (11), 145 (13), 144 (10), 143 (100), 141 (21), 133 (22), 115 (12), 113 (54), 109 (13); NMR no. 40.

1,1,2,3,3,3-Hexafluoro-1-[4-(1,1,2,3,3,3-hexafluoro-2-iodopropyl) cyclohexyl]-2-iodopropane and benzenethiol.

1,1,2,3,3,3-Hexafluoro-1-[4-(1,1,2,3,3,3-hexafluoro-2-iodopropyl)cyclohexyl]-2-iodopropane (**35**) (0.06 g, 0.094 mmol) and sodium benzenethiolate (0.05 g, 0.38 mmol) gave, after column chromatography over silica (petroleum ether 40/60), *1-{ difluoro[4-(1,1,2,3,3,3-hexafluoro-2-phenylthiopropyl)cyclohexyl]methyl}1,2,2,2-tetrafluoro-1-phenylthioethane* (**46**) (0.039 g, 70%) as a white solid; mp 93.8-94.6 °C (from hexane) (M^+, 600.081436. $C_{24}H_{20}F_{12}S_2$ requires m^+, 600.081483); ν_{max} (cm^{-1}) 2853 and 2923 (C-H); m/z (EI^+) 600 (M^+, 10.3 %), 209 (30), 110 (72), 109 (100), 81 (16), 77 (45); NMR no. 41.

1,4-Diiodooctafluorobutane and benzenethiol.

1,4-Diiodooctafluorobutane (1.5 g, 3.3 mmol) and sodium benzenethiolate (6.8 mmol) gave, after column chromatography over silica (petroleum ether 40/60), *1,1,2,2,3,3,4,4-octafluoro-4-iodo-1-phenylthiobutane* (**47**) (0.27 g,19%) as a colourless liquid; b.p. 188-189 °C (Found: C, 27.5; H, 1.1. $C_{10}H_5F_8SI$ requires C, 27.5; H, 1.1); ν_{max} (cm^{-1}) 1443 and 1475 (C=C); m/z (EI^+) 436 (M^+, 13.3 %), 309 (16), 159 (77), 131 (12), 127 (28), 109 (100), 108 (11), 100 (14), 65 (21); NMR no. 43 and *1,1,2,2,3,3,4,4-octafluoro-1,4-diphenylthiobutane* (**48**) (0.96 g, 70%) as white crystals; mp 51.8-52.3 °C (Found: C, 45.8; H, 2.4. $C_{16}H_{10}F_8S_2$ requires C, 45.9; H, 2.4%); ν_{max} (cm^{-1}) 1443 and 1475 (C=C); m/z (EI^+) 418 (M^+, 29.7 %), 159 (100), 109 (78), 77 (77), 69 (10), 65 (24); NMR no. 42.

1,4-Diiodooctafluorobutane and 1-octanethiol.

1,4-Diiodooctafluorobutane (1 g, 2.2 mmol) and sodium 1-octanethiolate (4.4 mmol) gave, after column chromatography over silica (hexane), *1,1,2,2,3,3,4,4-octafluoro-1,4-dioctylthiobutane* (**49**) (0.8 g, 72%) as a colourless oil; (M^+, 490.198241. $C_{20}H_{34}F_8S_2$ requires M^+, 490.197421); ν_{max} (cm^{-1}) 2857 and 2928 (C-H) ; m/z (EI^+) 490 (M^+, 1.3 %), 145 (100), 144 (13), 70 (14), 69 (16), 58 (31).

General procedure for oxidation of sulfides.

The solution of sulfides and chromium trioxide (3 fold molar excess) were heated at reflux in acetic acid for 3 hours. Then the crude mixture was carefully added to ice water, extracted with ether, dried ($MgSO_4$), concentrated and purified as stated below.

1-(Cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoro-1-phenylthioethane.

1-(Cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoro-1-phenylthioethane (**42**) (0.2 g, 0.58 mmol) and CrO_3 (0.2 g, 2 mmol) gave after vacuum transfer *1-(cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoro-1-(phenylsulfonyl)ethane* (**51**) (0.16 g, 74%) as a colourless liquid; b.p. 262-263°C ($(m+H)^+$, 375.084265. $C_{15}H_{17}F_6O_2S$ requires 375.085346); ν_{max}/cm^{-1} 2937 and 2860 (C-H), 1363 (S=O); m/z (CI^+) 392 ($(M+ NH_4)^+$, 84.6 %), 94 (11), 81 (15), 78 (72); NMR no. 45.

1-(Cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoro-1-octylthioethane

1-(Cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoro-1-octylthioethane (**43**) (0.46 g, 1.22 mmol) and CrO_3 (0.4 g, 4 mmol) gave after column chromatography over silica (hexane/DCM, 70/30) *1-(cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoro-1-(octylsulfonyl)-ethane* (**52**) (0.39 g, 78%) as a colourless oil; ν_{max}/cm^{-1} 2929 and 2858 (C-H), 1361 (S=O); bp 273-274°C; *m/z* (CI^+) 428 ($(M+ NH_4)^+$, 100%).

Attempted deiodofluorinations

Reaction of 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane with SbF_5

1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) (1.3 g, 3.6 mmol) was added to a mixture of SbF_5 (5 g, 23 mmol) in flutek PP11 (first degassed). After stirring at 0°C for 1 hour, only 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) was recovered by vacuum transfer on analysis by GC/MS. No reaction occurred either using arklone solvent at 0°C, 25°C. At reflux temperature, degradation occurred.

Direct fluorination of 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane

Elemental fluorine (5 mmol) diluted to a 10% solution in nitrogen was passed through a solution of 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) (1.5 g, 4.2 mmol) in dry acetonitrile (15 ml) at 0°C. The reaction mixture was poured into 10% aqueus sodium hydrogen carbonate and extracted with dichloromethane. The extract was washed with water several times, dried ($MgSO_4$) and solvent was removed by rotary evaporation. Only 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) was recovered on analysis by GLC/MS. No reaction occurred either using arklone as a solvent.

Using xenon difluoride

1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) (2.1 g, 5.9 mmol) was dissolved in chloroform and treated with 1 equivalent of XeF_2 (1 g, 5.9 mmol). The reaction mixture was refluxed for 2 days. After washing with sodium bisulfite and concentrating the chloroform, only 1-cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**) was recovered on analysis by GLC/MS.

APPENDICES

8. Appendices

8.1. NMR spectra

1. 2-Chloro-1-cyclopentyl-1,1-difluoroethane (**1**)
2. 2,2-Dichloro-1-cyclopentyl-1,1-difluoroethane (**4**)
3. (1,1,2,3,3,3-Hexafluoropropyl)cyclohexane (**6**)
4. 2-Cyclohexyl-1,1,1,2,3,3,3-hexafluoropropane (**6a**)
5. 1,x-Bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (x=2-4) (**7**)
6. 2*R*,2'*S*-*Trans*-1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (**7a**)
7. (1,1,2,3,3,3-Hexafluoropropyl)adamantane (**8**)
8. 1,3-Bis-(1,1,2,3,3,3-hexafluoropropyl)adamantane (**9**)
9. 1,3,5-Tris(1,1,2,3,3,3-hexafluoropropyl)adamantane (**10**)
10. 1,3,5,7-Tetrakis(1,1,2,3,3,3-hexafluoropropyl)adamantane (**11**)
11. 4,4-Dimethyl-1,1,1,2,3,3-hexafluoropentane (**12**)
12. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexanol (**14**)
13. 2-(1,1,2,3,3,3-Hexafluoropropyl)oxolane (**16**)
14. *Z*-2-Chloro-1-cyclopentyl-1-fluoroethene (**20**)
15. 2,2-Dichloro-1-cyclopentyl-1-fluoroethene (**21**)
16. (1*Z*)-1-Cyclohexyl-1,2,3,3,3-pentafluoropropene (**19**)
17. *Trans*-1,4-bis[(1*Z*)-pentafluoroprop-1-enyl]-cyclohexane (**22**)
18. 1[(1*Z*)-Pentafluoroprop-1-enyl]adamantane (**18*Z***)
19. 1[(1*E*)-Pentafluoroprop-1-enyl]adamantane (**18*E***)
20. 1,3,5,7-Tetrakis(*E*-pentafluoroprop-1-enyl)-adamantane (**23a**)
21. 1-(*Z*-Pentafluoroprop-2-enyl)-3,5,7-tris(*E*-pentafluoroprop-2-enyl)adamantane (**23b**)
22. (2*Z*)-1,1,1,2,3-Pentafluoro-4,4-dimethylpent-2-ene (**24**)
23. 2-((1*Z*)-1,2,3,3,3-Pentafluoroprop-1-enyl)oxolane (**17**)
24. 1-(1,1,2,3,3,3-Hexafluoropropyl)cyclohexene (**25**)
25. 1-(1,2,3,3,3-Pentafluoro-*Z*-prop-1-enyl)-cyclohexene (**26**)
26. 1,2-Dibromo-2,2-dichloro-1-cyclopentyl-1-fluoroethane (**27**)
27. 1,2,2,2-Tetrachloro-1-cyclopentyl-1-fluoroethane (**29**)

