Free radical syntheses of new organofluorine systems

Dunn, Stephen Norman

How to cite:

Dunn, Stephen Norman (1996) *Free radical syntheses of new organofluorine systems*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/5194/

UNIVERSITY OF DURHAM

Department of Chemistry

A thesis called

FREE RADICAL SYNTHESES OF NEW ORGANOFLUORINE SYSTEMS

by

Stephen Norman Dunn B.Sc.
(University of Northumbria at Newcastle)

A candidate for the degree of Doctor of Philosophy
1996

Acknowledgements

I would like to express many thanks to Professor R.D. Chambers and Dr. G. Sandford for their invaluable advice and encouragement throughout the course of this work.

For an amusing stay, I would like to thank the inmates of lab. CG115 i.e. Alan, Alex, Andrew, Anwar, Chris F., Chris H, Corinne, Julian, Keith, Matthew and Robert.

For services within the department I thank Dr. M. Jones, Dr. A. Kenwright, Dr. R. Matthews, Mrs. J. Say, Miss L.M. Turner, Mr. L. Lauchlan and Mr. D. Hunter. Also, I would like to express particular gratitude to Mr. T.F. Holmes whose presence is greatly missed.

Memorandum

The work described in this thesis was carried out at the University of Durham between October 1992 and December 1995. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

Copyright

Nomenclature

Throughout this thesis an ' F ' in the centre of a ring is used to denote that all unmarked bonds are to fluorine.

The following abreviations are also used.

HFP	Hexafluoropropene
DBP	Dibenzoyl peroxide
DTBP	Di-tert-butyl peroxide

Abstract

Free Radical Syntheses of New Organofluorine Systems

Use of the carbon hydrogen bond as a functional group in free radical addition reactions to fluoro - alkenes has been studied. Reactions involving additions of cyclic alcohols and cyclic as well as acyclic diols to hexafluoropropene, yielded selective hydroxyl group directed products in high yield.

The subsequent alcohol or diol - hexafluoropropyl adducts were easily dehydrated using thionyl chloride and pyridine, forming alkenes and dienes containing a polyfluoroalkyl moety, in good yield.

The resultant alkenes following bromination and epoxidation, were found to be electrophilic in nature. Furthermore, these alkenes were dehydrogenated using sulphur, yielding aromatic compounds containing the hexafluoropropyl moiety, in high yield.

Additions of hydrocarbons to hexafluoropropene gave complex final mixtures, illustrating the poor selectivity of such reactions.

Contents

Chapter 1 Introduction to free radical chemistry

Introduction

Alcohols and hydrocarbons

Results and Discussion

Chapter 2 The addition of cyclic / acyclic alcohols and diols to hexafluoropropene

Chapter 3 Fluoroalkene formation and subsequent reactions

Chapter 4 Reactions involving the use of a C-H bond in hydrocarbons as a functional group for insertion of fluoroalkenes

Experimental

Chapter 5 Experimental to chapter 2

Chapter 6 Experimental to chapter 3

Chapter 7 Experimental to chapter 4

Appendices and References

CHAPTER 1

INTRODUCTION TO FREE RADICAL CHEMISTRY

INTRODUCTION

1.1 History of free radical processes[1]

This thesis is based on the free radical additions of alcohols and hydrocarbons to fluoro alkenes and therefore begins with some general comments on free radical chemistry.

Radical processes occur in many fields of chemistry i.e. combustion, auto oxidation, pollution, biological and pathological chain reactions. The first radical based on triphenylmethyl was identified by Gomberg in 1900[1]. However, synthesis by radical pathways did not appear until 1937[1]. At this time, the homolytic phenylation of aromatic substrates and anti-Markovnikov free radical addition of hydrogen bromide to alkenes was discovered.

World War II was an important stimulus for the development of radical chemistry. Japanese occupation of South East Asia cut off supplies of latex to the United States. Consequently, chemists were called upon to find substitutes for natural rubber. Various workers[1] studied polymerisations of vinyl compounds and demonstrated polar character in reactions leading to electrophilic as well as nucleophilic radicals.

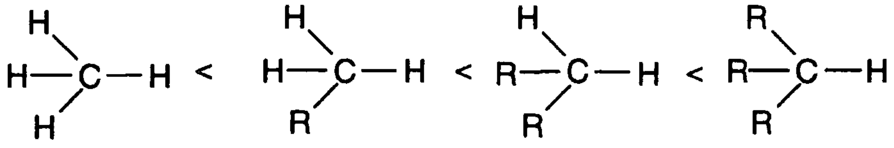
However, since 1970 there have been significant developments in synthetic methodology using free radical reactions.

GENERAL PRINCIPLES

2.1 Factors influencing the ease of hydrogen atom abstraction from a C-H bond

2.1.1. Effects of alkyl substitution on radical stability

Ease of attack on differently situated hydrogen atoms in an alkane is found to increase as follows :-

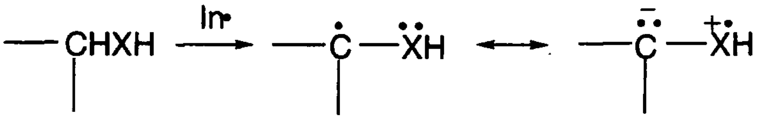


	1°	2°	3°
k_{rel}	1	4.4	6.7

This order reflects a weakening of C-H bond strength and increasing stability of product radicals. Figures quoted[2] reflect the relative rates of abstraction of hydrogen by chlorine radicals at 25°C.

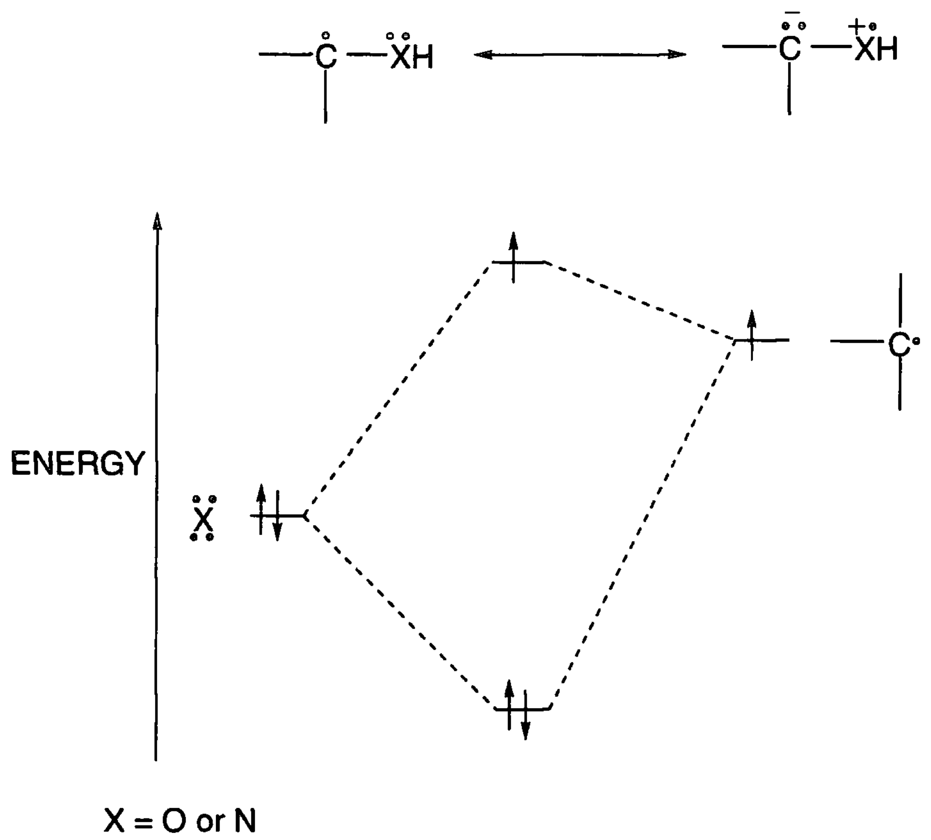
2.1.2. Effect of oxygen or nitrogen

An activating influence of oxygen or nitrogen[1] on the formation of a radical at attached C-H sites is shown below.



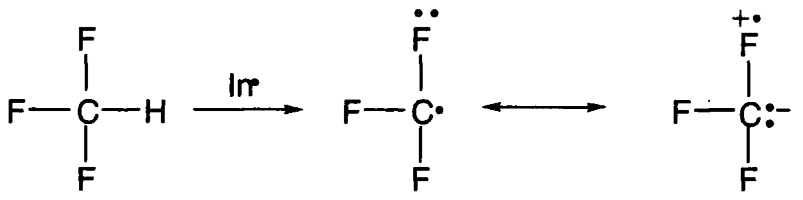
X = O or N
In• = initiator

The resulting radical is nucleophilic in nature and readily reacts with electron deficient (electrophilic in nature) alkenes. A molecular orbital explanation of such stabilisation is represented by scheme 1.



Scheme 1 :- Interaction of a radical SOMO and an oxygen or nitrogen lone pair[3]

2.1.3. Effect of halogen

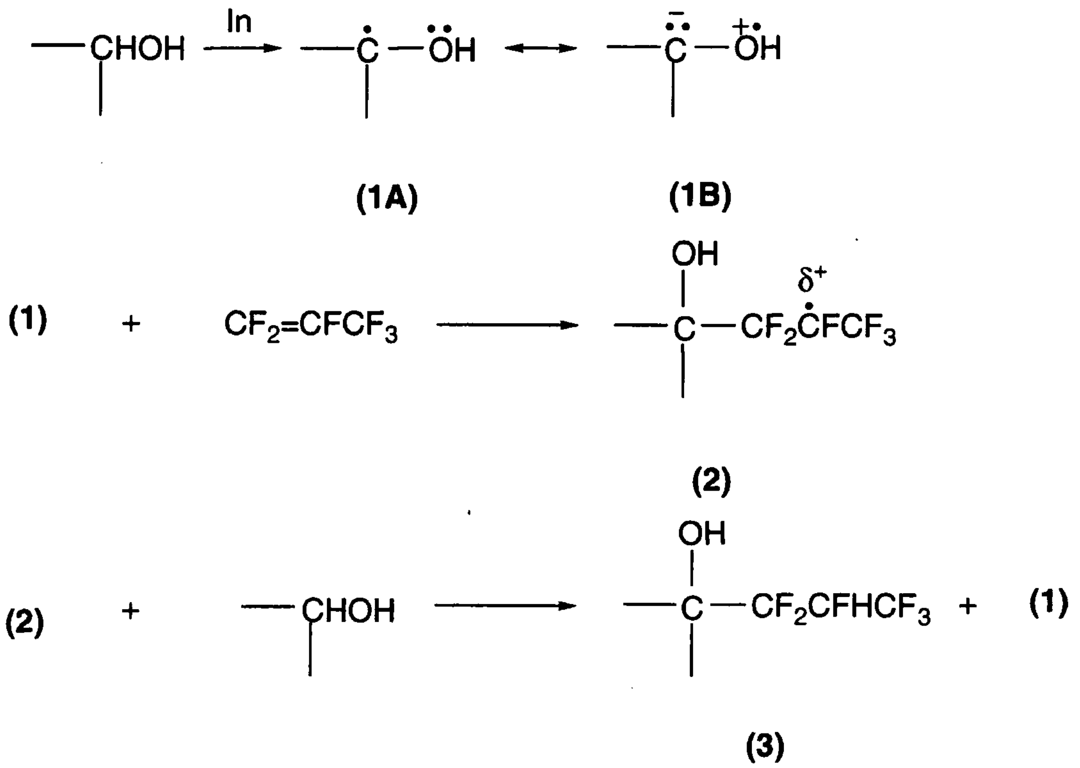


In = initiator

Halogens have two effects on a radical centre. Firstly, as illustrated above there is the possibility of resonance stabilisation. However, halogens withdraw electron density from an attached carbon centre making the radical more electronegative in nature.

2.2. Hydrogen abstraction reaction between an alcohol and hexafluoropropene[4, 5]

As well as being influenced by the above three factors, radical formation also depends on the nature of an attacking radical. For example, radical centres with attached electron withdrawing groups such as R_F, are electrophilic in nature and readily abstract a hydrogen atom from an electron rich C-H site.

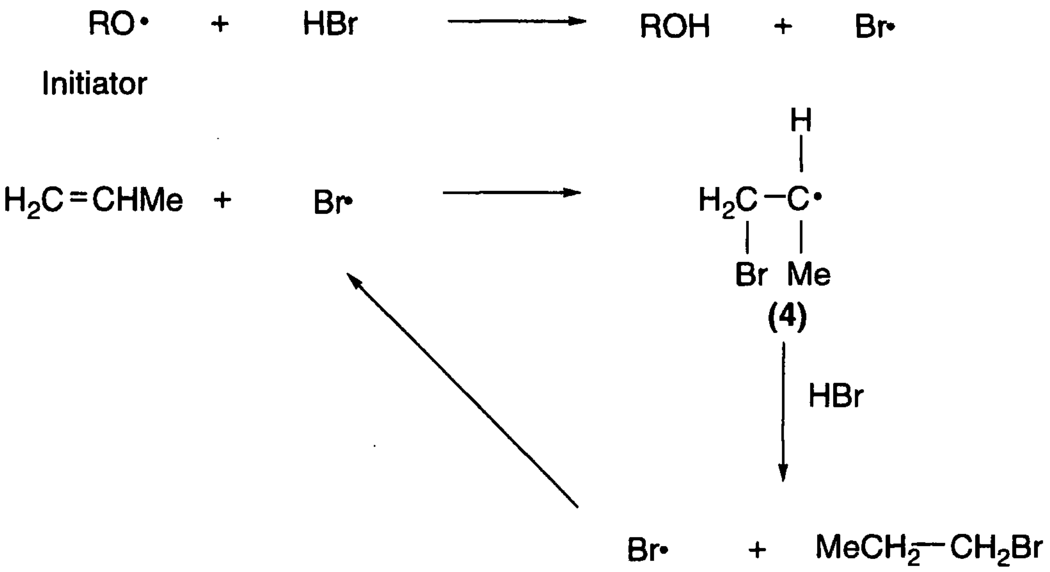


Scheme 2 :- Reaction of alcohols with hexafluoropropene

From scheme 2, electrophilic radical (2) abstracts a hydrogen atom from an electron rich alcohol, compared to attacking the electron deficient hexafluoropropene, which is an energetically unfavourable situation.

2.3. Factors influencing addition to alkenes

2.3.1. Radical stability[2]

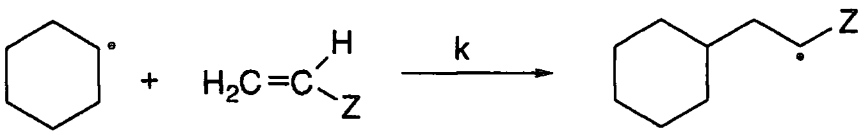


Scheme 3 :- Reactions of bromine radicals with propene[2]

Addition of an electrophilic bromine radical to an electron rich alkene e.g. propene is influenced by stability of the intermediate radical. Bromine radicals are added to the least substituted carbon site of propene, and consequently this reaction proceeds via a more stable secondary **(4)** than primary radical intermediate.

2.3.2. Polar effects[1, 6-8]

Alkenes and radicals can be nucleophilic or electrophilic in nature depending on the attached substituents. Electron donating groups enhance the electron density on a C=C double bond, and such an alkene is described as being nucleophilic in nature. Conversely, electron withdrawing groups lower electron density on a C=C double bond, and such an alkene is electrophilic. Furthermore, electron donating groups increase electron density at an attached carbon centre, and such radicals are nucleophilic in nature. Electron withdrawing groups reduce electron density at an attached carbon site, and such radicals are electrophilic. Nucleophilic radicals react easily with electrophilic alkenes. Conversely, electrophilic radicals favour addition to nucleophilic alkenes.

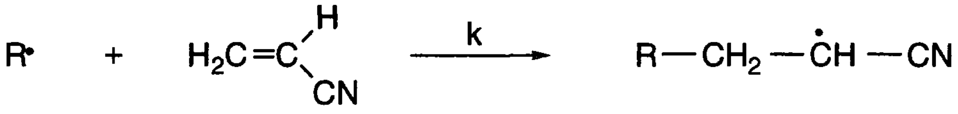


z	n-Bu	Ph	CO_2Me	CN	CHO
k_{rel}	1	84	3000	6000	8500

Table 1 :- Effects of substituents at C(alpha) on reactivity[1]

The above data[1] are explained in terms of polar effects. The nucleophilic cyclohexyl radical reacts faster with alkenes in which the C=C bond is more electron deficient (electrophilic in nature). Furthermore, stability of the radical formed is relatively unimportant compared to polar effects, since when Z = Ph, the reaction is about 100 times slower than with Z = CHO.

Examples of substituents attached to a radical centre effecting reactivity with an electron deficient alkene are shown below.



Radical R·	$R\cdot_{prim}$	$R\cdot_{sec}$	$R'-CH_2-\dot{C}H-CN$
k_{rel}	1	7.3	0.0015

Table 2 :- Effects of substituents attached to a radical centre on reactivity[1]

Clearly. the fastest rate of reaction occurs with a more nucleophilic secondary radical compared to an electrophilic secondary radical.

Table 3 shows the effect of changing a substituent attached to a C=C double bond to one that has the opposite electronic characteristics. This changes rates of addition by electrophilic or nucleophilic radicals.

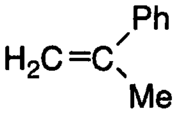
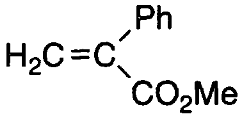
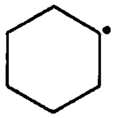
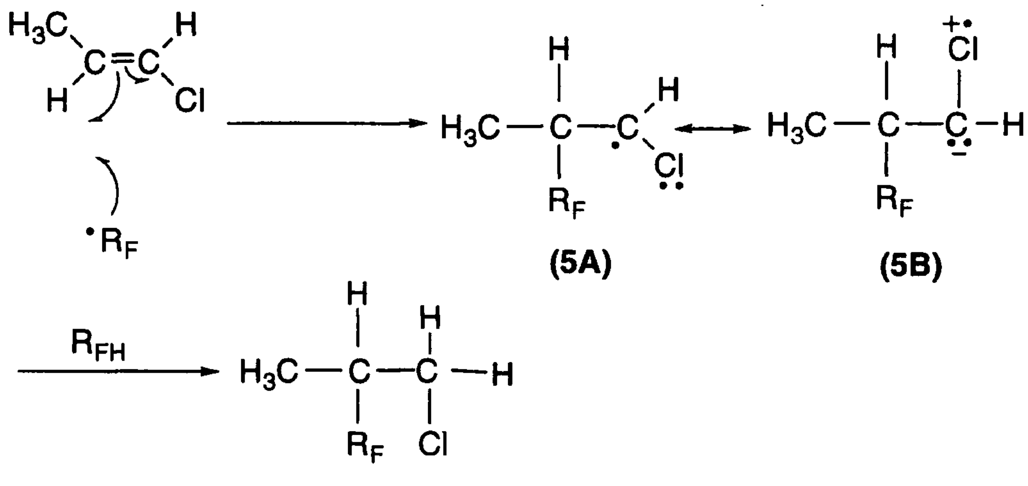
	 $H_2C{=}C(Ph)(Me)$	 $H_2C{=}C(Ph)(CO_2Me)$
$\cdot CH(CO_2Et)_2$	3.7	1
	1	42

Table 3 :- Reactions between radicals and alkenes with different electronic characteristics[1]

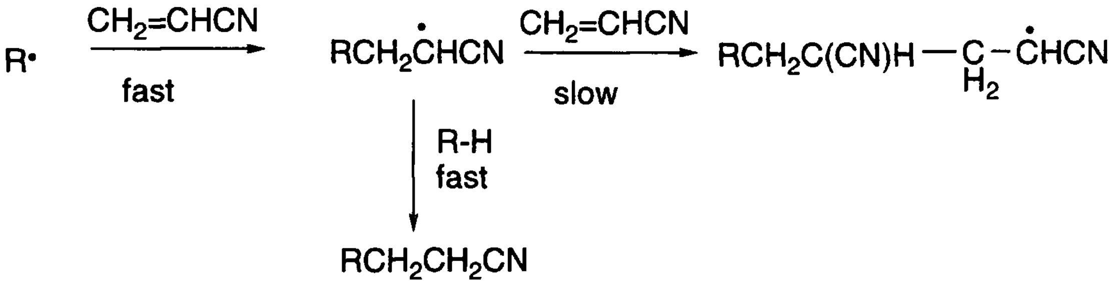
Additions to other alkenes are also influenced by polar effects. In scheme 4 below, an electrophilic radical is added to the most electron rich carbon in the C=C double bond, and the intermediate radical is stabilised (**5A** , **5B**) by resonance interaction with chlorine[1].



•R_F = perfluoroalkyl radical

Scheme 4 :- Addition of an electrophilic radical to 1-chloro-propene[1]

Polar effects strongly influence the outcome of radical addition reactions.



For example, the very favoured addition of a nucleophilic radical to acrylonitrile gives an electrophilic radical, which is unreactive towards acrylonitrile[1]. This means hydrogen transfer from the solvent is then preferred to polymerisation.

2.3.3. Steric effects[1, 8]

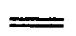
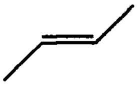
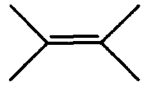
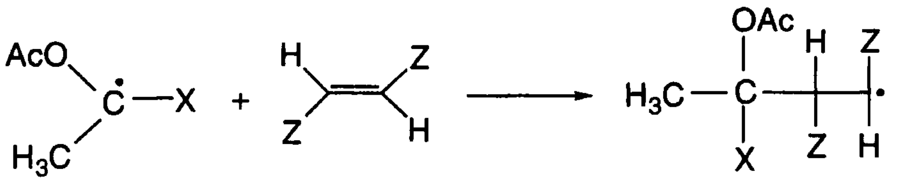
Alkene				
k_{rel}	1	0.7	0.33	0.20

Table 4 :- Additions of methyl radicals to various alkenes[1]

In the additions of methyl radicals to alkenes, polar effects are negligible. Clearly, steric effects of substituents attached to the alkene outweigh stability of intermediate radicals.

Additions to internal alkenes are influenced by steric factors to a greater extent than terminal alkenes. Thus a tertiary butyl substituent on an alkene reduces cyclohexyl radical addition by a factor of only 4 in terminal alkenes compared to 20000 with internal olefins[1].

Bulky substituents attached to a radical centre also influence reactivity.



(6) (7)

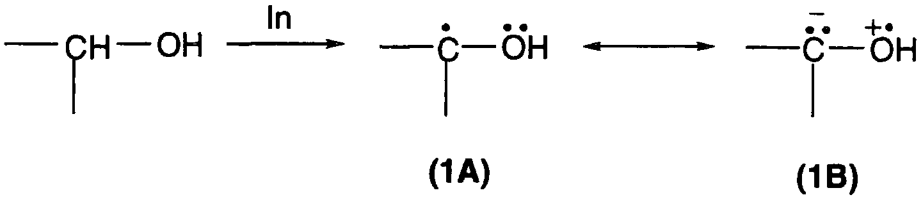
(6) X = t-Bu or Me

(7) Z = CO_2Et

For example, radical (6) reacts 260 times more slowly with compound (7) when X=t-Bu than X=Me. Here, steric effects of the attacking radical outweigh polar influences[1].

2.4. Characteristics of reactions of alcohols with hexafluoropropene

As mentioned earlier, alcohol radicals are nucleophilic in nature due to resonance stabilisation shown below.



In = initiator

Furthermore, fluoroalkenes are electrophilic in nature since electron withdrawal by fluorine lowers the electron density on the C=C double bond. Therefore, nucleophilic alcohol radicals readily react with electrophilic fluoroalkenes such as hexafluoropropene.

Hexafluoropropene is a non homo polymerisable fluoroalkene. In reactions with alcohols or hydrocarbons, rates of chain transfer are much greater than for chain growth, and therefore telomerisation is not observed. However, some fluoroalkenes such as tetrafluoroethene homopolymerise during free radical reactions. In such cases, rates of chain growth are much greater than for chain transfer, allowing telomerisation to compete effectively.

The forthcoming work covered in this thesis is based on additions of alcohols and hydrocarbons to non - homopolymerisable fluoroalkenes. Consequently, reactions of alcohols and hydrocarbons with homopolymerisable fluoroalkenes will not be discussed any further.

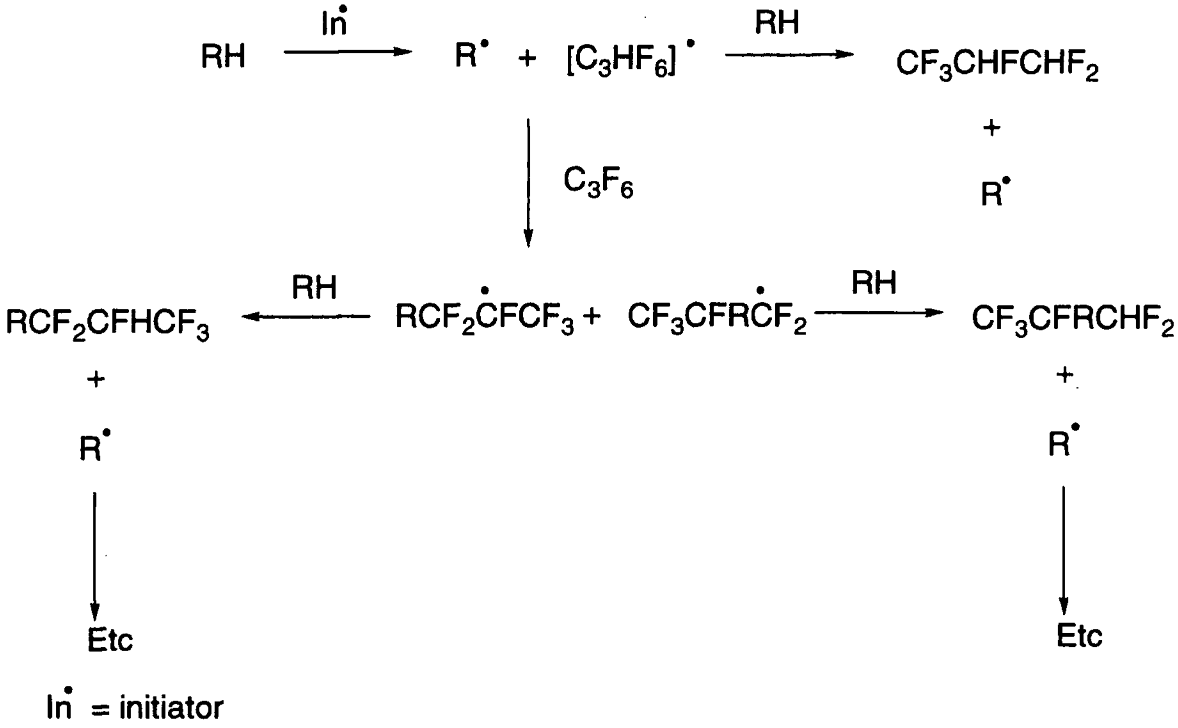
Alcohol radicals normally attack the difluoromethylene site of hexafluoropropene, since this is the most electron poor site and least sterically hindered[3]. Furthermore, the radical formed is more stable, being adjacent to fluorine, difluoromethylene and trifluoromethyl moieties. The fluorine atom attached to the carbon radical could provide a similar stabilisation to oxygen. Trifluoromethyl as well as difluoromethyl groups would be expected to stabilise radical canonical forms.

3.0. Previous work involving reactions of alcohols with fluoro-alkenes

3.1. Reactions of hexafluoropropene with:-

3.1.1. Acyclic alcohols

Reactions involving additions of alcohols to hexafluoropropene have been investigated[9-16] and a radical chain mechanism for R-H, initiated by excited fluoroalkenes was proposed[10, 17-22].



Scheme 5 :- Reactions of alcohols and hydrocarbons with hexafluoropropene[17, 18]

Examples of reactions involving the addition of alcohols to hexafluoropropene are shown in the table 5 below.