28. (1*Z*)-1-(1-Chloro-2-iodocylohexyl)-1,2,3,3,3-pentafluoroprop-1-ene (**30**)
29. 2-Bromo-1-(2-bromocyclohexylidene)-1,2,3,3,3-pentafluoropropane (**32**)
30. (1*Z*)-1-(1,2-Dibromocyclohexyl)-1,2,3,3,3-pentafluoroprop-1-ene (**33**)
31. 1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane (**34**)
32. 1,1,2,3,3,3-Hexafluoro-1-[4-(1,1,2,3,3,3-hexafluoro-2-iodopropyl)cylohexyl]-2-iodopropane (**35**)
33. 1,1,1,2,3,3-Hexafluoro-2-iodo-4,4-dimethylpentane (**36a**)
34. 2-(Cyclohexyldifluoromethyl)-1,1,1,2-tetrafluoro-4-iododecane (**40**)
35. [4-Cyclohexyldifluormethyl-4,5,5,5-tetrafluoro-2-iodopentyl]benzene (**39**)
36. (3*E*)-2-Cyclohexyldifluoromethyl-1,1,1,2-tetrafluoro-4-iodooct-3-ene (**41**)
37. 1-(Cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoro-1-phenylthioethane (**42**)
38. 1-(Cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoro-1-octylthioethane (**43**)
39. 1-(Cyclohexyldifluoromethyl)-1-{2—[1-(cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoroethylthio]ethylthio}-1,2,2,2-tetrafluoroethane (**44**)
40. 1-(Cyclohexyldifluoromethyl)-1-{8-[1-(cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoroethylthio}-1,2,2,2-tetrafluoroethane (**45**)
41. 1-{Difluoro[4-(1,1,2,3,3,3-hexafluoro-2-phenylthiopropyl)cyclohexyl]methyl}1,2,2,2-tetrafluoro-1-phenylthioethane (**46**)
42. 1,1,2,2,3,4,4-Octafluoro-1,4-diphenylthiobutane (**48**)
43. 1,1,2,2,3,3,4,4-Octafluoro-4-iodo-1-phenylthiobutane (**47**)
44. 1,1,2,2,3,3,4,4-Octafluoro-1,4-dioctylthiobutane (**49**)
45. 1-(Cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoro-1-(phenylsulfonyl)ethane (**51**)
46. 1-(Cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoro-1-(octylsulfonyl)ethane (**52**)

Chemical shifts are quoted in ppm relative to an internal tetramethylsilane reference (^1H and ^{13}C spectra) or an external trichlorofluoromethane reference (^{19}F spectra).

For an AB system, chemical shifts are quoted as the 'centre of gravity', calculated from :

$$(\delta_1-\delta_3) = (\delta_2-\delta_4) = (\Delta v^2 + J^2)^{1/2}$$

where δ_n is the chemical shift of the nth peak, Δv is the difference in chemical shifts between the two resonances of the nucleii and J is the coupling constant.

The following abbreviations are used :

s singlet

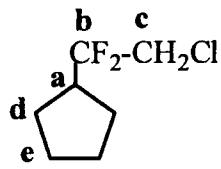
d doublet

t triplet

q quartet

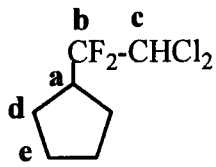
m multiplet

No. 1 2-Chloro-1-cyclopentyl-1,1-difluoroethane (**1**)



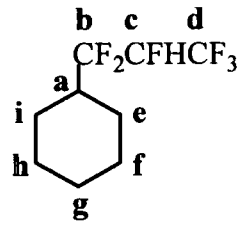
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.6-1.8	m		8	d, e
2.56	m		1	a
3.67	t	$^{3}J_{H\text{-}F}$ 12.8	2	c
^{19}F				
-108.9	dt	$^{3}J_{H\text{-}F}$ 14.3 $^{3}J_{H\text{-}F}$ 12.9	2	b
^{13}C				
26.1	s			e
26.2	t	$^{3}J_{C\text{-}F}$ 3.8		d
42.6	t	$^{2}J_{C\text{-}F}$ 23.3		a
44.4	t	$^{2}J_{C\text{-}F}$ 34.4		c
122.7	t	$^{1}J_{C\text{-}F}$ 244.5		b

No. 2 2,2-Dichloro-1-cyclopentyl-1,1-difluoroethane (**4**)



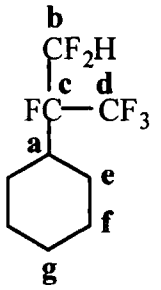
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.6-1.7	m		4	d_{ax}, e_{ax}
1.8-1.9	m		4	d_{eq}, e_{eq}
2.7	m		1	a
5.7	t	$^{3}J_{H-F}$ 8.7	1	c
^{19}F				
-113.8	dd	$^{3}J_{H-F}$ 8.6 $^{3}J_{H-F}$ 14.7	2	b
^{13}C				
25.6	s			e
26	t	$^{3}J_{C-F}$ 3.4		d
42.1	t	$^{2}J_{C-F}$ 22.3		a
70.1	t	$^{2}J_{C-F}$ 35.1		c
121	t	$^{1}J_{C-F}$ 251		b

No. 3 (1,1,2,3,3,3-Hexafluoropropyl)cyclohexane (**6**)



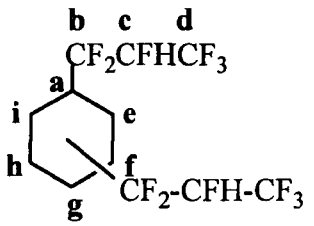
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^1H				
1.21	m		5	e_{ax}, f_{ax}, g_{ax}, $h_{ax.}$ i_{ax}
1.76	m		6	e_{eq}, f_{eq}, g_{eq}, $h_{eq.}$ i_{eq}, a
4.82	ddqd	$^2J_{H-F}$ 43.6 $^3J_{H-F}$ 15.6 $^3J_{H-F}$ 12.0 $^3J_{H-F}$ 12.0	1	c
^{19}F				d
-74.5	m		3	
-118.34	A of AB		2	b
-119.06	B of AB			
-212	dq	$^2J_{F-H}$ 43.6 $^3J_{F-F}$ 10	1	c
^{13}C				
23.8	t	$^3J_{C-F}$ 4.5		e
25.2	s			g
25.3	s			f
25.4	m			i
25.6	s			h
41.3	t	$^2J_{C-F}$ 21.3		a
84.6	ddqd	$^1J_{C-F}$ 194.6 $^2J_{C-F}$ 36.8 $^2J_{C-F}$ 33.7 $^2J_{C-F}$ 30.9		c
119.7	ddd	$^1J_{C-F}$ 248.4 $^1J_{C-F}$ 246.6 $^2J_{C-F}$ 23.9		b
120.9	qd	$^1J_{C-F}$ 281 $^2J_{C-F}$ 25		d

No. 4 2-Cyclohexyl-1,1,1,2,3,3,3-hexafluoropropane (**6a**)



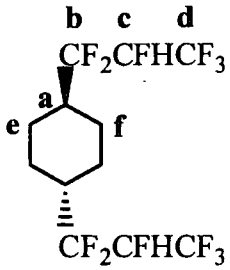
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
5.97	t	$^2J_{H-F}$ 53.2	1	b
	d	$^3J_{H-F}$ 6.8		

No. 5 1,x-Bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (x=2-4) (**7**)



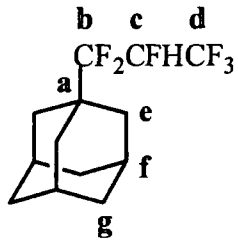
Chemical shift (ppm)	Multiplicity	Coupling constant	Relative intensity	Assignment
^{1}H				
1.35	m			a,e,f,g,h,i
1.70	m			a,e,f,g,h,i
2.09	m			a,e,f,g,h,i
4.84	dm	$^2J_{H-F}$ 41		c
^{19}F				
-74.7	s		3	d
-118.2	m		2	b
-212	s		1	c

No. 6 2*R*,2'*S*-*Trans*-1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (**7a**)



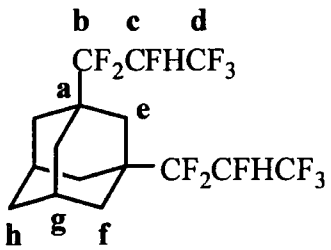
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.42	m		2	e_{ax}, f_{ax}
2.04	m		3	a, e_{eq}, f_{eq}
4.83	dm	$^{2}J_{H-F}$ 44	1	c
^{19}F				
-74.5	m			d
-117.6	A of AB		J_{AB} 268	b
-118.8	B of AB			
-211.5	dq	$^{2}J_{H-F}$ 44		c
		$^{3}J_{F-F}$ 8		
^{13}C				
22.9	t	$^{3}J_{C-F}$ 4.6		e
24.3	t	$^{3}J_{C-F}$ 3.1		f
40.7	t	$^{2}J_{C-F}$ 22		a
85.9	ddqd	$^{1}J_{C-F}$ 196.2		c
		$^{2}J_{C-F}$ 34.7		
		$^{2}J_{C-F}$ 34.4		
		$^{2}J_{C-F}$ 32.4		
119.4	ddd	$^{1}J_{C-F}$ 253.4		b
		$^{1}J_{C-F}$ 249.2		
		$^{2}J_{C-F}$ 24.8		
122.4	qd	$^{1}J_{C-F}$ 282		d
		$^{2}J_{C-F}$ 25.9		

No. 7 (1,1,2,3,3,3-Hexafluoropropyl)adamantane (**8**)



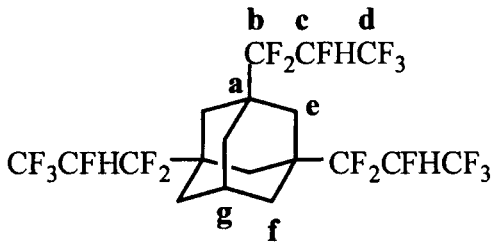
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.78	m		12	e, g
2.09	br s		3	f
4.94	ddq	$^2J_{H-F}$ 44 $^3J_{H-F}$ 20 $^3J_{H-F}$ 6.5	1	c
^{19}F				
-74.3	m		3	
-122.6	A of AB	J_{AB} 274	2	d
-130.0	B of AB			b
-206.9	dm	$^2J_{H-F}$ 43.9	1	c
^{13}C				
27.8	s			f
34.9	q			e
36.7	s			g
40.0	t			a
83.8	ddqd	$^1J_{C-F}$ 197.5 $^2J_{C-F}$ 41.7 $^2J_{C-F}$ 33.5 $^2J_{C-F}$ 25.9		c
119.8	ddd	$^1J_{C-F}$ 260.6 $^1J_{C-F}$ 246.6 $^2J_{C-F}$ 22.1		b
121.5	qd	$^1J_{C-F}$ 283.1 $^2J_{C-F}$ 25.9		d

No. 8 1,3-Bis-(1,1,2,3,3,3-hexafluoropropyl)adamantane (**9**)



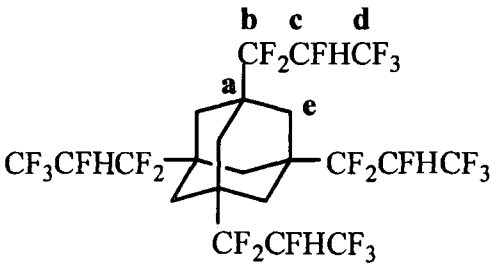
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^1H				
1.80	m		6	g, e, f
2.28	br s		1	h
4.95	ddq	$^2J_{H-F}$ 44 $^3J_{H-F}$ 20 $^3J_{H-F}$ 6	1	a
^{19}F				
-74.3	m		3	d
-121.7	A of AB	J_{AB} 275	2	
-129.4	B of AB			b
-207.1	dm	$^2J_{H-F}$ 43	1	c
^{13}C				
27.2	s			g
31.1	s			e
34.0	s			f
35.4	s			h
40.8	t	$^2J_{C-F}$ 22		a
84.0	ddqd	$^1J_{C-F}$ 197.7 $^2J_{C-F}$ 41.7 $^2J_{C-F}$ 34.1 $^2J_{C-F}$ 26.4		c
119.3	ddd	$^1J_{C-F}$ 261.4 $^1J_{C-F}$ 247 $^2J_{C-F}$ 22.5		b
121.3	qd	$^1J_{C-F}$ 283.6 $^2J_{C-F}$ 26.4		d

No. 9 1,3,5-Tris(1,1,2,3,3,3-hexafluoropropyl)adamantane (**10**)



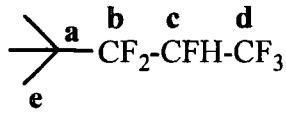
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.88	m		12	e, f
2.14	s		1	g
4.96	m		3	c
^{19}F				
-74.8	m		3	d
-120.7	A of AB	J_{AB} 274	2	b
-128.7	B of AB			
-207.8	dm	$^{2}J_{F-H}$ 29	1	c
^{13}C				
26.9	s			g
31.7	s			f
33.3	s			e
41.5	t	$^{2}J_{C-F}$ 22		a
84.0	dm	$^{1}J_{C-F}$ 197.2		c
119.2	ddd	$^{1}J_{C-F}$ 261.4		b
		$^{1}J_{C-F}$ 247.6		
		$^{2}J_{C-F}$ 22.5		
121.4	qd	$^{1}J_{C-F}$ 283.1		d
		$^{2}J_{C-F}$ 25.9		

No. 10 1,3,5,7-Tetrakis(1,1,2,3,3,3-hexafluoropropyl)adamantane (**11**)



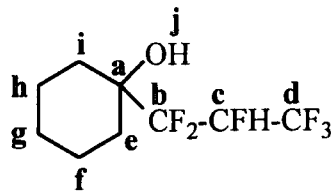
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
2.09	m		3	e
6.01	ddq	$^{2}J_{H-F}$ 42	1	c
		$^{3}J_{H-F}$ 20		
		$^{3}J_{H-F}$ 6		
^{19}F				
-74.2	m		3	d
-121.1	A of AB	J_{A-B} 276	2	b
-127.6	B of AB			
-207.1		$^{2}J_{F-H}$ 29	1	c
^{13}C				
30.1	s			e
40.5	t	$^{2}J_{C-F}$ 21.3		a
82.0	dm	$^{1}J_{C-F}$ 192.8		c
117.9	ddd	$^{1}J_{C-F}$ 260.9		b
		$^{1}J_{C-F}$ 248.5		
		$^{2}J_{C-F}$ 21.6		
120.3	qd	$^{1}J_{C-F}$ 282.6		d
		$^{2}J_{C-F}$ 25.9		

No. 11 4,4-Dimethyl-1,1,1,2,3,3-hexafluoropentane **(12)**



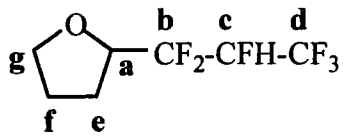
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.13	br s		9	e
4.92	ddqd	$^{2}J_{H-F}$ 44	1	c
		$^{3}J_{H-F}$ 20		
		$^{3}J_{H-F}$ 6		
		$^{3}J_{H-F}$ 1		
^{19}F				
-74.7	m		3	d
-117.6	A of AB	J_{AB} 270	2	b
-126.1	B of AB			
-207.0	dm	$^{2}J_{H-F}$ 44.2	1	c
^{13}C				
23.8	s			e
38.7	t	$^{2}J_{C-F}$ 21.5		a
84.8	ddqd	$^{1}J_{C-F}$ 200.8		c
		$^{2}J_{C-F}$ 41.8		
		$^{2}J_{C-F}$ 33.4		
		$^{2}J_{C-F}$ 25.9		
120.9	ddd	$^{1}J_{C-F}$ 260.9		b
		$^{1}J_{C-F}$ 247		
		$^{2}J_{C-F}$ 22.5		
121.5	qd	$^{1}J_{C-F}$ 282.9		d
		$^{2}J_{C-F}$ 25.9		

No. 12 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexanol **(14)**



Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.2-1.9	m		10	e-i
3.60	m		1	j
5.24	ddqd	$^{2}J_{H-F}$ 43.6	1	c
		$^{3}J_{H-F}$ 17.6		
		$^{3}J_{H-F}$ 6.4		
		$^{3}J_{H-F}$ 1.2		
^{19}F				
-74.5	m		3	d
-127.7	A of AB	J_{AB} 275.5	2	b
-128.4	B of AB			
-207.8	dm	$^{2}J_{F-H}$ 46.4	1	c
^{13}C				
20.7	s			f
20.8	s			h
25.4	s			g
29.4	m			e
29.7	m			i
74.3	t	$^{2}J_{C-F}$ 24.2		a
83.1	ddqd	$^{1}J_{C-F}$ 195.8		c
		$^{2}J_{C-F}$ 37.2		
		$^{2}J_{C-F}$ 33.7		
		$^{2}J_{C-F}$ 24.1		
118.3	ddd	$^{1}J_{C-F}$ 264.7		b
		$^{1}J_{C-F}$ 250.4		
		$^{2}J_{C-F}$ 21.3		
121.6	qd	$^{1}J_{C-F}$ 282.8		d
		$^{2}J_{C-F}$ 26.1		

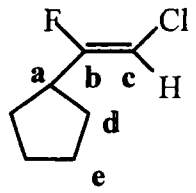
No. 13 2-(1,1,2,3,3,3-Hexafluoropropyl)oxolane (**16**)



Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.9-2.2	m		4	e, f
3.88	m		2	g
4.26	m		1	a
5.09	ddqd	$^{2}J_{H-F}$ 43	1	c
		$^{3}J_{H-F}$ 21		
		$^{3}J_{H-F}$ 6		
		$^{3}J_{H-F}$ 5.8		
^{19}F				
-74.5	m		3	d minor
-75.1	m		3	d major
-122.4	A of AB	J_{AB} 269.6	2	b minor
-123.1	B of AB			
-127.8	A of AB	J_{AB} 269.4	2	b major
-128.5	B of AB			
-213.6	dm	$^{2}J_{F-H}$ 43	1	c minor
-218.9	dm	$^{2}J_{F-H}$ 44	1	c major
^{13}C				
24.4	s			e or f
24.5	s			e or f
25.9	s			e or f
26.1	s			e or f
70.2	br s			g
70.3	br s			g
75.6	dd	$^{2}J_{C-F}$ 34.2		a
		$^{2}J_{C-F}$ 23.1		