Table 5 :- Additions of alcohols to hexafluoropropene

Alcohol	**Cond^{n}**	**Rec hfp (%)**	**Product**	**Yie-lds (%)**	**Ref**
MeOH	110-120°C 3d[a] Pyrex ampoule	25 - 30	$CF_3CHFCF_2CH_2OH$ **(8)**	90	11
MeOH	280°C 4d Pyrex ampoule	2	**(8)** + $CHF_2CF(CF_3)CH_2OH$ **(9)**	**(8)** 85 **(9)** 4	10
MeOH	40°C 4d[c] Silica ampoule	10	**(8)** + **(9)**	**(8)** 95 **(9)** 2	10
MeOH	150°C 0.83d[a] Pyrex ampoule	0.2	**(8)** + **(9)**	**(8)** 93 + **(9)** 2	10
MeOH	140°C 1H[a] auto-clave	40	**(8)**	N/Y	9
MeOH	12H[c]		**(8)**	N/Y	13
MeOH	12H[c]		**(8)**	N/Y	13
MeOH	8H[a]		**(8)**	N/Y	15
CH_3CH_2OH	280°C 4d Pyrex ampoule	44	$CH_3CH(OH)CF_2CFHCF_3$ **(10)**	79	10

CH_3CH_2OH	40°C 4d^{c} Silica ampoule	45	**(10)**	92	10
CH_3CH_2OH	150°C 0.83d^{a} Pyrex ampoule	30	**(10)**	86	10
CH_3CH_2OH	17H^{c}		**(10)**	N/Y	14
$(CH_3)_2CHOH$	280°C 4d Pyrex ampoule	44	$(CH_3)_2C(OH)CF_2CFHCF_3$ **(11)**	86	10
$(CH_3)_2CHOH$	40°C 4d^{c} Silica ampoule	2	**(11)**	95	10
$(CH_3)_2CHOH$	150°C 0.83d^{a} Pyrex ampoule	2	**(11)**	89	10
$(CH_3)_2CHOH$	140°C 1H auto-clave	5	**(11)**	N/Y	9
$(CH_3)_2CHOH$	29H^{c}		**(11)**	N/Y	14
$(CH_3)_2CHOH$	6H^{a}		**(11)**	N/Y	15
$CH_3CH_2CH(OH)CH_3$	280°C 4d Pyrex ampoule	62	$CH_3CH_2C(OH)(CF_2CFHCF_3)$-$CH_3$	91	10
$CH_3CH_2CH(OH)CH_3$	40°C 3d^{c} Silica ampoule	1.5	$CH_3CH_2C(OH)(CF_2CFHCF_3)$-$CH_3$	97	10

$CH_3CH_2CH(OH)CH_3$	6H[c]		$CH_3CH_2C(OH)(CF_2CFHCF_3)$-$CH_3$	N/Y	15
$CH_3(CH_2)_2CH_2OH$	40°C 5d[c] Silica ampoule	53	$CH_3(CH_2)_2CH(OH)CF_2CFHCF_3$	94	10
$CH_3(CH_2)_3CHOH$	80°C[a]		$CH_3(CH_2)_3COHCF_2CFHCF_3$	N/Y	15
CF_3CH_2OH	320°C 0.7d Pyrex ampoule	43	$CF_3CH(OH)CF_2CFHCF_3$	95	10
$(CF_3)_2CHOH$	320°C 5d Pyrex ampoule	100	NO REACTION		10
(8)	385°C 1.5d Pyrex ampoule	98.5	NO REACTION		10

a) Peroxide initiated
b) γ rays initiated
c) UV initiated
N/Y = no percentage yield quoted

Table 5 shows that high yields of 1:1 adducts are found in all reactions except those involving $(CF_3)_2CHOH$ and compound **(8)**. Also photochemical and peroxide initiated reactions gave higher yields than thermal conditions.

Haszeldine[10] found in contrast to previous work[11], that methanol addition to hexafluoropropene also occurs by radical attack at the central carbon, under extreme conditions as well as the normal difluoromethylene site. Bi-directional alcohol addition to hexafluoropropene is not observed with other alcohols as a consequence of the greater steric bulk of the attacking radicals inhibiting addition at the central carbon of this fluoroalkene.

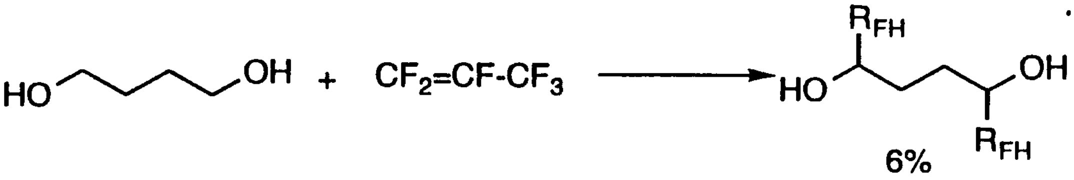
Radical $[CF_3CHOH]^{\cdot}$ is not as nucleophilic as those systems mentioned above. However, this radical is still sufficiently nucleophilic to react with hexafluoropropene giving the expected 1:1 adduct under extreme conditions. Alcohols $(CF_3)_2CHOH$ and compound **(8)** with more electron withdrawing substituents than CF_3CH_2OH, are deactivated towards addition to hexafluoropropene.

Lazerte[11] investigated effects of reaction conditions on conversions and yields. It was discovered that highest fluoroalkene conversions (70-75%) were achieved using a 3:1 or 5:1 excess of alcohol to hexafluoropropene.

The above examples are all additions of acyclic alcohols to hexafluoropropene. It has also been reported[11] that attempted additions of cyclohexanol to hexafluoropropene, initiated by benzoyl peroxide was unsuccessful. The forthcoming work in this thesis shows a significant development in additions of cyclic alcohols to hexafluoropropene.

3.1.2. Acyclic diol

In 1994 Paleta[23] reported the addition of 1,4-butanediol to hexafluoropropene giving a monoadduct and diadduct in low yield.

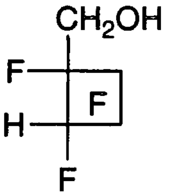
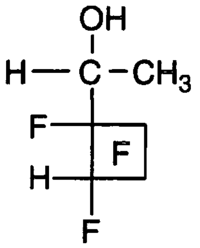
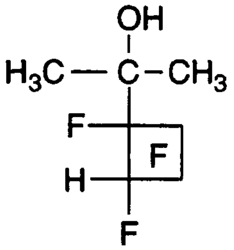
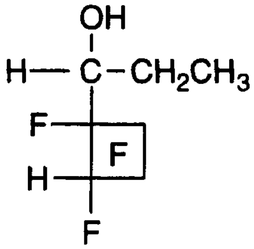
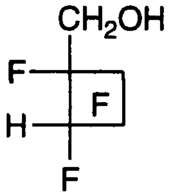
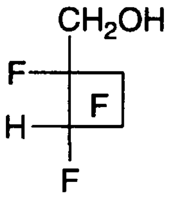
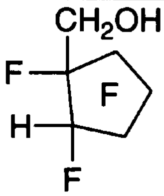


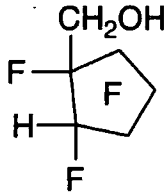
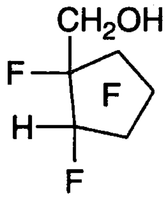
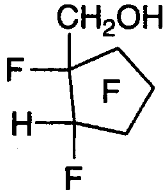
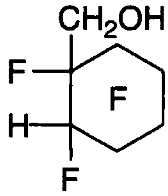
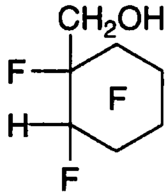
This represents the only addition of a diol to hexafluoropropene but with limited success. The forthcoming work in this thesis shows a significant development in addition of cyclic / acyclic diols to hexafluoropropene.

3.2. Additions of alcohols to cyclic perfluoroalkenes

Reactions involving additions of alcohols to perfluorocycloalkenes[11, 24-31] are shown in table 6.

Table 6 :- Reactions of alcohols with perfluorocycloalkenes

Alcohol	Cond^n	Fluoro-alkene	Product	Trans : cis ratio	Yield or conv^n	Ref
CH_3OH	25°C 2.7^a glass tube			B 70.6 A 14.1	84.7	29
C_2H_5OH	25°C 2.9^a glass tube			B 50.3 A 7.7	69.7	29
i-C_3H_7OH	25°C 2.9^a glass tube			B 50.3 A 7.7	67.0	29
n-C_3H_7OH	25°C 2.9^a glass tube				79.9	29
CH_3OH	25°C 3.0^a glass tube			8.7 : 1	85 conv^n	24
CH_3OH	85°C 24.5h auto- clave			5.0 : 1	57	24
CH_3OH	110°C 8H Pyrex tube			N/Q	80.1	31

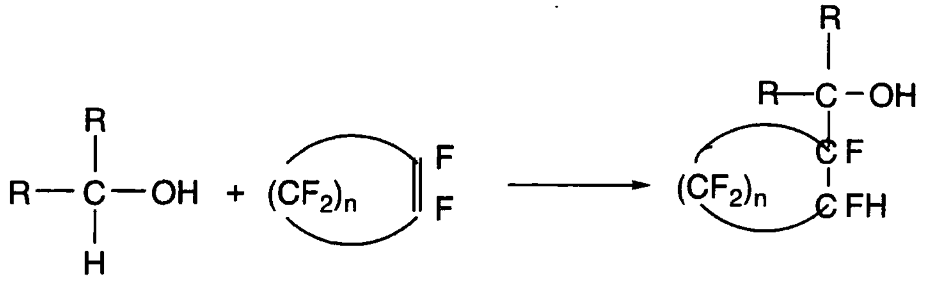
CH_3OH	110°C 8H Metal autoclave			N/Q	29.7	31
CH_3OH	25°C 3.0^a glass tube			1.0 :1	68 conv^n	24
CH_3OH	85°C 24.5H Metal autoclave			1.4 : 1	64 conv^n	24
CH_3OH	25°C 3.0^a glass tube			0.7 : 1	79 conv^n	24
CH_3OH	85°C 24.5H Metal autoclave			0.4 : 1	67 conv^n	24

a) γ rays x 10^7 rad

B Trans, A Cis Isomers

N/Q = not quoted

In 1955, Lazerte[11] reported that the free radical addition of methanol to perfluorocyclohexene occurred in low conversion, giving the normal 1:1 adduct and unexpected unsaturated products. However, later work[24-26, 29, 30] has shown that free radical additions of alcohols to perfluorocyclobutene, perfluorocyclopentene as well as perfluorocyclohexene occur easily under a variety of conditions giving the 1:1 adducts as mixtures of cis and trans stereo isomers (scheme 6).



R = alkyl n = 2,3,4 **(12)** cis + trans isomers

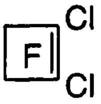
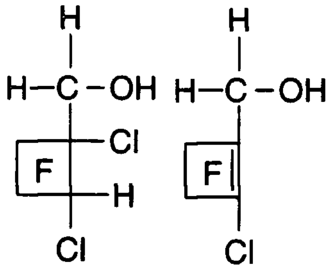
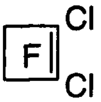
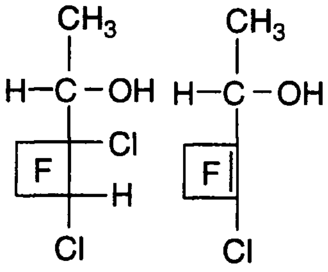
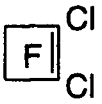
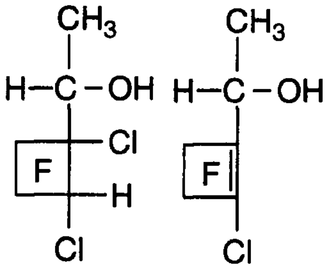
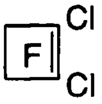
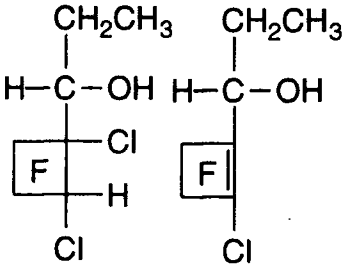
Scheme 6 :- Free radical additions of alcohols to perfluorocycloalkenes

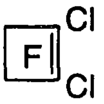
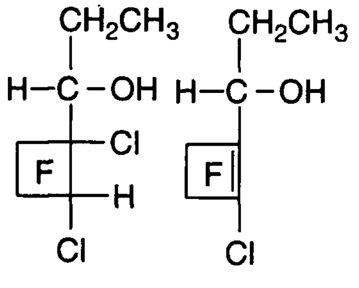
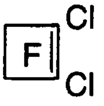
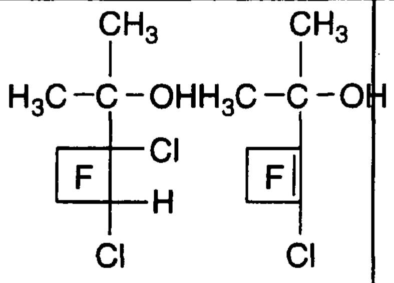
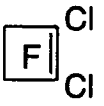
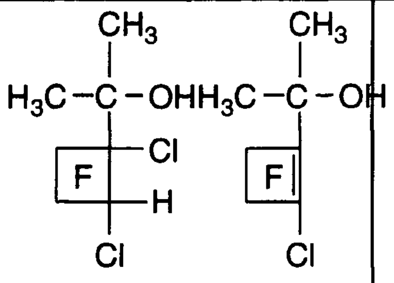
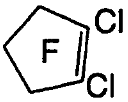
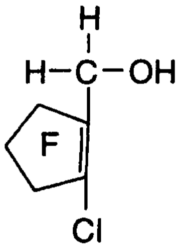
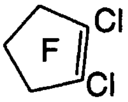
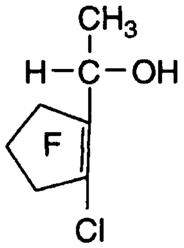
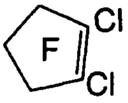
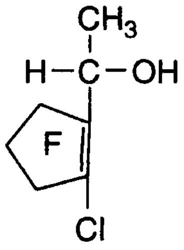
Furthermore, in such reactions telomerisation is not observed. Chambers et al[24] investigating the stereo chemistry of products **(12)**, discovered that with a given alcohol, from perfluorocyclobutene to perfluorocyclohexene there is an increase in proportions of cis isomers to trans.