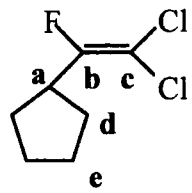
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
77.1	dd	$^{2}J_{C-F}$ 29.9		a
		$^{2}J_{C-F}$ 24.5		
83.8	ddqd	$^{1}J_{C-F}$ 192.5		c
		$^{2}J_{C-F}$ 39.9		
		$^{2}J_{C-F}$ 34.5		
		$^{2}J_{C-F}$ 23.7		
85.3	dm	$^{1}J_{C-F}$ 198.2		c
117.7	dd	$^{1}J_{C-F}$ 253		b
		$^{2}J_{C-F}$ 19		
118.1	ddd	$^{1}J_{C-F}$ 252.3		b
		$^{1}J_{C-F}$ 255.7		
		$^{2}J_{C-F}$ 25.7		
121.1	qd	$^{1}J_{C-F}$ 281.8		d
		$^{2}J_{C-F}$ 26.1		
121.4	qd	$^{1}J_{C-F}$ 282.2		d
		$^{2}J_{C-F}$ 26.0		

No. 14 *Z*-2-Chloro-1-cyclopentyl-1-fluoroethene (**20**)



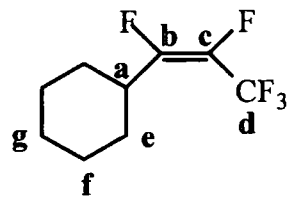
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.4-1.9	m		8	e, d
2.60	m		1	a
5.31	dd	$^{3}J_{trans\ H\text{-}F}$ 24.8 $^{4}J_{H\text{-}H}$ 0.8	1	c
^{19}F				
-109.8	dd	$^{3}J_{trans\ H\text{-}F}$ 24.8 $^{3}J_{F\text{-}H}$ 24.4	1	b
^{13}C				
25.5	s			e
26.0	s			d
41.4	d	$^{2}J_{C\text{-}F}$ 23.6		a
94.9	d	$^{2}J_{C\text{-}F}$ 19.4		c
160	d	$^{1}J_{C\text{-}F}$ 262		b

No. 15 2,2-Dichloro-1-cyclopentyl-1-fluoroethene (**21**)



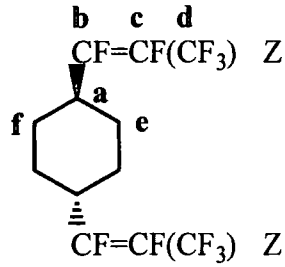
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.4-1.9	m		8	e, d
3.10	dp	$^{3}J_{H-F}$ 30.4 $^{3}J_{H-H}$ 8.4	1	a
^{19}F				
-113.4	d	$^{3}J_{F-H}$ 30.5	1	b
^{13}C				
25.9	s			e
29.0	s			d
38.8	d	$^{2}J_{C-F}$ 23.6		a
105.5	d	$^{2}J_{C-F}$ 46.5		c
159.5	d	$^{1}J_{C-F}$ 262.9		b

No. 16 (1Z)-1-Cyclohexyl-1,2,3,3,3-pentafluoropropene (**19**)



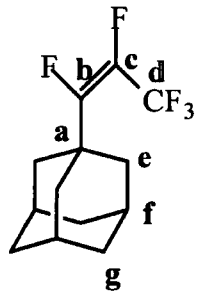
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.2-1.4	m		5	e, f, g_{ax}
1.6-1.8	m		5	e, f, g_{eq}
2.49	dt	$^{3}J_{H-F}$ 32.8	1	a_{ax}
		$^{3}J_{H-H}$ 12		
^{19}F				
-66.1	s		3	d
-131.3	dm	$^{3}J_{F-H}$ 32	1	b
-161.6	m		1	c
^{13}C				
25.4	s			g
25.7	s			f
28.8	d	$^{3}J_{C-F}$ 2.7		e
36.5	d	$^{2}J_{C-F}$ 21		a
120.2	qdd	$^{1}J_{C-F}$ 270		d
		$^{2}J_{C-F}$ 34.7		
		$^{3}J_{C-F}$ 9.6		
134.7	dqd	$^{1}J_{C-F}$ 250		c
		$^{2}J_{C-F}$ 40.4		
		$^{2}J_{C-F}$ 24		
156.5	ddq	$^{1}J_{C-F}$ 256.9		b
		$^{2}J_{C-F}$ 9.6		
		$^{3}J_{C-F}$ 3.4		

No. 17 *Trans*-1,4-bis[(1Z)-pentafluoroprop-1-enyl]-cyclohexane (**22**)



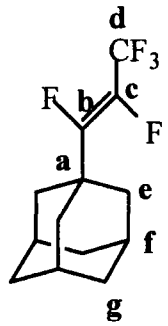
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.4-1.6	m		4	e, f_{ax}
1.7-1.9	m		4	e, f_{eq}
2.56	dm	$^{3}J_{H-F}$ 32	2	a
^{19}F				
-65.9	br s		3	d
-132.1	dm	$^{3}J_{H-F}$ 32	1	b
-159.3	br s		1	c
^{13}C				
27.1	s			e, f
34.8	d	$^{3}J_{C-F}$ 21		a
120.1	qdd	$^{3}J_{C-F}$ 270		d
		$^{3}J_{C-F}$ 33		
		$^{3}J_{C-F}$ 9.3		
135.3	dqd	$^{3}J_{C-F}$ 251		c
		$^{3}J_{C-F}$ 40		
		$^{3}J_{C-F}$ 24		
155.4	dd	$^{3}J_{C-F}$ 265		b
		$^{3}J_{C-F}$ 10		

No. 18 1[(1*Z*)-Pentafluoroprop-1-enyl]adamantane (**18Z**)



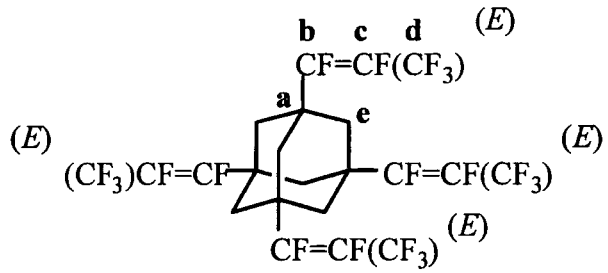
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.77	m		6	e
1.95	d	$^{3}J_{H-H}$ 2.5	6	g
2.07	s		3	f
^{19}F				
-60.1	t	$^{3}J_{F-F}$, $^{4}J_{F-F}$ 9.1	3	d
-125.0	q	$^{4}J_{F-F}$ 9.1	1	b
-154.8	q	$^{3}J_{F-F}$ 9	1	c
^{13}C				
28.1	s			f
36.5	s			e
38.2	m			g
39.4	s			a
120.3	qdd	$^{1}J_{C-F}$ 258.1		d
		$^{2}J_{C-F}$ 35.6		
		$^{3}J_{C-F}$ 9.1		
138.4	dd	$^{1}J_{C-F}$ 245.2		c
		$^{2}J_{C-F}$ 29.2		
160.9	ddq	$^{1}J_{C-F}$ 263.8		b
		$^{2}J_{C-F}$ 12.9		
		$^{3}J_{C-F}$ 4.3		

No. 19 1[(1*E*)-Pentafluoroprop-1-enyl]adamantane (**18*E***)



Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.76	m		6	e
1.96	d	$^{3}J_{H-H}$ 1	6	g
2.05	br s		3	f
^{19}F				
-67.6	dd	$^{3}J_{F-F}$ 23.7		d
		$^{4}J_{F-F}$ 9.8		
-149.3	dq	$^{3}J_{trans\ F-F}$ 131.7		b
		$^{4}J_{F-F}$ 22.6		
-175.6	dq	$^{3}J_{trans\ F-F}$ 131.4		c
		$^{3}J_{F-F}$ 9.4		
^{13}C				
27.9	s			f
36.6	s			e
38.1	t	$^{5}J_{C-F}$ 4.4		g
39.4	s			a
119.7	qdd	$^{1}J_{C-F}$ 272.5		d
		$^{2}J_{C-F}$ 35.9		
		$^{3}J_{C-F}$ 3.4		
138.4	ddq	$^{1}J_{C-F}$ 242.2		c
		$^{2}J_{C-F}$ 53.8		
		$^{2}J_{C-F}$ 38.8		
160.5	ddq	$^{1}J_{C-F}$ 260.1		b
		$^{2}J_{C-F}$ 35.9		
		$^{3}J_{C-F}$ 2.9		

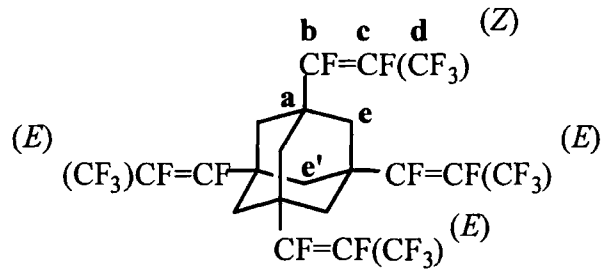
No. 20 1,3,5,7-Tetrakis(*E*-pentafluoroprop-1-enyl)-adamantane (**23a**)



Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
2.21	br s		12	e
^{19}F				
-68.1	dd	$^{3}J_{F\text{-}F}$ 22.9	3	d
		$^{4}J_{F\text{-}F}$10.2		
-150.1	dq	$^{3}J_{trans\ F\text{-}F}$ 134.3	1	b
		$^{4}J_{F\text{-}F}$22.9		
-170.8	dq	$^{3}J_{trans\ F\text{-}F}$ 133.6	1	c
		$^{4}J_{F\text{-}F}$10.2		
^{13}C				
36.4	s			e
38.5	dd	$^{2}J_{C\text{-}F}$ 21.1		a
		$^{3}J_{C\text{-}F}$ 4.3		
118.8	qdd	$^{1}J_{C\text{-}F}$ 273		d
		$^{2}J_{C\text{-}F}$ 35.9		
		$^{3}J_{C\text{-}F}$ 3.3		
139.7	ddq	$^{1}J_{C\text{-}F}$ 247.6		c
		$^{2}J_{C\text{-}F}$ 51.7		
		$^{2}J_{C\text{-}F}$ 39.9		
156.2	ddq	$^{1}J_{C\text{-}F}$ 260.6		b
		$^{2}J_{C\text{-}F}$ 35.9		
		$^{3}J_{C\text{-}F}$ 2.4		

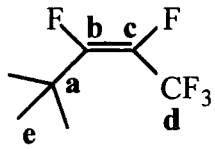
No. 21 1-(*Z*-Pentafluoroprop-2-enyl)-3,5,7-tris(*E*-pentafluoroprop-2-enyl)adamantane

(23b)



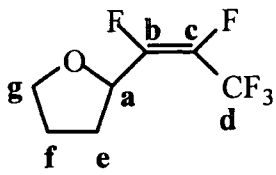
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
2.18	br s		6	e
2.20	br s		6	e'
^{19}F				
-60.3	br s		3	d (*Z*)
-67.9	dd	$^{3}J_{F\text{-}F}$ 22.9 $^{4}J_{F\text{-}F}$ 9.1	9	d (*E*)
-126.5	br s		1	b (*Z*)
-149.9	dq	$^{3}J_{trans\ F\text{-}F}$ 132.8 $^{4}J_{F\text{-}F}$ 22.9	3	b (*E*)
-150	m		1	c (*Z*)
-172.4	dq	$^{3}J_{trans\ F\text{-}F}$ 132.5 $^{4}J_{F\text{-}F}$ 9.1	3	c (*E*)

No. 22 (2Z)-1,1,1,2,3-Pentafluoro-4,4-dimethylpent-2-ene (**24**)



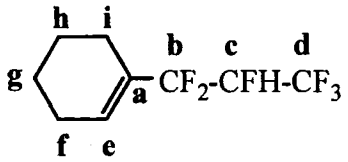
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.21	br s			e
^{19}F				
-61.2	t	$^{3}J_{F-F}$ and $^{4}J_{F-F}$ 9.4	3	d
-118.6	d	$^{3}J_{F-F}$ 7.1	1	b
-154.8	q	$^{3}J_{F-F}$ 9.1	1	c
^{13}C				
27.6	m			a
31.4	s			e
120.1	qdd	$^{1}J_{C-F}$ 269.9		d
		$^{2}J_{C-F}$ 35.3		
		$^{3}J_{C-F}$ 9.2		
137.4	dqd	$^{1}J_{C-F}$ 263.4		c
		$^{2}J_{C-F}$ 42.5		
		$^{2}J_{C-F}$ 28.4		
161.2	ddq	$^{1}J_{C-F}$ 265.3		b
		$^{3}J_{C-F}$ 13		
		$^{4}J_{C-F}$ 4.2		

No. 23 2-((1Z)-1,2,3,3,3-Pentafluoroprop-1-enyl)oxolane **(17)**



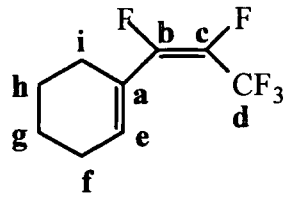
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.9-2.2	m		4	e, f
3.92	m		2	g
4.78	dm	$^{3}J_{H-F}$ 29.2	1	a
^{19}F				
-66.3	dd	$^{3}J_{F-F}$ 11.7	3	d
		$^{4}J_{F-F}$ 8.6		
-140.3	dqd	$^{3}J_{F-H}$ 29.7	1	b
		$^{4}J_{F-F}$ 8.6		
		$^{3}J_{cis\ F-F}$ 2.2		
-155.7	qm	$^{3}J_{F-F}$ 11.7	1	c
^{13}C				
26.8	s			f
28.9	t	$^{3}J_{C-F}$ 2.3		e
70.1	s			g
71.9	dq	$^{2}J_{C-F}$ 21.5		a
		$^{4}J_{C-F}$ 3.2		
119.7	qdd	$^{1}J_{C-F}$ 270.6		d
		$^{2}J_{C-F}$ 34.5		
		$^{3}J_{C-F}$ 8.8		
136.4	ddd	$^{1}J_{C-F}$ 256.5		c
		$^{2}J_{C-F}$ 41.3		
		$^{2}J_{C-F}$ 22.5		
151.9	ddq	$^{1}J_{C-F}$ 269.5		b
		$^{2}J_{C-F}$ 10.3		
		$^{3}J_{C-F}$ 3.4		

No. 24 1-(1,1,2,3,3,3-Hexafluoropropyl)cyclohexene (**25**)



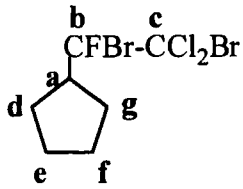
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.6-1.8	m		4	g, h
2.1-2.2	m		4	f, i
5.60	dm	$^{2}J_{H-F}$ 42.1	1	c
6.30	m		1	e
^{19}F				
-74.9	m			
-110.9	A of AB	J_{AB} 260	3	d
-113.7	B of AB		2	b
-212.9	dq	$^{2}J_{H-F}$ 42.4	1	c
		$^{3}J_{F-F}$ 13.9		
^{13}C				
22.1	s			g
22.5	s			h
23.5	s			i
25.4	s			f
86.1	ddqd	$^{1}J_{C-F}$ 194		c
		$^{2}J_{C-F}$ 37		
		$^{2}J_{C-F}$ 33.1		
		$^{2}J_{C-F}$ 30.9		
117.8	ddd	$^{1}J_{C-F}$ 249		b
		$^{1}J_{C-F}$ 246		
		$^{2}J_{C-F}$ 22.1		
122.1	qdd	$^{1}J_{C-F}$ 282		d
		$^{2}J_{C-F}$ 26.4		
		$^{3}J_{C-F}$ 3		
130.1	t	$^{2}J_{C-F}$ 21.7		a
130.3	t	$^{3}J_{C-F}$ 9.2		e

No. 25 1-(1,2,3,3,3-Pentafluoro-*Z*-prop-1-enyl)-cyclohexene (**26**)



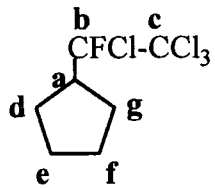
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.6-1.7	m		4	g, h
2.1-2.2	m		4	f, i
6.14	m		1	e
^{19}F				
-65.9	dd	$^{3}J_{F-F}$ 12.4 $^{4}J_{F-F}$ 8.6	3	d
-117.6	m		1	b
-158.0	p	$^{3}J_{F-F}$ 12.4	1	c
^{13}C				
21.5	s			g
22.1	s			h
25.4	s			i
25.7	d	$^{4}J_{C-F}$ 0.8		f
120.1	qdd	$^{1}J_{C-F}$ 269.9 $^{2}J_{C-F}$ 34.9 $^{3}J_{C-F}$ 8.7		d
125.7	dd	$^{2}J_{C-F}$ 21.3 $^{3}J_{C-F}$ 1.2		a
135.2	dqd	$^{1}J_{C-F}$ 254.4 $^{2}J_{C-F}$ 39.6 $^{2}J_{C-F}$ 26.1		c
137.5	m			e
153.2	ddq	$^{1}J_{C-F}$ 261.2 $^{2}J_{C-F}$ 12.7 $^{3}J_{C-F}$ 3.5		b

No. 26 1,2-Dibromo-2,2-dichloro-1-cyclopentyl-1-fluoroethane (**27**)



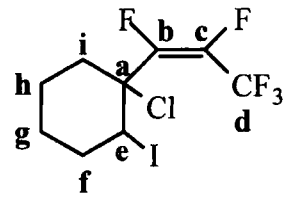
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.6-2.0	m		8	d-g
2.90	dm	$^{3}J_{H-F}$ 23.2	1	a
^{19}F				
-119.6	d	$^{3}J_{F-H}$ 25.9		b
^{13}C				
25.0	s			e
26.4	s			f
31.5	d	$^{3}J_{C-F}$ 3		d
32.2	d	$^{3}J_{C-F}$ 4.9		g
48.4	d	$^{2}J_{C-F}$ 19.1		a
85.7	d	$^{2}J_{C-F}$ 35		c
119.8	d	$^{1}J_{C-F}$ 267.9		b

No. 27 1,2,2,2-Tetrachloro-1-cyclopentyl-1-fluoroethane (**29**)



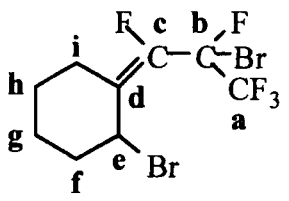
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.4-1.7	m		4	d-g_{ax}
1.7-2.0	m		4	d-g_{eq}
3.01	m		1	a
^{19}F				
-99.8	d	$^{3}J_{F-H}$ 5.6		b
^{13}C				
25.1	s			e
26.3	s			f
29.6	d	$^{3}J_{C-F}$ 3.4		d
30.5	d	$^{3}J_{C-F}$ 4.9		g
46.9	d	$^{2}J_{C-F}$ 20.6		a
101.8	d	$^{2}J_{C-F}$ 35		c
120.2	d	$^{1}J_{C-F}$ 259		b