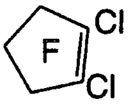
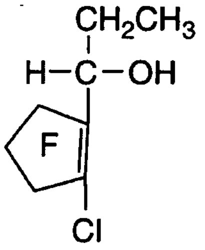
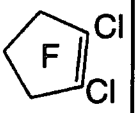
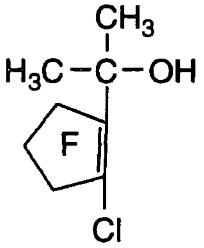
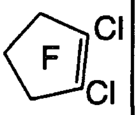
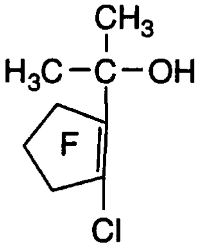
3.3. Additions of alcohols to cyclic chlorofluoroalkenes

Free radical reactions of alcohols with 1,2-dichlorotetrafluorocyclobutene and 1,2-dichlorohexafluorocyclopentene[32, 33] are shown in table 7.

Table 7 :- Reactions involving additions of alcohols to cyclic chlorofluoroalkenes

Alcohol	Cond^n	Fluoro Chloro Alkene	Product % composition	Trans : cis ratio of sat. prod^t	Yield of prod %	Ref .
CH_3OH	25°C 33^a glass tube		 57% 43%	51 : 49	21	33
CH_3CH_2OH	25°C 30^a glass tube		 74% 26%	33 : 67	61	33
CH_3CH_2OH	25°C 22^a glass tube		 75% 25%	36 : 64	71	33
n-C_3H_7OH	25°C 31^a glass tube		 54% 46%	32 : 68	19	33

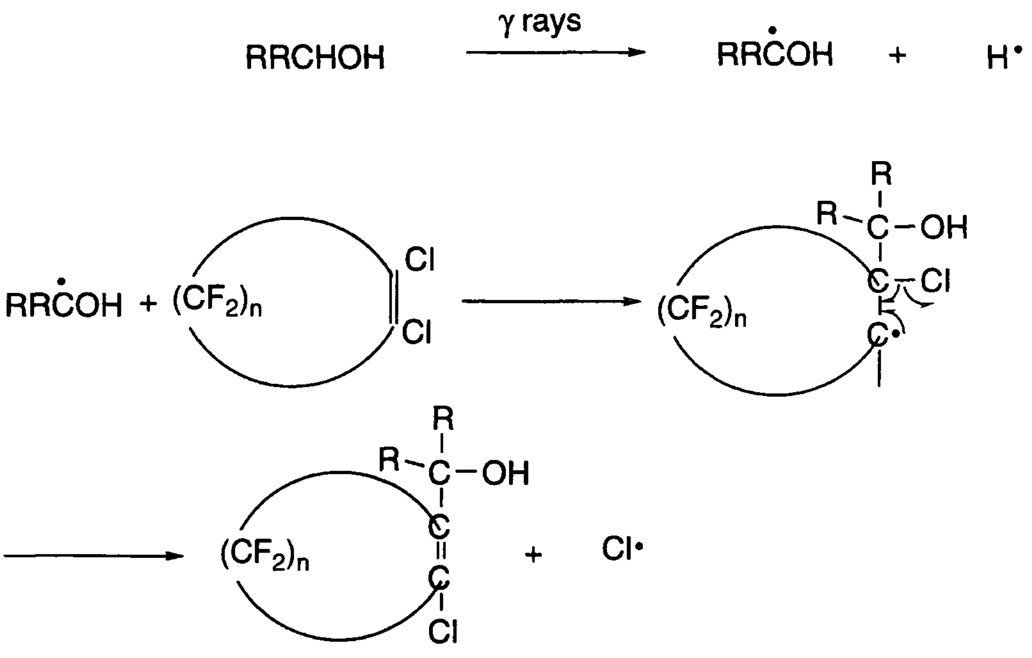
n-C_3H_7OH	25°C 29^a glass tube		 52% 48%	36 : 64	23	33
i-C_3H_7OH	25°C 22^a glass tube		 7% 93%	7 : 93	49	33
i-C_3H_7OH	25°C 38^a glass tube		 7% 93%	5 : 95	64	33
CH_3OH	620°C furn- ace				60	32
CH_3CH_2OH	25°C 3.1^a glass tube				46	33
CH_3CH_2OH	620°C furn- ace				N/Y	32

$CH_3(CH_2)_2$ OH	25°C 3.1[a] glass tube				28	33
i-C_3H_7OH	25°C 3.1[a] glass tube				81	33
i-C_3H_7OH	620°C furn- ace				N/Y	32

a) γ rays X 10^6 rad

N/Y = no yield quoted

From table 7, reactions of alcohols with 1,2-dichlorotetrafluorocyclobutene gave two main products. Formation of the dehydrochlorinated adducts (scheme 7) may have occurred by the following reaction competing with abstraction of a hydrogen atom from the alcohol giving the characteristic 1:1 adducts[33].



Scheme 7 :- Formation of dehydrochlorinated adducts from reactions of alcohols with 1,2-dichlorotetrafluorocyclobutene[33]

Differences in product ratios from methanol and ethanol is explained[33] by the latter forming a more nucleophilic radical favouring formation of 1:1 adducts compared to dehydrochlorinated products. However, a sterically hindered attacking radical as associated with isobutanol favours formation of dehydrochlorinated product compared to the normal 1:1 adducts.

As shown in table 7, alcohols reacting with 1,2-dichlorohexafluorocyclopentene give almost exclusively dehydrochlorinated 1:1 products.

3.4. Additions of alcohols to other non-homopolymerisable alkenes

Reactions of alcohol free radicals with 1,2,2-trichloro-1-fluoroethene[34] and 1,2-dichlorodifluoroethene[34-36] giving non homopolymerisable products are shown in table 8.

Table 8 :- Free radical additions of alcohols to non homopolymerisable halogenalkenes

Alcohol	Halogeno-alkene	Cond^{n}	Product	Yield (%)	Conv^{nb} (%)	Ref
MeOH	$Cl_2C=CFCl$	25°C^{c} 353 H	$HOCH_2CFClCHCl_2$	13	N/Q	34
CH_3CH_2OH	$Cl_2C=CFCl$	25°C^{c} 353 H	$HOC(CH_3)CFClCHCl_2$	67	N/Q	34
$CH_3(CH_2)_2OH$	$Cl_2C=CFCl$	25°C^{c} 353 H	$HOC(CH_3CH_2)CFClCHCl_2$	42	N/Q	34
$(CH_3)_2CHOH$	$Cl_2C=CFCl$	25°C^{c} 353 H	$HOC(CH_3)_2CFClCHCl_2$	60	N/Q	34
CH_3OH	$ClFC=CFCl$	25°C^{c} 353 H	$HOCH_2CFClCHFCl$	16	N/Q	34
CH_3OH	$ClFC=CFCl$	150°C^{a} 5H autoclave	$HOCH_2CFClCHFCl$	N/Q	10	35, 36
CH_3CH_2OH	$ClFC=CFCl$	25°C^{c} 353 H	$HOCH(CH_3)CFClCHFCl$	40	N/Q	34
CH_3CH_2OH	$ClFC=CFCl$	150°C^{a} 5H autoclave	$HOCH(CH_3)CFClCHFCl$	N/Q	15	35, 36
$CH_3(CH_2)_2OH$	$ClFC=CFCl$	25°C^{c} 353 H	$HOCH(CH_3CH_2)CFClCHFCl$	43	N/Q	34
$CH_3(CH_2)_2OH$	$ClFC=CFCl$	150°C^{a} 5H autoclave	$HOCH(CH_3CH_2)CFClCHFCl$	N/Q	17	35, 36

$(CH_3)_2CHOH$	ClFC=CFCl	25°C[c] 353 H	$HOC(CH_3)_2CFClCHFCl$	86	N/Q	34
$(CH_3)_2CHOH$	ClFC=CFCl	150°C[a] 5H auto-clave	$HOC(CH_3)_2CFClCHFCl$	N/Q	30	35, 36

a) Reactions with Peroximon DB
Molar ratio reactant : alkene = 9:1
Molar ratio alkene : peroxide = 2:1
b) Based on alkene
c) γ ray dosage 2.9×10^7 r.
N/Q = not quoted

In terms of orientation of addition to perhalogeno alkenes , an alcohol radical attacks the end of a C=C double bond that has the fewer chlorine substituents, and this may be explained by steric factors.

Order of reactivity is influenced by combination of the nucleophilicity of an attacking alcohol radical and the steric hindrance from chlorine substitution in the perhalogeno alkenes. Reactivity order for additions of alcohols to 1,2-dichlorodifluoroethene is as shown below , and these reactions appear to depend on the nucleophilicity of attacking radicals.

$(CH_3)_2CHOH > CH_3(CH_2)_2OH, CH_3CH_2OH > CH_3OH$

However, in additions of alcohols to 1,2,2-trichloro-1-fluoroethene, yields with ethanol are higher than isopropanol or propan-1-ol[34]. In this case decrease in reactivity of isopropanol is due to steric interference of bulky chlorine atoms attached to the perhalogeno alkenes. The 1:1 adducts were thought to be formed by the addition of alpha-hydroxy-alkyl radicals to the halogenoalkenes by the mechanism of Urry[16] and co-workers.

4.0. Previous work involving reactions of hydrocarbons with hexafluoropropene

Insertion of hexafluoropropene into the C-H bonds of halogenoalkanes[21], alkanes[17-20] and alkyl benzenes[22] has been investigated, and a radical chain mechanism has been proposed[10, 17-22] (see scheme 5 earlier).

Recent developments in the functionalisation of hydrocarbons by the addition of radicals to hexafluoropropene are as follows.

4.1. Reactions of hexafluoropropene with:-

4.1.1. Halogenalkanes[21]

Haszeldine et al[21] have investigated the thermal and / or photochemical reactions of hexafluoropropene with various fluoro-, chloro as well as chlorofluoro alkanes and some results are shown in table 9.

Table 9 :- Reactions of fluoro, chloro and chlorofluoroalkanes with hexafluoropropene

Alkane	Temp (°C)	Time (days)	C_3F_6 recovery (%)	1:1 adducts (%)	Ref.
MeCl	280	4	65	$CH_2ClCF_2CHFCF_3$ (75) $CH_2ClCF(CF_3)CHF_2$ (8)	21
CH_2Cl_2	280	4	14	$CHCl_2CF_2CHFCF_3$ (85) $CHCl_2CF(CF_3)CHF_2$ (12)	21
$CHCl_3$	280	4	87	$CCl_3CF_2CHFCF_3$ (80) $CCl_3CF(CF_3)CHF_2$ (trace)	21
MeF	280	4	69	$CH_2FCF_2CHFCF_3$ (76)	21
CH_2F_2	280	4	91	CHF_2CHFCF_3 (85)	21
CHF_2Cl	275	3	15	$CF_2ClCF_2CHFCF_3$ (52) $CF_2ClCF(CF_3)CHF_2$ (2)	21
EtF	295	4	58	$CH_3CHFCF_2CHFCF_3$ (96)	21
$MeCHF_2$	290	4	97	$CH_3CF_2CF_2CHFCF_3$ (65)	21
$MeCF_3$	310	6	84	$CF_3CH_2CF_2CHFCF_3$ (71)	21

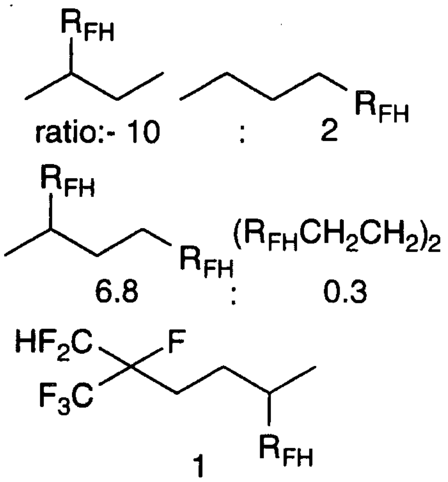
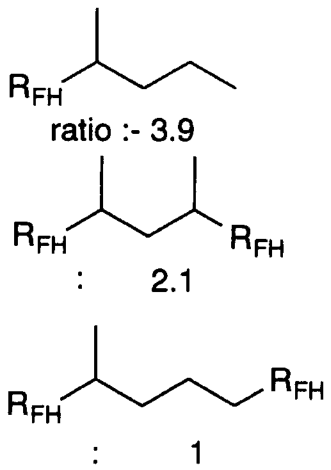
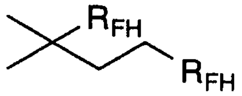
As can be seen from table 9, reasonable yields were achieved with halogenomethanes as well as fluoroethanes, but with $MeCHF_2$ insertion apparently only involved the fluorinated site. However, conversions in most cases were very low.

4.1.2. Aliphatic hydrocarbons

A summary of the reactions involving free radical addition of aliphatic hydrocarbons[17, 18, 37, 38] to hexafluoropropene under various conditions is shown in table 10. All reactions were carried out on a small scale and involved low conversions of reactants.

Table 10 :- Free radical addition of aliphatic hydrocarbons to hexafluoropropene
$R_{FH} = CF_2CFHCF_3$

Hydrocarbon	Conditions	Recov. HFP (%)	Products, Yields, (%) or N/R -not recorded)	Ref
CH_4	D.T.B.P. 140°C		No reaction	37
CH_3CH_3	300°C / 4d Pyrex ampoule	46	CH_3CH_2-R_{FH} , N/R	18
$CH_3CH_2CH_3$	γ rays / r.t. Pyrex Tube		$CH_3CH(R_{FH})CH_3$ (21) $CH_3CH_2CH_2$-R_{FH}	37
$CH_3CH_2CH_3$	295°C / 4d Pyrex Ampoule	32	$(CH_3)_2CH$-R_{FH} , N/R	18
$CH_3CH_2CH_3$	UV, 40-60°C 24h silica ampoule	80	$(CH_3)_2C$-R_{FH}, N/R	17
$(CH_3)_3CH$	γ rays r.t. Pyrex tube		$(CH_3)_3C$-R_{FH} (42)	37
$(CH_3)_3CH$	UV, 40-60°C 24h silicon ampoule	71	$(CH_3)_3C$-R_{FH}, N/R	17
$(CH_3)_3CH$	295°C / 4d	30	$(CH_3)_3C$-R_{FH}, N/R	18
n-C_4H_{10}	γ rays r.t. Pyrex tube		$CH_3CH(R_{FH})CH_2CH_3$ (6) $CH_3CH(R_{FH})(CH_2)_2R_{FH}$ (11)	37

n-C_4H_{10}	295°C / 5d tube		 + at least eleven other products + charred residue	38
n-C_4H_{10}	UV, 40-60°C 24h silicon ampoule	85	products as above except ratio is :- 39 : 7 : 11 : 0 : 3 : 1 + others	38
n-C_4H_{10}	D.T.B.P. (2 mol%), 130°C 70h pyrex tube	60	products as above except ratio is :- 18 : 1 : 40 : 0 : 6 : 3	38
n-C_5H_{12}	300°C / 5d autoclave	22	 + tarry residue and other products	38
$(CH_3)_2CHCH_2$ CH_3	γ rays r.t. Pyrex tube		$(CH_3)_2C(R_{FH})CH_2CH_3$ $(CH_3)_2CHCH(R_{FH})CH_3$ $(CH_3)_2CHCH_2CH_2R_{FH}$ ratio 8.8 : 3 : 1 (5.2%)  14%	37

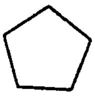
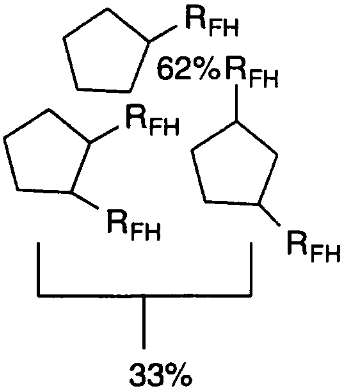
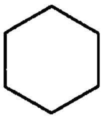
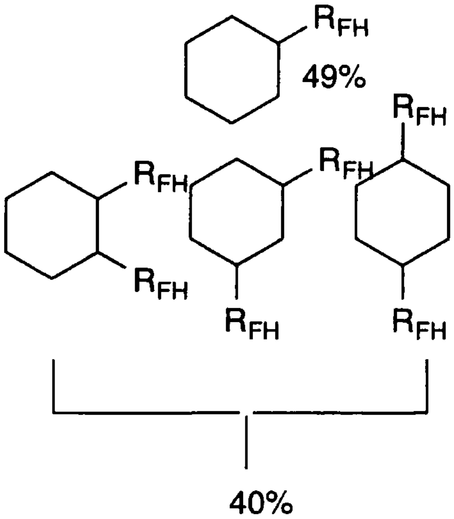
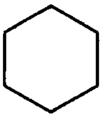
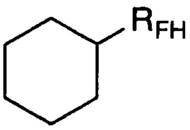
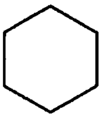
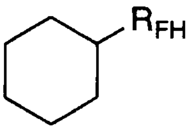
n-C_6H_{14}	D.T.B.P. 140°C		 $(R_{FH})_n$ = 1-3 n = 1, 1.1% n = 2, 7.7% n = 3, 5.2%	37

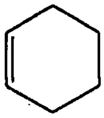
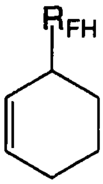
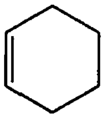
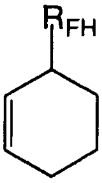
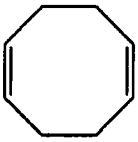
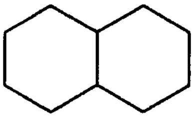
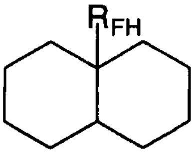
As can be seen from table 10, reactions with ethane and isobutane exclusively afforded mono-addition products, but polysubstitution occurred in systems that contained four or more carbons in a straight chain. Furthermore, major products from these reactions are formed by addition at the most stable C-H site of a hydrocarbon.

4.1.3. Cyclic hydrocarbons

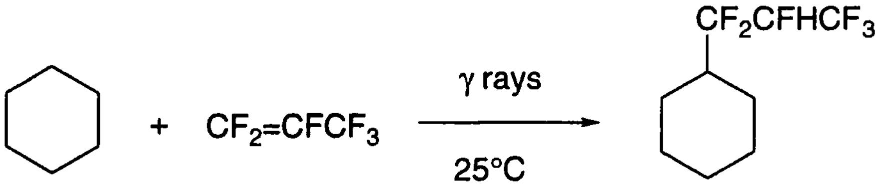
Saturated and unsaturated cyclic hydrocarbons[17, 18, 37, 39] react with hexafluoropropene under a variety of conditions to yield cyclic hydrocarbon-hexafluoropropene adducts. A summary of such reactions is shown in table 11.

Table 11 :- Reactions of various cyclic hydrocarbons with hexafluoropropene
$R_{FH} = CF_2CFHCF_3$

Hydrocarbon	Conditions	Rec. HFP (%)	Yield(%), N/Y = no yield recorded	Ref.
	310°C 4d autoclave	87	 N/Y	18
	γ rays r.t. Pyrex tube	100	No Reaction	37
	γ rays r.t. Pyrex tube			37
	D.T.B.P. 140°C 24H autoclave			37
	280°C 3d autoclave	40	 N/Y	18
	UV 40-60°C silica ampoule	40	 N/Y	17

	D.T.B.P. 140°C autoclave		 < 3%	37
	320°C 4d	4	 N/Y	17
	γ rays D.T.B.P.		No Reaction	37
	γ rays D.T.B.P.		 N/Y	37

Podkhalyuzin et al[39], in kinetic studies, reacted a 3 : 2 excess of cyclohexane with hexafluoropropene under gamma rays producing (1,1,2,3,3,3-hexafluoropropyl)-cyclohexane (**13**) in reasonable yield.



(13) 60%

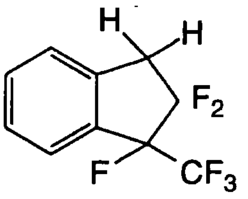
The alkylation reaction was only partly inhibited by water but completely inhibited by iodine and benzene.

4.1.4. Alkylbenzenes[19, 22]

Haszeldine et al[19, 22] have reported results on the thermal reaction of a series of alkylbenzenes with hexafluoropropene in the absence of added initiator. Considering toluene, the range of products formed by carrying out reactions in either metal tubes or autoclaves are as follows :-

$PhCH_2CF_2CFHCF_3$

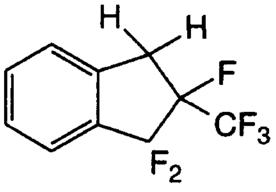
(14)



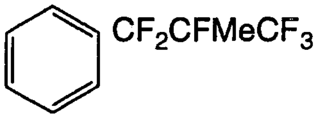
(15)

$PhCH_2CF(CF_3)CHF_2$

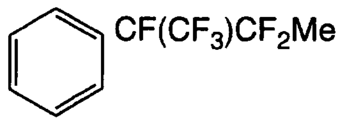
(16)



(17)

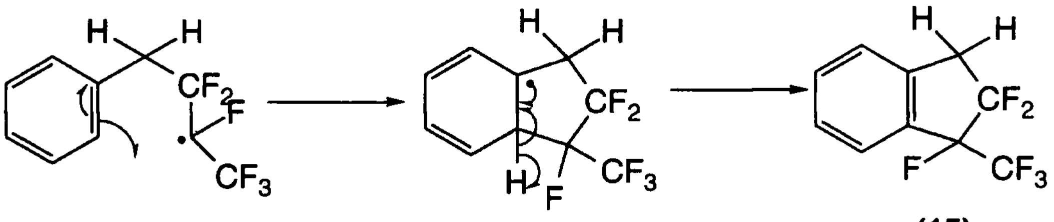


(18)



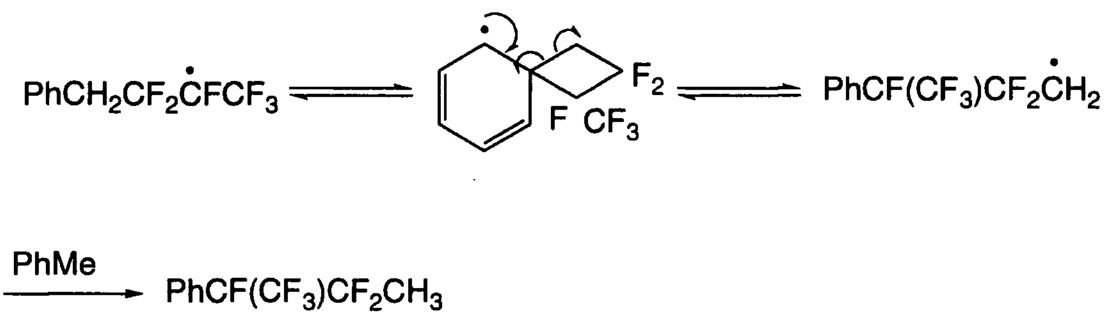
(19)

Toluene adducts **(14)** as well as **(16)** and the indanes **(15)** / **(17)** arise by bi-directional addition to hexafluoropropene. Indane formation is likely to occur as follows:-



(15)

The other adducts **(18)** and **(19)** have probably arisen from rearrangement of intermediate radicals.

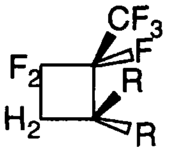


(19)

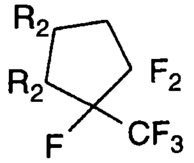
The thermal reaction of diphenylmethane[22] with hexafluoropropene gives $Ph_2CHCF_2CFHCF_3$ and a major adduct $PhCH_2CF_2CFPhCF_3$ due to rearrangement. As mentioned previously a radical from toluene undergoes bi-directional addition to hexafluoropropene. However, the more bulky $(Ph)_2CH\cdot$ radical exclusively attacks the difluoromethylene site of hexafluoropropene on steric grounds.

4.1.5. Alkenes

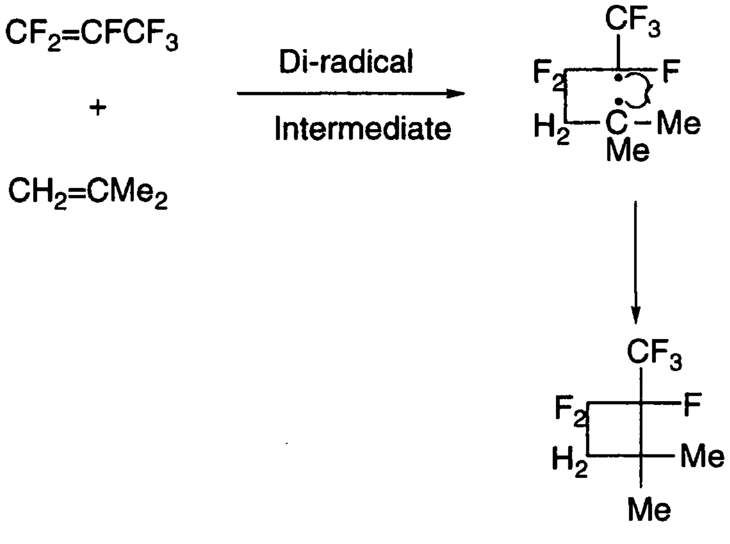
In 1966[40], after confused earlier reports[41, 42], the structures of thermal cyclodimers of hexafluoropropene were established. Since then several cyclodimerisation reactions between hexafluoropropene and hydrocarbon alkenes e.g. $CH_2{=}CH_2$[43], $CH_2{=}CHMe$[44] and $CH_2{=}CMe_2$[45] have been investigated; and it was observed that the rates of cyclodimer formation were slower than from tetrafluoroethene under similar conditions. However, in 1982 Haszeldine et al[20] showed that thermal reactions of hydrocarbon alkenes with hexafluoropropene gave rise to three different types of product.



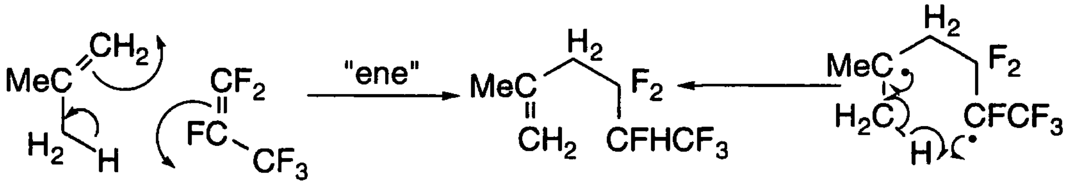
$R^1R^2C{=}CR^3CH_2CFHCF_2CF_3$



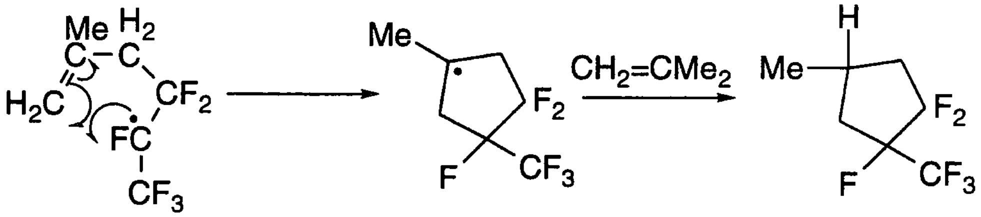
Under thermal conditions, cis and trans 1,2-disubstituted cyclobutanes have been reported to form in a 1:1 ratio. This is explained[20] on the basis of free rotation of diradical intermediates giving equal probability for closure to cis and trans structures. The mechanism below is suggested[20] to explain cyclobutane formation.



Hexafluoroalkenes are suggested[20] to have been formed by concerted "ene" or diradical mechanisms.



For non terminal alkenes e.g. $Me_2C=CHMe$ and $Me_2C=CMe_2$, formations of cyclobutanes as well as hexafluoroalkenes is reported[20] as being slow, allowing cyclopentane formation (see below) to become competitive.