No. 28 (1Z)-1-(1-Chloro-2-iodocylohexyl)-1,2,3,3,3-pentafluoroprop-1-ene (**30**)



Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.7	m		2	h
1.8	m		2	i
1.9	m		1	g
2.1	m		2	f
2.6	m		1	g
4.9	m		1	e
^{19}F				
-62.1	br s		3	d
-124.8	br s		1	b
-147.1	br s		1	c
^{13}C				
20.6	d	$^{3}J_{C-F}$ 2.3		h
21.1	s			i
29.9	m			g
31.4	s			f
34.6	m			e
69.3	d	$^{2}J_{C-F}$ 21.7		a
119.2	qdd	$^{1}J_{C-F}$ 271.5		d
		$^{2}J_{C-F}$ 35.2		
		$^{3}J_{C-F}$ 7.5		
138.5	dqd	$^{1}J_{C-F}$ 259.3		c
		$^{2}J_{C-F}$ 44		
		$^{2}J_{C-F}$ 27.4		
155.3	ddq	$^{1}J_{C-F}$ 263.9		b
		$^{2}J_{C-F}$ 18.6		
		$^{3}J_{C-F}$ 4		

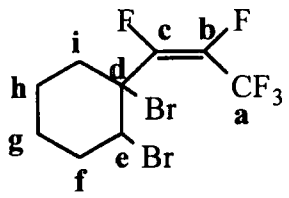
No. 29 2-Bromo-1-(2-bromocyclohexylidene)-1,2,3,3,3-pentafluoropropane (**32**)



Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{19}F				
-79.4	d	$^3J_{F-F}$ 10.8		a
-79.6	d	$^3J_{F-F}$ 10.8		a
-78.6	d	$^3J_{F-F}$ 9.1		a
-78.9	d	$^3J_{F-F}$ 10.1		a
-115.2	m			c
-117.1	m			c
-125.0	m			c
-127.5	dq	$^3J_{F-F}$ 24.4		b
		$^3J_{F-F}$ 9.7		
-128.7	dq	$^3J_{F-F}$ 25.8		b
		$^3J_{F-F}$ 10.3		
-129.7	dq	$^3J_{F-F}$ 25.4		b
		$^3J_{F-F}$ 10.3		
-129.9	dq	$^3J_{F-F}$ 27.3		b
		$^3J_{F-F}$ 9.9		

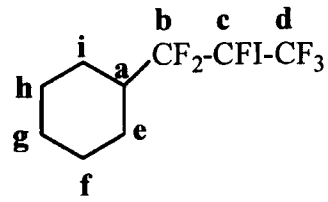
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{13}C				
94.2	ddq	$^{1}J_{C-F}$ 263.9		b
		$^{2}J_{C-F}$ 43.8		
		$^{2}J_{C-F}$ 38.6		
119.4	qd	$^{1}J_{C-F}$ 271.4		a
		$^{2}J_{C-F}$ 27.5		
118.9	qdd	$^{1}J_{C-F}$ 273.3		a
		$^{2}J_{C-F}$ 33.6		
		$^{3}J_{C-F}$ 3.8		
120.1	qdd	$^{1}J_{C-F}$ 283.5		a
		$^{2}J_{C-F}$ 29.4		
		$^{3}J_{C-F}$ 2.5		
120.3	qdd	$^{1}J_{C-F}$ 281.7		a
		$^{2}J_{C-F}$ 29.9		
		$^{3}J_{C-F}$ 2.5		
127.2	d	$^{2}J_{C-F}$ 13.5		d
127.3	d	$^{2}J_{C-F}$ 15.7		d
127.8	d	$^{2}J_{C-F}$ 14.9		d
127.9	d	$^{2}J_{C-F}$ 16.7		d
141.1	dd	$^{1}J_{C-F}$ 250.9		c
		$^{2}J_{C-F}$ 25.9		
141.2	dd	$^{1}J_{C-F}$ 250.5		c
		$^{2}J_{C-F}$ 26.4		
141.9	dd	$^{1}J_{C-F}$ 250.5		c
		$^{2}J_{C-F}$ 26.2		

No. 30 (1Z)-1-(1,2-Dibromocyclohexyl)-1,2,3,3,3-pentafluoroprop-1-ene (**33**)



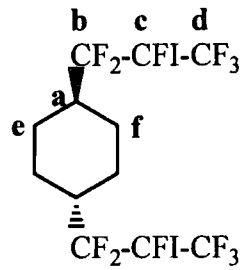
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{19}F				
-68.1	m		3	a
-147.6	m		1	c
-163.9	m		1	b
^{13}C				
64.8	dd	$^{2}J_{C-F}$ 20.5		d
		$^{3}J_{C-F}$ 5.2		
120.0	m			a
137.9	ddq	$^{1}J_{C-F}$ 254.8		b
		$^{2}J_{C-F}$ 50.9		
		$^{2}J_{C-F}$ 40.1		
153.6	dd	$^{1}J_{C-F}$ 254.5		c
		$^{2}J_{C-F}$ 33.6		

No. 31 1-Cyclohexyl-1,1,2,3,3,3-hexafluoro-2-iodopropane **(34)**



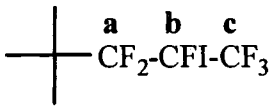
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.2-1.3	m		5	e-i_{ax}
1.7-2	m		5	e-i_{eq}
2.41	m		1	a
^{19}F				
-73.3	m		3	d
-107.4	A of AB	J_{AB} 267	2	b
-108.1	B of AB			
-140.1	sextet	$^{3}J_{F-F}$ 14	1	c
^{13}C				
25.1	t	$^{3}J_{C-F}$ 4.2		e
25.4	s			g
25.4	m			i
25.5	s			f
25.6	s			h
42.7	t	$^{2}J_{C-F}$ 22		a
81.3	d	$^{1}J_{C-F}$ 267		c
	sextet	$^{2}J_{C-F}$ 34		
118.9	ddd	$^{1}J_{C-F}$ 258.2		b
		$^{1}J_{C-F}$ 255		
		$^{2}J_{C-F}$ 24.4		
120.7	qdd	$^{1}J_{C-F}$ 285		d
		$^{2}J_{C-F}$ 28		
		$^{3}J_{C-F}$ 3		

No. 32 1,1,2,3,3,3-Hexafluoro-1-[4-(1,1,2,3,3,3-hexafluoro-2-iodopropyl)cylohexyl]-2-iodopropane **(35)**



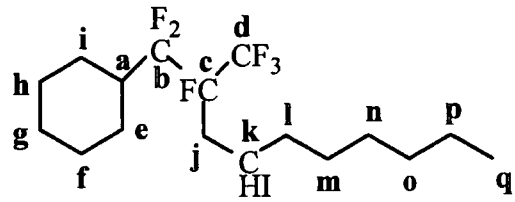
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.2-1.6	m		4	e,f_{ax}
2-2.3	m		4	e,f_{eq}
2.4	m		1	a
^{19}F				
-73.2	m		3	d
-107.4	A of AB	J_{AB} 263	2	b
-108.1	B of AB			
-140.6	m		1	c
^{13}C				
24.2	t	$^{3}J_{C-F}$ 4.2		e
24.4	t	$^{3}J_{C-F}$ 4.2		f
42.0	t	$^{2}J_{C-F}$ 22.5		a
82.7	m			c
118.8	ddd	$^{1}J_{C-F}$ 255.9		b
		$^{1}J_{C-F}$ 258.7		
		$^{2}J_{C-F}$ 24.7		
120.8	qdd	$^{1}J_{C-F}$ 287.6		d
		$^{2}J_{C-F}$ 28.2		
		$^{3}J_{C-F}$ 3.4		

No. 33 1,1,1,2,3,3-Hexafluoro-2-iodo-4,4-dimethylpentane (**36a**)



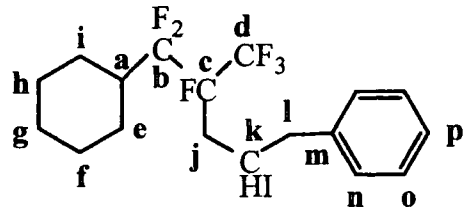
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{19}F				
-79.9	m		3	c
-106.5	A of AB	J_{AB} 262	2	a
-105.1	B of AB			
-139.5	m		1	b

No. 34 2-(Cyclohexyldifluoromethyl)-1,1,1,2-tetrafluoro-4-iododecane (**40**)



Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
0.92	t	$^{3}J_{H-H}$ 7.2	3	q
1.2-2	m		20	e-i, l-p
2.7	m		1	a
2.9	m		2	j
4.4	m		1	k
^{19}F				
-75.6	m		3	d minor
-75.9	m		3	d major
-112.5	A of AB	J_{AB} 260	2	b minor
-113.3	B of AB			
-113.9	A of AB	J_{AB} 259	2	b major
-114.7	B of AB			
-181.4			1	c minor
-181.5			1	c major
^{13}C				
14.4	s			q
25.3	m			e
25.7	m			g
25.9	m			f
26.1	m			i
26.1	m			h
26.6	s			k
26.8	s			k
22.9, 22.9, 28.5, 28.5, 30.1, 30.2, 31.7, 31.9, 40.8, 41.1, 41.5 and 41.6	12 distinct singlets			j, l-p
42.5	t	$^{2}J_{C-F}$ 22		a
42.6	t	$^{2}J_{C-F}$ 22.3		a
96	m			c
120.3	m			b
121.9	m			d