CHAPTER 2

THE ADDITION OF CYCLIC / ACYCLIC ALCOHOLS AND DIOLS TO HFP

5.0. Introduction

A general review of free radical reactions involving alcohols and fluoroalkenes is given in chapter 1.

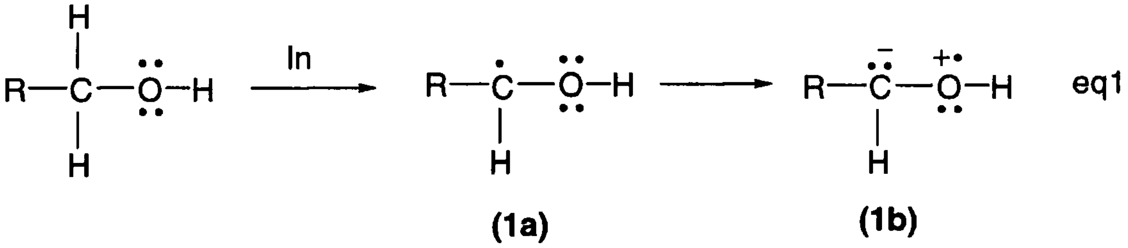
5.1. Our approach for the introduction of fluoroalkenes into C-H bonds

The aims of our research were as follows :-

1. To investigate free radical reactions of cyclic alcohols and cyclic diols with hexafluoropropene.
2. Similarly, investigate free radical reactions of acyclic diols with hexafluoropropene.

5.2. Review of theory involving reactions of alcohols with hexafluoropropene

Again, alcohols form radicals readily especially at sites attached to oxygen and furthermore, stabilisition by oxygen renders the radical nucleophilic in character (**eq 1**).



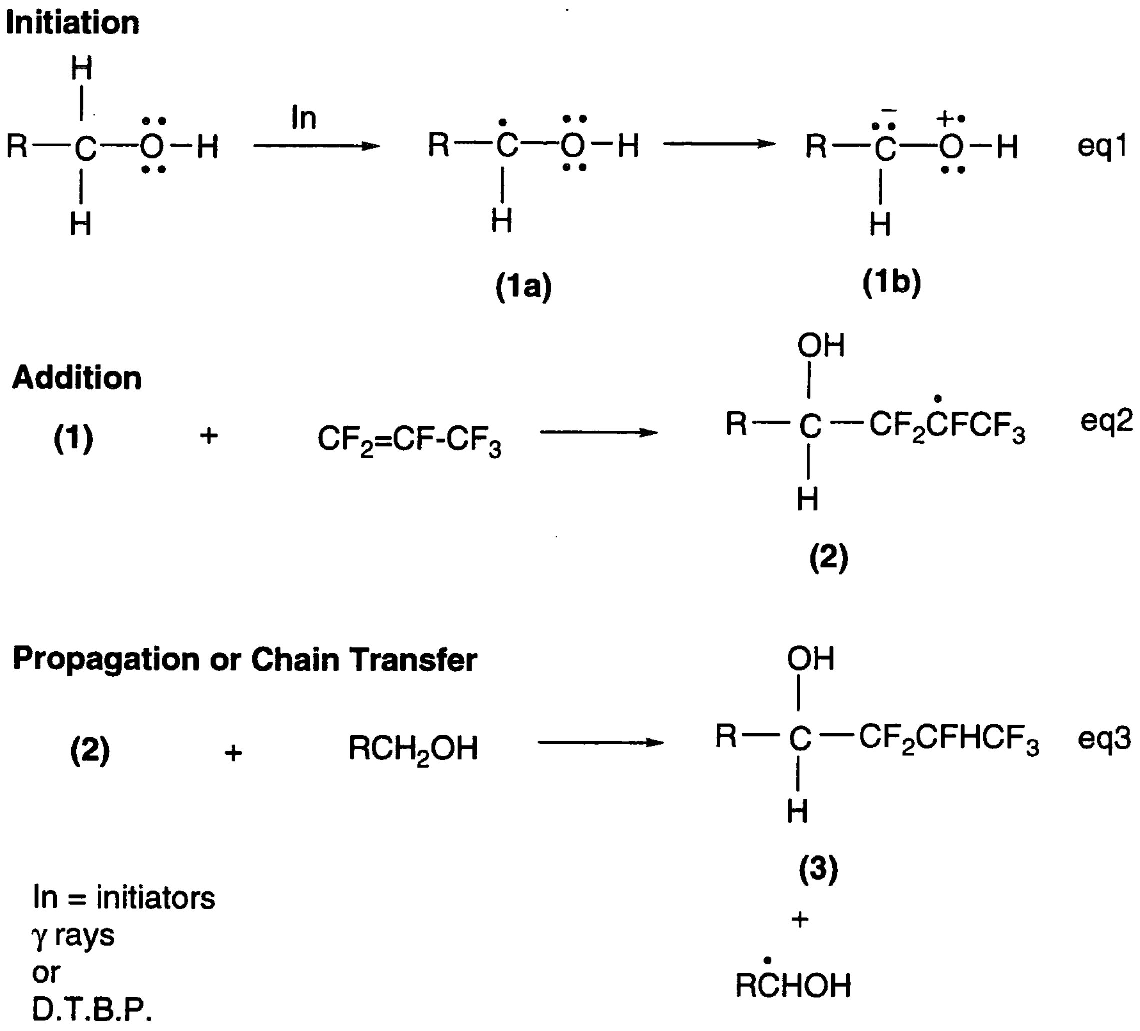
In = γ rays or di-tert-butyl peroxide (D.T.B.P.).

It is also well established[46] that *HFP* being electrophilic in nature is very susceptible to attack from *nucleophilic* radicals. The process for the addition is outlined in Scheme 8[4, 5].

Initiation (eq1) :-
This process involves the loss of a hydrogen atom from the carbon attached to oxygen, creating a *nucleophilic* radical (**1b**) as a consequence of resonance stabilisation.

Addition (eq2) :-
Nucleophilic radical (**1a, b**) attacks *HFP* exclusively at the difluoromethyl site to give an extremely *electrophilic* radical (**2**).

Propagation (Chain Transfer) (eq3) :-
Electrophilic radical (**2**) abstracts a hydrogen atom from the electron rich reacting alcohol to give the product (**3**), as well as regenerating a reacting radical (**1a, b**).

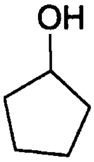
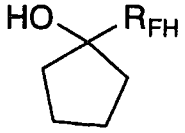
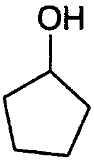
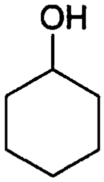
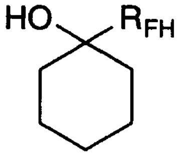
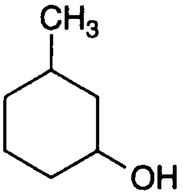
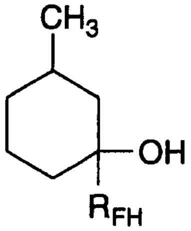
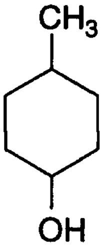
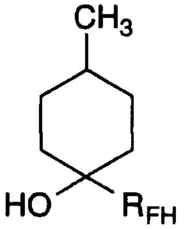
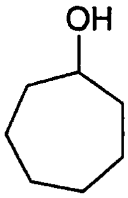
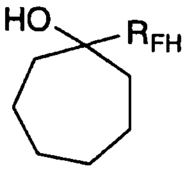
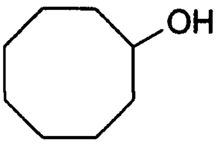
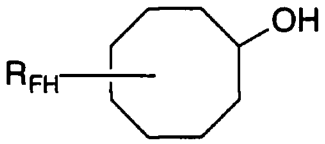


Scheme 8 :- Mechanism for reaction of an alcohol with hexafluoropropene

5.3. **Results and discussion**

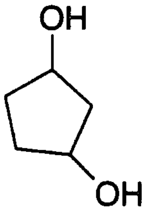
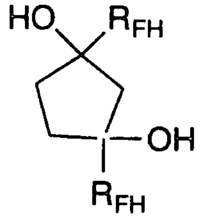
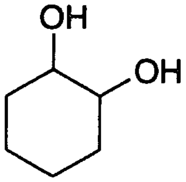
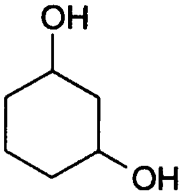
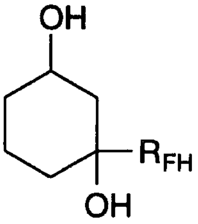
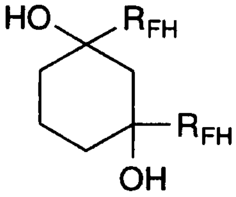
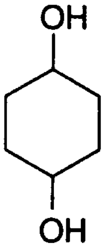
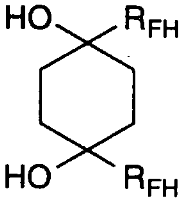
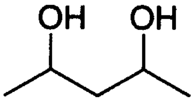
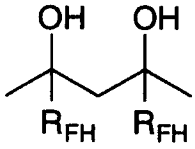
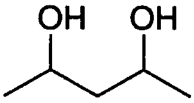
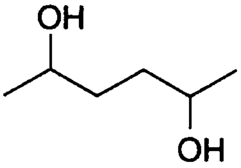
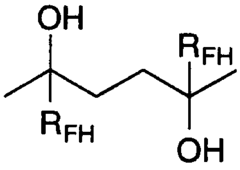
There has been no previously successful work on additions of cyclic alcohols to hexafluoropropene, and Lazerte[11] et al have stated that there is no reaction between cyclohexanol and this fluoroalkene. However, in contrast with earlier work[11-15, 23], successful reactions involving gamma ray or di-tert-butyl peroxide (D.T.B.P.) initiated additions of cyclic or acyclic alcohol / diols to excess hexafluoropropene, contained in evacuated Carius tubes or metal autoclaves, is shown in tables 12 and 13.

Table 12 :- Addition of cyclic alcohols to hexafluoropropene

Starting Alcohol	Conditions[ab] HFP : ROH	Mono - adducts and yields (%) $R_{FH} = CF_2CFHCF_3$	Yield of di-adducts (%)
	1.26[a]	 **(20)** 78%	10
	1.11[b]	(20) 80%	ca 8
	1.42[a]	 **(22)** 78%	19
	1.58[a]	 **(27)** 81%	ca 10
	1.10[a]	 **(29)** 82%	ca 10
	1.25[a]	 **(24)** 80%	12
	1.30[a]	 **(25)** N/C	N/I

a) γ rays, 25°C, 10 days.
b) Di-tert butyl peroxide, 140°C, 24 hours
N/C = not fully characterised. N/I = not isolated.

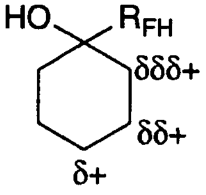
Table 13 :- Addition of cyclic / acyclic diols to hexafluoropropene

Starting Alcohol	Conditions^{ab} HFP : ROH	Mono-adduct and yield (%) R_{FH}= CF_2CFHCF_3	Di-adduct and yield (%) RFH= CF_2CFHCF_3
	2.10^a	-	 **(31)** 71%
	2.19^a	-	-
	2.39^a	 **(32)** 42%	 **(33)** 56%
	2.39^a	-	 **(34)** 97%
	2.12^a	-	 **(36)** 84%
	2.30^b	-	(36) 50%
	2.19^a	-	 **(37)** 51%

a) γ source, 25°C, 10 days
b) D.T.B.P., 140°C, 24 hours

For reactions involving cyclic alcohols with hexafluoropropene (table 12), initiation has been effected by gamma rays (25°C) and, in one example, di-tertiary butyl peroxide (140°C). It is obvious that there was no discernible difference between overall yields nor in site selectivity for the two processes. Only with cyclooctanol did the mono-adduct contain a small amount (ca 5%) of product formed as a consequence of attack at a C-H site removed from the oxygen centre. The addition procedure was outlined earlier in scheme 8, following a normal radical chain process[4, 5].

These results emphasise the importance of polar effects in free radical reactions. In the addition process as a consequence of polar effects, *nucleophilic* alcohol radicals (**1a, 1b**) attack *HFP* at the difluoromethyl sites to give an extremely *electrophilic* radicals (**2**). However a second polar effect arises i.e. inductive electron withdrawal by oxygen inhibits attack by propagating electrophilic radicals (**2**). The effect is significant at the 2-, 3-, and 4- positions but is less evident for larger rings (see cyclooctanol).

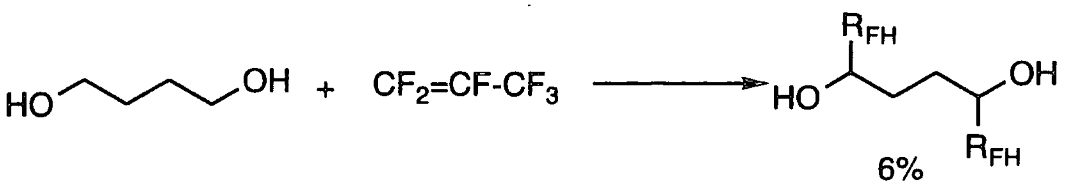


(22)

This deactivation was sufficient to allow mono addition adducts to be the major products, even with a slight excess of hexafluoropropene. However, some di and poly addition products were observed and understandably these increase with a greater excess of HFP as well as longer reaction times. Small amounts of product are obtained from cyclooctanol in which addition is not at the hydroxyl carbon because oxygen is now sufficiently far removed from the methylene site and so selectivity is not under full control.

Eq 1 shows attack of a nucleophilic radical exclusively at the difluoromethyl site of HFP. This has been rationalised[3] on the grounds that it is the most electron poor as well as being the least sterically hindered site. Furthermore, the radical formed is more stable, being adjacent to fluorine , and the difluoromethylene as well as the trifluoromethyl moieties. Also the fluorine atom on the carbon radical will provide a similar stabilisation to oxygen in eq1. The trifluoromethyl and difluoromethylene groups will cause electron withdrawal from the radical site, and so would be expected to stabilise the canonical form (**1b**) similar to the " capto dative[47] " effect.

The only successfully reported[23] addition of a diol to hexafluoropropene produced a diadduct in low yield (6%).

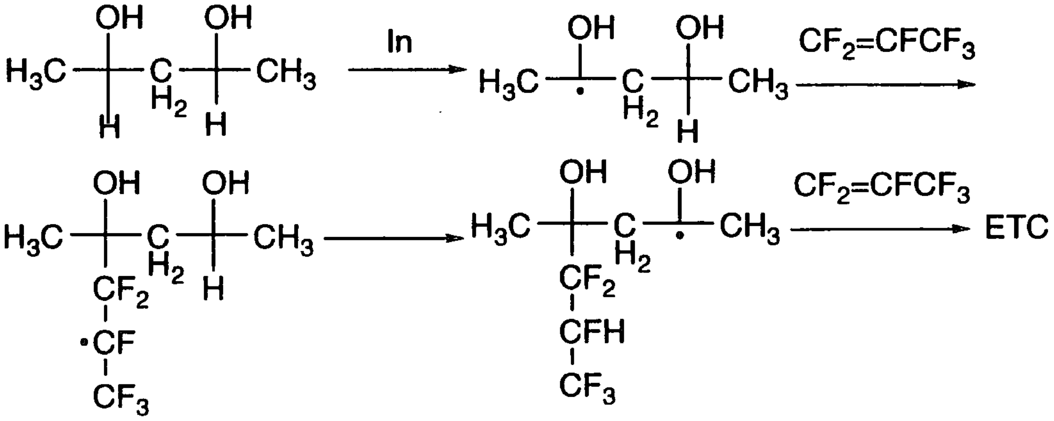


However, it is now found that addition of various diols to HFP proceeds quite smoothly and examples of cyclic and acyclic systems which can be efficiently polyfluoroalkylated by this process to give products are shown in table13. This provides a convenient route to new difunctional monomers containing polyfluoroalkyl groups and further chemistry on these systems is proceeding.

1,2-Cyclohexanediol did not yield significantly useful products, whereas 1,3-cyclohexanediol gave mono as well as di-adducts and 1,4-cyclohexanediol formed only di-adducts in quantitative conversion. 1,5-Cyclooctane diol also gave quantitative conversion of starting material to mainly di-adducts but the exact structures have not been further investigated since the final reaction was too complicated.

Clearly, free-radical additions to these diols are governed by the same factors that affect cyclic alcohols outlined above that lead to site specific polyfluoroalkylated products. However, when the hydroxyl groups are at adjacent positions, as in 1,2-cyclohexanediol then both alcohol centres are too deactivated due to sigma electron withdrawal by oxygen and so radical addition does not occur. It can be seen that reactions involving acyclic diols proceed easily, forming di-alcohol-hfp adducts in good yield for the same reasons outlined in cyclic diols.

A further reaction involving the addition of 2,4-pentane diol to half a molar equivalent of hexafluoropropene produced only di-alcohol-hfp adduct with starting material and no mono adduct. This is another illustration of a back biting mechanism[48] involving a six membered transition state as shown in scheme 9.

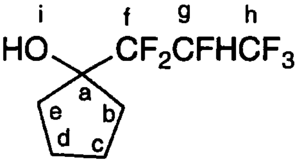


Scheme 9 :- Back biting mechanism involved in the addition of 2,4-pentanediol to hexafluoropropene

Furthermore, a competition reaction between 2,4-pentanediol and 2,5-hexanediol revealed little difference in reaction rate with the latter slightly faster. This suggests little difference between back biting mechanisms[48] that involve either 6 or 7 membered transition states.

5.4. Characterisation of products :-

5.4.1. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclopentanol (20)



(20)

A number of questions need to be answered to establish the site selective addition of alcohols to hexafluoropropene. Firstly, what spectral evidence is there to confirm this reaction has taken place? Three signals from ^{19}F NMR, at -74.5 ppm (int. = 3F), -121.4 / -127.1 ppm (int. 2F) and -210.0 ppm (int. 1F), confirm[49] addition to the difluoromethylene end of hexafluoropropene. Individually, singlets at -74.5 ppm (int. 3F) are assigned[49] as arising from CF_3. Doublets of multiplets at -210.0 ppm (int. = 1F) with a coupling constant (J 42 Hz) characteristic of $^2J_{H\text{-}F}$ coupling, are assigned[49] as arising from CFH. AB systems at -121.4 / -127.1 ppm (int. = 2F) are assigned[49] as arising from CF_2. Since **C(f)** is attached to a stereogenic centre **C(g)**, fluorines on the former are diastereotopic resulting in inequivalence, giving rise to an AB system.

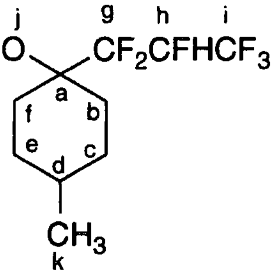
^1H NMR and ^{13}C NMR further confirms the presence of a polyfluoroalkyl group.

From ^1H NMR, doublets, doublets of quartets at 5.2 ppm (int. = 1H) are assigned[49] as arising from CFH.

From ^{13}C NMR, quartets of doublets at 121.9 ppm are assigned[49] as arising from CF_3. The splitting pattern is characteristic of $^1J_{C\text{-}F}$ as well as $^2J_{C\text{-}F}$ coupling with fluorines attached to **C(h)** and **C(g)** respectively. Doublets, doublets of doublets at 119.1 ppm are assigned[49] as arising from CF_2. The splitting pattern arises from $^1J_{C\text{-}F}$ coupling between each in-equivalent fluorine attached to **C(f)** and $^2J_{C\text{-}F}$ coupling with CFH. Doublets of multiplets at 82.2 ppm are assigned[49] as arising from CFH.

To which cyclopentanol ring carbon has the hexafluoropropyl moiety become attached? The answer to this question is revealed by ^{13}C NMR data. The triplets at 81.7 ppm with a coupling constant characteristic of $^2J_{C\text{-}F}$ coupling are assigned[49] on the basis of chemical shift, as arising from **C(a)**.

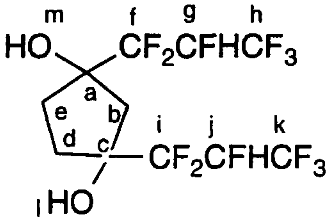
5.4.2. 4-Methyl cyclohexanol (29)



(29)

The presence of the polyfluoroalkyl group is confirmed[49] as previously by ^{19}F, ^{1}H and ^{13}C NMR. The question raised with this type of compound is, does the hexafluoropropyl moiety attach at **C(a)** or **C(d)** ? From ^{13}C NMR, on the basis of chemical shift, a triplet at 74.1 ppm confirms[49] hexafluoropropyl addition to **C(a)**, and the coupling constant (J 24.4 Hz) is characteristic of $^{2}J_{C-F}$ coupling with CF_2. Furthermore, singlets at 32.0 as well as 32.1 ppm are assigned[49] as arising from **C(d)**, in cis and trans stereochemical forms. Also, pairs of signals for all other ring carbons shows cis and trans stereochemical forms.

5.4.3. 1,3 - Di-(1,1,2,3,3,3-hexafluoro)-cyclopentane-1,3-diol (31)



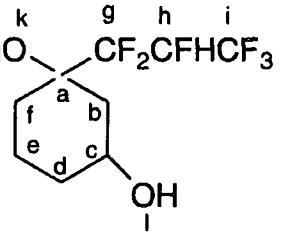
(31)

What spectral evidence confirms addition of 1,3-cyclopentanediol to two units of hexafluoropropene ? From ^{1}H NMR, doublets of multiplets (int. = 2H) at 5.8 ppm with an equal intensity as doublets attributed to OH (int. = 2H), are assigned[49] as arising from **CFH** , confirming di-hexafluoropropyl adduct formation.

A plane of symmetry exists from **C(b)** extending through the **C(d)-C(e)** bond axis. Consequently, this compound has four stereogenic centres at **C(a)**, **C(c)**, **C(g)** as well as **C(j)**. This complicates ^{19}F NMR spectra, in which signals for CF_3, CF_2 and CFH are all observed as multiplets indicating diastereostereoisomers.

From ^{13}C NMR, multiplets at 83.18ppm confirm[49] addition of the hexafluoropropyl moieties at **C(a)** and **C(c)**. Again, pairs of signals for all ring carbons arise from cis and trans stereo chemical forms.

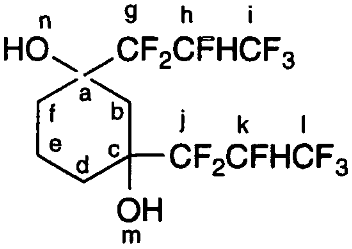
5.4.4. 1-(1,1,2,3,3,3-Hexafluoro)-1,3-cyclohexane diol (32)



(32)

The presence of the polyfluoroalkyl group is confirmed as previously by ^{19}F, ^{1}H and ^{13}C NMR spectra. How many hexafluoropropyl units have attached to this diol? From the ^{1}H NMR spectra, doublets of multiplets at 5.71ppm (int. = 1H) due to CF**H** confirm[49] attachment of only one hexafluoropropyl group.

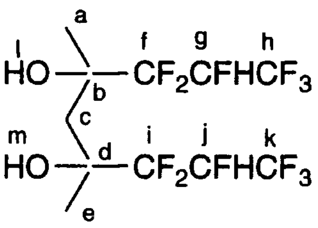
5.4.5. 1,3-Di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexane-1,3-diol (33)



(33)

What spectral evidence confirms addition of 1,3-cyclohexane diol to two units of hexafluoropropene? From ^{1}H NMR, multiplets at 5.6-6.0 ppm (int. = 2H), assigned[49] as arising from CF**H**, confirm di-hexafluoropropyl adduct formation.

5.4.6. 2,4-Di-(1,1,2,3,3,3-hexafluoro)-pentane-2,4-diol (36)



(36)

Again, di-alcohol-hexafluoropropyl adduct formation is confirmed by ^{1}H NMR, in which multiplets (area = 2H) at 5.8 ppm are assigned[49] as arising from CF**H**.

Compound (**36**) has four chiral centres at **C(b)**, **C(d)**, **C(g)**, **C(j)** and this complicates the ^{19}F NMR spectra. From these spectra, two AB systems[49] at -124.4,

-126.3 ppm , as well as a smaller signal in the same region clearly show different stereo chemical forms of compound **(36)**.

^{13}C NMR data confirm addition of hexafluoropropene at **C(b)** and **C(d)** as previously discussed. Furthermore, multiplets at 19.3 and 20.3 ppm, assigned[49] to equivalent carbons **C(a)** as well as **C(e)** show different stereo chemical forms of compound **(30)**. Similarly multiplets at 34.7 and 35.4 ppm are assigned[49] as arising from **C(c)**.

5.5. Summary and conclusions

1. Reactions of various cyclic alcohols (C5, C6, C7) with a small molar excess of hexafluoropropene, gives high yield site selective adducts, in which the fluoroalkene is added to the same carbon that the hydroxyl group is attached.
2. Larger cyclic alcohols (C8) react with hexafluoropropene giving a mixture of mono-adducts in which the total site selectivity mentioned above is not observed.
3. 1,3- and 1,4- cyclic diols (C5 + C6) react easily with two molar equivalents of hexafluoropropene giving site selective di-adducts in high yield. This again reflects activating as well as deactivating effects of oxygen.
4. 1,2-Cyclohexanediol does not react with excess hexafluoropropene as a result of deactivating effects of each hydroxyl oxygen on adjacent carbon sites.
5. 2,4-Pentanediol and 2,5-hexanediol react easily with two molar equivalents of hexafluoropropene giving oxygen directed site selective products.
6. Reactions of acyclic diols with a molar deficiency of hexafluoropropene yields di-adducts only (no mono adducts). Hence such reaction proceed by a back biting mechanism.

CHAPTER 3

FLUOROALKENE FORMATION AND SUBSEQUENT REACTIONS

6.1. Previous developments in the chemistry of alkenes of general formula R_F-$CH=CH_2$, in which R_F = polyfluoroalkyl

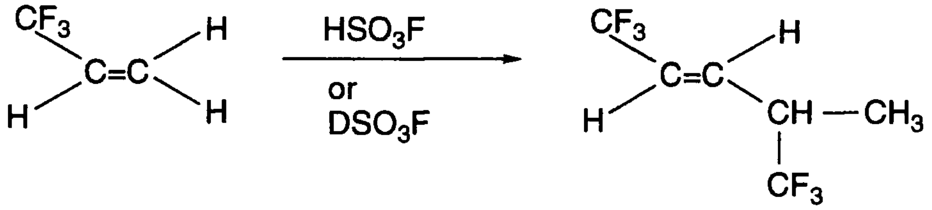
The chemistry of fluorinated alkenes is well studied[46, 50] in organic chemistry but alkenes with both hydrocarbon as well as fluorocarbon substituents are relatively rare. A brief review involving the chemistry of alkenes with the general formula R_F-$CH=CH_2$ now follows[51-57].

Perfluoroalkylethenes are typically synthesised as follows[58].

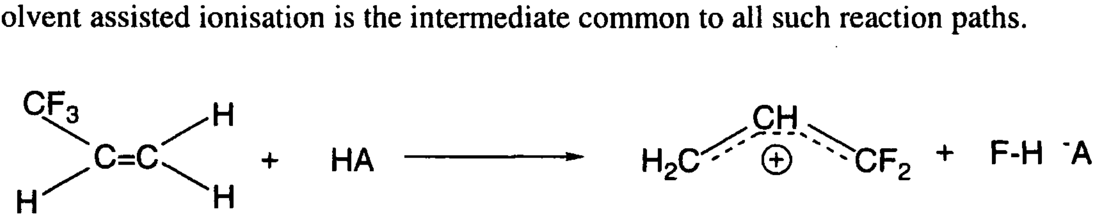
$$R_FI \xrightarrow{CH_2=CH_2} R_FCH_2CH_2I \xrightarrow{-HI} R_F\overset{\delta^-}{C}H=\overset{\delta^+}{C}H_2$$

$R_F = C_4F_9$. C_6F_{13}, C_8F_{17}

Very few reactions have been performed on R_F-$CH=CH_2$ systems. The first electrophilic reaction was reported[51] in 1950 by Henne and Kaye, who found that CF_3-$CH=CH_2$ did not react with excess anhydrous HCl (6 eq) at autogeneous pressure, but that upon the addition of aluminium chloride, a reaction took place at ambient temperature yielding exclusively $CF_3CH_2CH_2Cl$. However, in 1970 Myhre reported[54] two products for the same reaction i.e. $CF_3CH_2CH_2Cl$ and $CF_2ClCH_2CH_2Cl$. Furthermore, Myhre found that fluorosulphuric acid did not undergo addition to 3,3,3-trifluoropropene. Rather, in freshly distilled solvent, CF_3-$CH=CH_2$ undergoes dimerisation, yielding exclusively trans 1,1,1,5,5,5-hexafluoro-4-methyl-2-pentene, without incorporation of protons from the solvent.