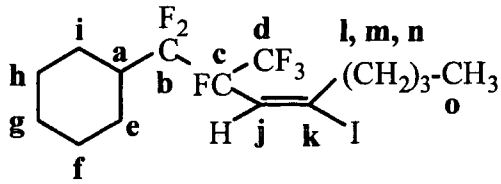
No. 35 [4-Cyclohexyldifluormethyl-4,5,5,5-tetrafluoro-2-iodopentyl]benzene (**39**)



Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1-1.3	m		5	e-i_{ax}
1.5-2	m		5	e-i_{eq}
2.6	m		1	a
2.9	m		2	j
4.5	m		1	k
7.2-7.4	m		5	n, o, p
^{19}F				
-75.6	m		3	d minor
-75.7	m		3	d major
-112.1	A of AB	J_{AB} 278.5	2	b minor
-112.9	B of AB			
-113.3	A of AB	J_{AB} 278.5	2	b major
-114.1	B of AB			
-180.3	m		1	c major
-181.0	m		1	c minor
^{13}C				
25.2, 25.2	2 m			e
25.7, 25.7	2 m			i
25.8	br s			g
25.9, 25.9	2 s			f
26.1, 26.2	2 s			h
40.5	2 d	$^{2}J_{C-F}$ 19.4		j

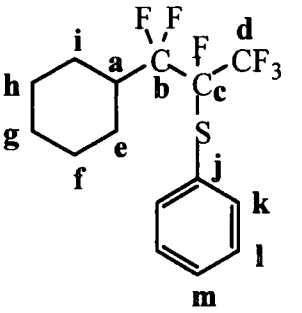
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
42.5	t	$^{2}J_{C-F}$ 21.8		a
42.6	t	$^{2}J_{C-F}$ 14.6		a
47.9	d	$^{4}J_{C-F}$ 2.4		l
48.1	d	$^{4}J_{C-F}$ 3.2		l
ca. 96	2 dm	$^{1}J_{C-F}$ 205		c
119.9	dd	$^{1}J_{C-F}$ 254.9		b
		$^{1}J_{C-F}$ 255.7		
120.4	dd	$^{1}J_{C-F}$ 254.9		b
		$^{1}J_{C-F}$ 255.3		
121.8	qdd	$^{1}J_{C-F}$ 286.8		d
		$^{2}J_{C-F}$ 28.9		
		$^{3}J_{C-F}$ 7.6		
122.3	qdd	$^{1}J_{C-F}$ 286.9		d
		$^{2}J_{C-F}$ 34.5		
		$^{3}J_{C-F}$ 5.8		
127.3	s			p
128.8 and 128.8	2 s			o
129.3 and 129.3	2 s			n
139.6	s			m

No. 36 (3*E*)-2-Cyclohexyldifluoromethyl-1,1,1,2-tetrafluoro-4-iodooct-3-ene (**41**)



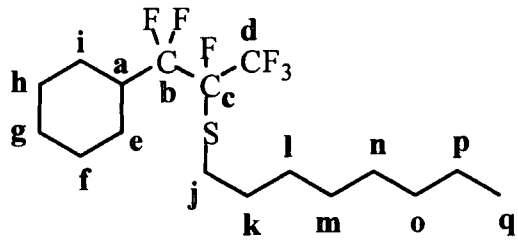
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
0.92	t	$^{3}J_{H-H}$ 7.6	1	o
1.1-2	m		16	e-i, l-n
2.63	m		1	a
6.21	d	$^{3}J_{H-F}$ 26	1	j
^{19}F				
-75.7	m		3	d
-110	m		2	b
-179.5	d	$^{3}J_{F-H}$ 26	1	c
^{13}C				
14.2	s			o
22.1	s			n
25.4	t	$^{3}J_{C-F}$ 4.6		e
25.4	t	$^{3}J_{C-F}$ 5		i
25.8	s			g
25.8	s			f
26.0	s			h
32.5	s			m
41.1	d	$^{4}J_{C-F}$ 9.6		l
42.5	t	$^{2}J_{C-F}$ 22.2		a
96.2	dq	$^{1}J_{C-F}$ 206.7		c
		$^{2}J_{C-F}$ 30.7		
117.9	s			k
119.9	ddd	$^{1}J_{C-F}$ 268.9		b
		$^{1}J_{C-F}$ 255		
		$^{2}J_{C-F}$ 25.6		
121.3	qd	$^{1}J_{C-F}$ 287.1		d
		$^{2}J_{C-F}$ 29.9		
126.3	d	$^{2}J_{C-F}$ 14.2		j

No. 37 1-(Cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoro-1-phenylthioethane **(42)**



Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.2-1.3	m		5	e-i_{ax}
1.7-2	m		5	e-i_{eq}
2.21	m		1	a
7.2-7.7	m		5	k-m
^{19}F				
-71.7	d	$^{3}J_{F-F}$ 14.7	3	d
	t	$^{4}J_{F-F}$ 10.2		
-111.6	A of AB	J_{AB} 269	2	b
-112.3	B of AB			
-152.9	qm	$^{3}J_{F-F}$ 10.5	1	c
^{13}C				
24.7	t	$^{3}J_{C-F}$ 4.2		e
25.4	s			f
25.5	s			g
25.6	t	$^{3}J_{C-F}$ 4.2		i
25.7	s			h
42.5	t	$^{2}J_{C-F}$ 22		a
101.8	dm	$^{1}J_{C-F}$ 245.9		c
120.3	ddd	$^{1}J_{C-F}$ 262.5		b
		$^{1}J_{C-F}$ 254.4		
		$^{2}J_{C-F}$ 24.3		
121.5	qd	$^{1}J_{C-F}$ 288		d
		$^{2}J_{C-F}$ 34.9		
125.0	s			m
129.0	s			k
130.5	s			l
137.3	s			j

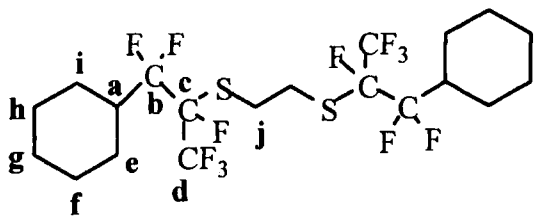
No. 38 1-(Cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoro-1-octylthioethane (**43**)



Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
0.81	t	$^{3}J_{H-H}$ 6.8	3	q
1.2-1.4	m		15	e-$i_{ax,}$ l-p
1.6	m		2	k
1.7-1.8	m		5	e-i_{eq}
2.2	m		1	a
2.9	m		2	j
^{19}F				
-72.8	d	$^{3}J_{F-F}$ 14.3	3	d
	t	$^{4}J_{F-F}$ 10.5		
-112.1	A of AB	J_{AB} 269.1	2	b
-112.8	B of AB			
-158.4	m		1	c
^{13}C				
14	s			q
22.6	s			p
24.7	t	$^{3}J_{C-F}$ 4.5		e
25.4	s			o
25.4	s			h
25.5	t	$^{3}J_{C-F}$ 4.5		i
25.5	s			f
25.7	s			g

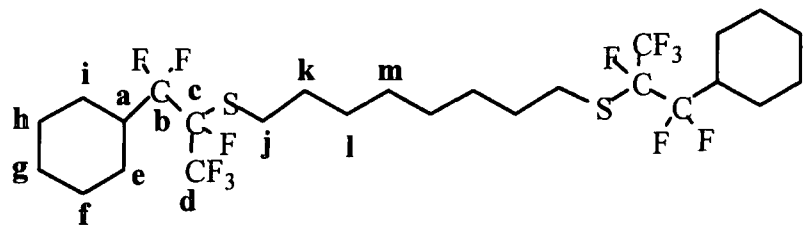
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
28.7, 28.8, 28.9, 29.1	singlets			k-n
31.7	s			j
42.4	t	$^{2}J_{C-F}$ 22.5		a
101.5	dm	$^{1}J_{C-F}$ 242.2		c
121.8	ddd	$^{1}J_{C-F}$ 262.4		b
		$^{1}J_{C-F}$ 254		
		$^{2}J_{C-F}$ 24		
122.3	qd	$^{1}J_{C-F}$ 287.5		d
		$^{2}J_{C-F}$ 35.2		

No. 39 1-(Cyclohexyldifluoromethyl)-1-{2—[1-(cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoroethylthio]ethylthio}-1,2,2,2-tetrafluoroethane **(44)**



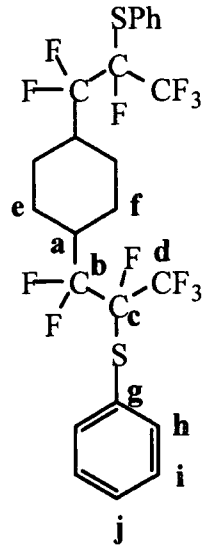
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.2-1.3	m		5	e-i_{ax}
1.6-2.1	m		5	e-i_{eq}
2.2	m		1	a
3.1	m		5	j
^{19}F				
-73.4	m		3	d
-111.4	A of AB	J_{AB} 270.2	2	b
-112.1	B of AB			
-158.5	qm	$^{3}J_{F-F}$ 10.1	1	c
^{13}C				
25.1	t	$^{3}J_{C-F}$ 3.9		e
25.6	s			h
25.6	t	$^{3}J_{C-F}$ 3.9		i
25.7	s			f
25.9	s			g
35.6	s			j
42.6	t	$^{2}J_{C-F}$ 21.7		a
101.4	dm	$^{1}J_{C-F}$ 245.3		c
120.5	ddd	$^{1}J_{C-F}$ 261.3		b
		$^{1}J_{C-F}$ 254.4		
		$^{2}J_{C-F}$ 24		
122.1	qd	$^{1}J_{C-F}$ 287.6		d
		$^{2}J_{C-F}$ 34.3		

No. 40 1-(Cyclohexyldifluoromethyl)-1-{8-[1-(cyclohexyldifluoromethyl)-1,2,2,2-tetrafloroethylthio}-1,2,2,2-tetrafluoroethane **(45)**



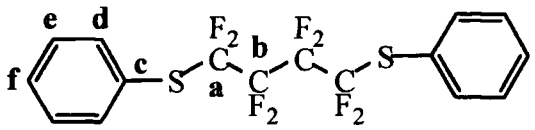
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1-1.4	m		18	e-i_{ax}, l, m
1.6-2	m		14	e-i_{eq}, k
2.2	m		2	a
2.8	m		4	j
^{19}F				
-72.8	m		3	d
-112.0	A of AB	J_{AB} 267.6	2	b
-112.7	B of AB			
-158.4	qm	$^{3}J_{F-F}$ 8.6	1	c
^{13}C				
24.7	t	$^{3}J_{C-F}$ 4.2		e
25.4	s			g
25.4	s			f
25.6	t	$^{3}J_{C-F}$ 4.2		i
25.7	s			h
28.5	s			m
28.8	s			l
28.9	s			k
39.0	s			j
42.4	t	$^{2}J_{C-F}$ 21.7		a
101.4	dm	$^{1}J_{C-F}$ 242.7		c
120.6	ddd	$^{1}J_{C-F}$ 262.1		b
		$^{1}J_{C-F}$ 253.7		
		$^{2}J_{C-F}$ 24		
122.3	qd	$^{1}J_{C-F}$ 287.6		d
		$^{2}J_{C-F}$ 35.2		

No. 41 1-{Difluoro[4-(1,1,2,3,3,3-hexafluoro-2-phenylthiopropyl)cyclohexyl]methyl}1,2,2,2-tetrafluoro-1-phenylthioethane (**46**)



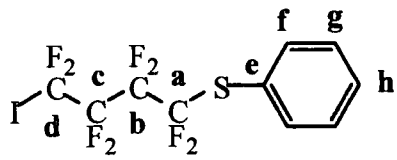
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.4-1.5	m		4	e, f_{ax}
2.15	m		2	a
2.2-2.3	m		4	e, f_{eq}
^{19}F				
-71.7	m		6	d
-111.7	A of AB	J_{AB} 270.2	4	b
-112.4	B of AB			
-153.0	m		2	c
^{13}C				
23.9	s			e
24.6	s			f
41.9	t	$^{2}J_{C-F}$ 22.4		a
101.8	m			c
121.8	ddd	$^{1}J_{C-F}$ 287.9		b
		$^{1}J_{C-F}$ 287.8		
		$^{2}J_{C-F}$ 34.6		
121.3	qd	$^{1}J_{C-F}$ 258.1		d
		$^{2}J_{C-F}$ 25.2		
124.9	s			j
129.0	s			h
131.0	s			i
137.8	s			g

No. 42 1,1,2,2,3,3,4,4-Octafluoro-1,4-diphenylthiobutane (**48**)



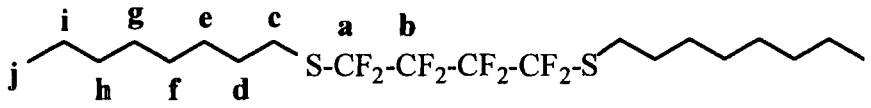
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
7.4-7.7	m			d-f
^{19}F				
-87.1	t	$^{3}J_{F\text{-}F}$ 9.0		a
-118.9	t	$^{3}J_{F\text{-}F}$ 10.1		b
^{13}C				
111.6	tt	$^{1}J_{C\text{-}F}$ 268.9 $^{2}J_{C\text{-}F}$ 32.9		b
123.3	tt	$^{1}J_{C\text{-}F}$ 288.4 $^{2}J_{C\text{-}F}$ 32.4		a
123.4	s			f
129.5	s			d
131.1	s			e
137.6	s			c

No. 43 1,1,2,2,3,3,4,4-Octafluoro-4-iodo-1-phenylthiobutane (**47**)



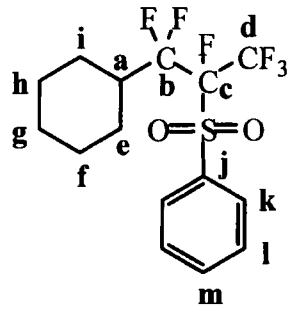
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
7.4-7.7	m			f-h
^{19}F				
-58.8	t	$^{3}J_{F\text{-}F}$ 14.5		d
-87.2	m			a
-112.7	m			i
-118.6	m			b
^{13}C				
94.5	tt	$^{1}J_{C\text{-}F}$ 321.5		d
		$^{2}J_{C\text{-}F}$ 42.2		
109.1	tt	$^{1}J_{C\text{-}F}$ 266.8		c
		$^{2}J_{C\text{-}F}$ 32.7		
110.4	tt	$^{1}J_{C\text{-}F}$ 268.7		b
		$^{2}J_{C\text{-}F}$ 33.6		
123.2	tt	$^{1}J_{C\text{-}F}$ 291.7		a
		$^{2}J_{C\text{-}F}$ 34.3		
123.1	s			h
129.6	s			f
131.2	s			g
137.6	s			e

No. 44 1,1,2,2,3,3,4,4-Octafluoro-1,4-dioctylbutane (**49**)



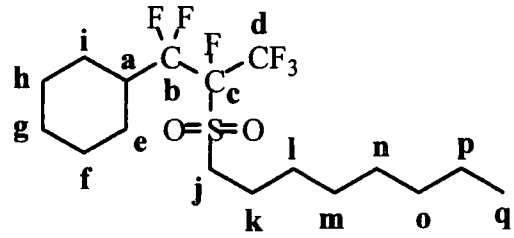
Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
0.92	t	$^{3}J_{H-H}$ 6.8	3	j
1.2-1.4	m		10	e-i
1.7	m		2	d
2.93	t	$^{3}J_{H-H}$ 7.4	2	c
^{19}F				
-87.8	t	$^{3}J_{F-F}$ 8.6	4	a
-119.6	t	$^{3}J_{F-F}$ 8.6	4	b
^{13}C				
14.3	s			j
22.8, 28.8, 28.8, 29.1, 29.3, 29.7	s			d-i
31.9	s			c
111.3	tt	$^{1}J_{C-F}$ 267.9		b
		$^{2}J_{C-F}$ 33.5		
125.1	tt	$^{1}J_{C-F}$ 290		a
		$^{2}J_{C-F}$ 33.7		

No. 45 1-(Cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoro-1-(phenylsulfonyl)ethane (**51**)



Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
1.2-1.3	m		5	e-i_{ax}
1.8-2.2	m		5	e-i_{eq}
2.41	m		1	a
7.6-8.0	m		5	k, l, m
^{19}F				
-69.5	m		3	d
-107.8	A of AB	J_{AB} 274.7	2	b
-108.6	B of AB			
-162.5	m		1	c
^{13}C				
25.0	m			e
25.6	br s			f, g
25.6	m			i
25.9	s			h
43.2	t	$^{2}J_{C-F}$ 21.2		a
100.7	dm	$^{1}J_{C-F}$ 248		c
119.8	ddd	$^{1}J_{C-F}$ 290.6		b
		$^{1}J_{C-F}$ 290.7		
		$^{2}J_{C-F}$ 26.1		
121.6	qd	$^{1}J_{C-F}$ 258.2		d
		$^{2}J_{C-F}$ 24.5		
123.7	s			m
129.4	s			k
131.2	s			l
135.9	s			j

No. 46 1-(Cyclohexyldifluoromethyl)-1,2,2,2-tetrafluoro-1-(octylsulfonyl)ethane (**52**)



Chemical shift (ppm)	Multiplicity	Coupling constant (Hz)	Relative intensity	Assignment
^{1}H				
0.91	t		3	q
1.2-1.3	m		15	e-i_{ax}, k-p
1.6-2	m		5	e-i_{eq}
2.4	m		1	a
3.2	m		2	j
^{19}F				
-69.9	m		3	d
-108.2	A of AB	J_{AB} 284.9	2	b
-108.9	B of AB			
-167.5	m		1	c
^{13}C				
14.4	s			q
20.8, 22.9	singlets			p, o
25.1	m			e
25.6	s			n
25.6	s			g
25.6	s			f
25.7	m			i
25.9	s			h
28.8, 29.1, 29.2	singlets			k, l, m
31.9	s			j
43.1	t	$^{2}J_{C-F}$ 22.5		a
101.7	dm	$^{1}J_{C-F}$ 238.8		c
119.9	qd	$^{1}J_{C-F}$ 288.3		d
		$^{2}J_{C-F}$ 29.9		
120.2	ddd	$^{1}J_{C-F}$ 262		b
		$^{1}J_{C-F}$ 257		
		$^{2}J_{C-F}$ 24.5		

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