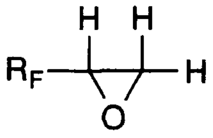


Hence, the kinds of products obtained from reaction of CF_3-$CH=CH_2$ with strong acids varied. Under the appropriate reaction conditions it was possible to obtain addition and addition substitution products[54, 55] as well as those derived from hydrolysis[51, 59] / dimerisation[54, 57]. It was suggested[55] that the 1,1-difluoroallyl cation (**38**) formed by solvent assisted ionisation is the intermediate common to all such reaction paths.



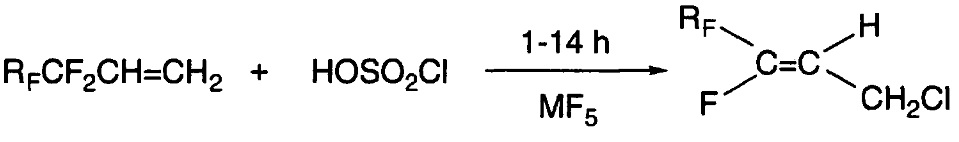
(38)

In 1984, Coudures reported[58] that the Hg^{2+} catalysed addition of a mixture of bromine as well as AcOH, to olefins of the type R_F-$CH=CH_2$, gave R_F-$CHBr$-CH_2OAc ($R_F = C_4F_9$ C_6F_{13}, C_8F_{17}). in good yield. The product from this reaction was hydrolysed using 50% sodium hydroxide, and following displacement of bromine using ${}^tBuOK$/ THF / H_2O, yielded epoxides of the general formula :-



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

More recently, Petrov[56] reported new reactions of alkenes of the type R_F-$CH=CH_2$ with different Bronsted acids to form allylic halides of the formula R_F-$CF=CHCH_2X$, and the further chemistry of such products has also been investigated. In general the following reaction was established.



(39) **(40)**

R_F = n-C_3F_7, n-C_5F_{11}, n-C_7F_{15}
M = Nb, Ta

6.2. A brief review of previous methodology for the introduction of polyfluoroalkyl groups into aromatic rings[60]

Most research in this field of organic chemistry has involved the synthesis of aromatic compounds containing a trifluoromethyl moiety.

Trifluoromethylated compounds have found a large number of industrial uses including their use in dyes, polymers, pharmaceuticals and agrochemicals. In biologically active molecules, the trifluoromethyl group is often associated with increased lipophilicity[61]. The dye industry has often found that trifluoromethylation of chromophores results in increased light fastness as well as a shift in colour (both bathochromic and hypsochromic) compared to their non fluorinated counterparts[62, 63].

6.2.1. Conversion of $ArCX_3$ to $ArCF_3$

It has been found that hydrogen fluoride can fluorinate benzotrichloride to yield the trifluoride but such a method has the disadvantage of working with H-F[64]. This fact has lead to the development of milder alternative reagents[65-68] and certain benzotrifluorides have been found to be quantitatively converted to their trichloride using aluminium trichloride as well as fluorotrichloromethane.

6.2.2. Use of trifluoromethyl copper

Trifluoromethylcopper has been particularly successful in reactions with haloaromatics. Reactions involving iodoaromatic compounds with trifluoromethyl copper are thought to be nucleophilic in nature, and consequently the presence of electron withdrawing groups attached to the aromatic ring favour such a process.

There are many sources of " Cu CF_3 " for addition to iodoaromatics[69-75], with each system having its own advantages / disadvantages based on cost, toxicity, reagent availability as well as reaction conditions.

When bromoaromatics[69, 70, 73, 74, 76-79] are used instead of iodoaromatics, lower yields are recorded and reactions can be complicated by the formation of perfluoroethyl as well as dehalogenated aromatics.

Reactions of chloroaromatics[71, 73, 80-84] are less studied but it has been reported that such processes are favoured by the presence of an electron deficient ortho substituent e.g. NO_2, CHO, CO_2Me, COR.

6.2.3. Use of trifluoromethyl radicals

This radical is electrophilic in nature, and may be generated by photochemical[85-97], electrochemical[98-100], thermal[79, 93, 101-108] or chemical reactions[109-114]. However, the highest yields recorded for the trifluoromethylation of benzene are when iodotrifluoromethane and mercury (65%) were used[85]. Furthermore, trifluoromethyl radicals are not highly specific but they do prefer sites of high electron density in the HOMO[115].

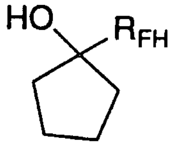
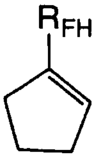
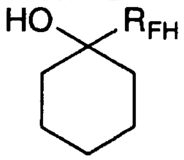
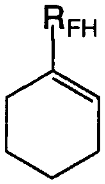
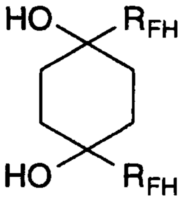
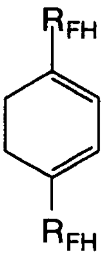
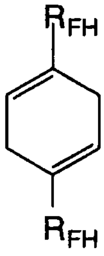
6.3. Our approach towards synthesis of alkenes, dienes and aromatics containing the hexafluoropropyl moiety

Our work discussed in the previous chapter illustrates that using alcohols as well as diols, it was possible to introduce polyfluoroalkyl groups at sites directed by the influence of the hydroxyl group(s). In the present work such alcohol and / or diol HFP adducts have been successfully dehydrated using thionyl chloride and pyridine at room temperature[116-118], yielding monoenes or mixtures of dienes containing the polyfluoroalkyl moiety. Furthermore, various electrophilic reactions have been performed on such monoenes and the further chemistry of selected products has been explored. Also, dehydrogenation of the monoenes and diene mixtures with sulphur[119, 120] at 225°C, gave aromatic compounds which contained a polyfluoroalkyl moiety, in quantitative yield.

6.4. Dehydration of alcohols containing an attached hexafluoropropyl moiety

We have explored various methodologies for converting the fluorinated alcohols and diols to corresponding cycloalkene or cyclodiene derivatives. Dehydration of the polyfluoroalkylated alcohols using reagents such as concentrated sulphuric acid[121-123] or phosphorus pentoxide[124, 125] was unsuccessful, probably reflecting the adverse influence of a polyfluoroalkyl group on developing carbocation centres. However, formation of the chloride followed by subsequent base induced elimination of hydrogen chloride was successful, and this reaction is most conveniently carried out using a " one pot" procedure[116-118] in which the alcohol or diol are mixed with a combination of thionyl chloride and pyridine at room temperature. Indeed, earlier workers[116] had applied this procedure for dehydration of an alcohol with an attached electron withdrawing group. A range of such reactions has been performed on various alcohol - hexafluoropropyl adducts as shown in table 14.

Table 14 :- Products from the dehydration of various alcohol - HFP adducts[ab]

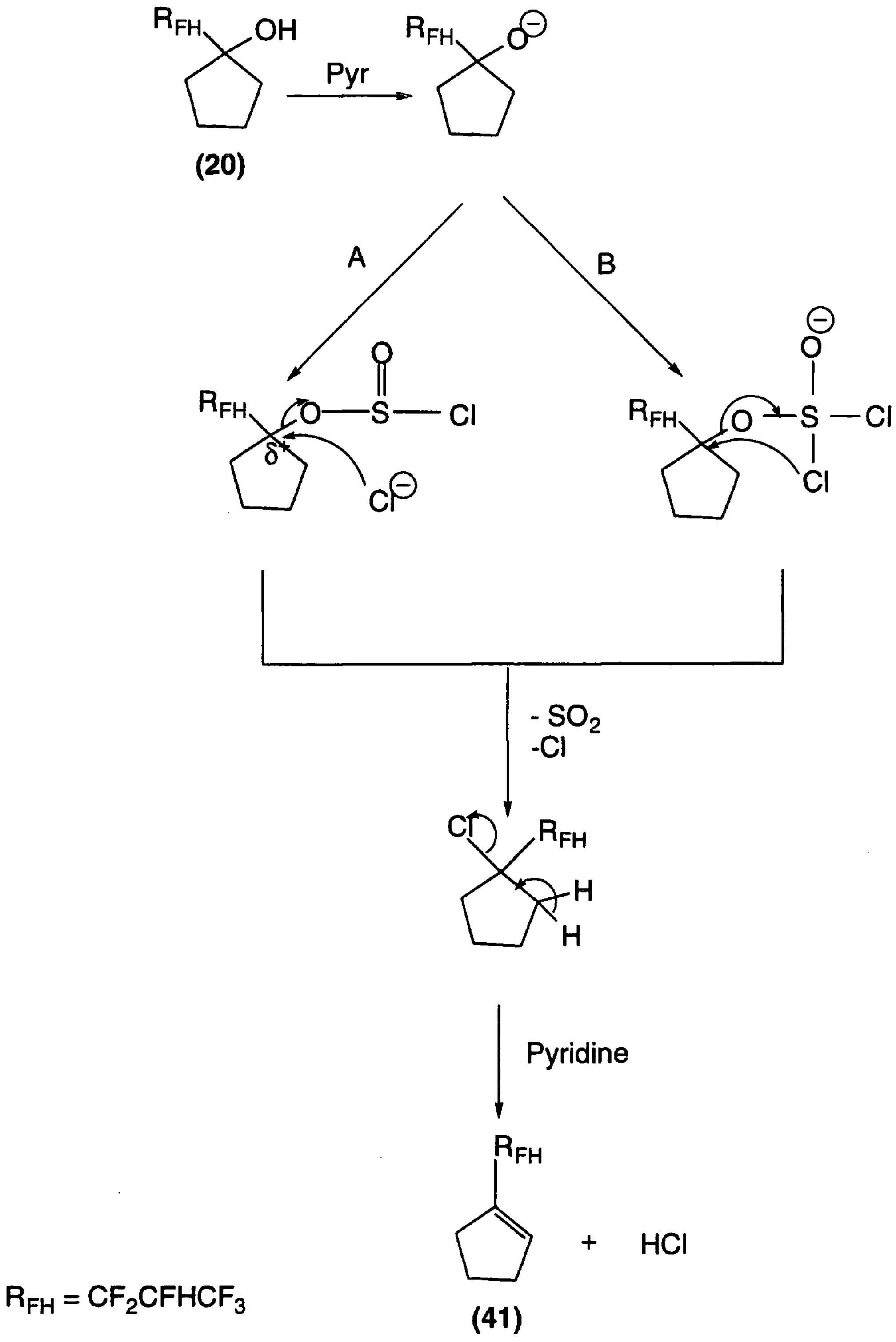
Starting Material	Products / Yields (%)[c]
 **(20)**	 **(41)** 61%
 **(22)**	 **(42)** 55%
 **(34)**	 +  **(44)** **(43)** 70%

a) $SOCl_2$ / pyridine / 25°C / 24H

b) $R_{FH} = CF_2CFHCF_3$

c) Isolated yields

A possible mechanism for the reaction of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentanol **(20)** with thionyl chloride and pyridine is suggested below.



Scheme 10 :- Mechanism for dehydration of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentanol (20) using thionyl chloride and pyridine

From scheme 10, route B should be preferred to route A since SN_2 processes at tertiary sites are unlikely.

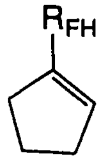
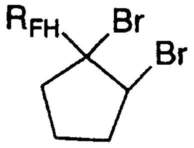
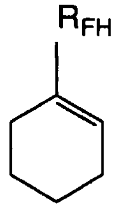
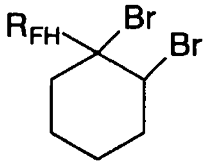
An attempted chlorination of compound (**20**) using thionyl chloride only, was unsuccessful. This suggests that in the dehydration mechanism (scheme 10), chlorination depends on an initial stage involving proton removal using pyridine, followed by attack of thionyl chloride.

6.5. Reactions of alkenes containing a hexafluoropropyl group attached directly to the C=C double bond

6.5.1. Bromination

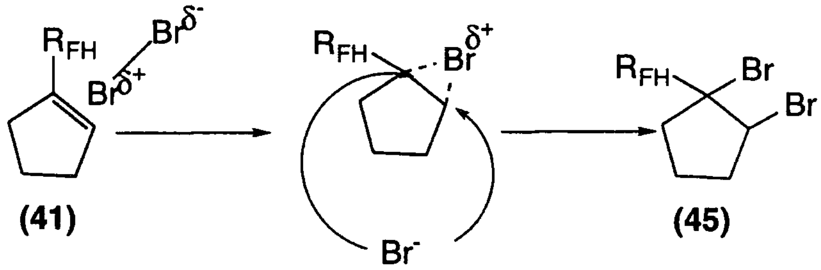
The aim was to investigate the effect of the polyfluoroalkyl group on C=C double bond reactivity. Firstly, attempted brominations[126] of compounds (**41**) and (**42**) proved successful (table 15), showing that such alkenes remained electrophilic in nature despite the presence of a polyfluoroalkyl group. However, such reactions occurred at a slower rate[126] than the parent cycloalkenes. These observations agree with previous work on the reaction of acyclic systems such as $R_F\text{-}CH=CH_2$[58].

Table 15 :- Brominations of alkenes [ab]containing the hexafluoropropyl moiety directly attached to a C=C double bond

Starting Material	Products / Yields (%)[c]
 **(41)**	 **(45)** 80%
 **(42)**	 **(46)** 70%

a) Br_2 / 0°C / 1H
b) $R_{FH} = CF_2CFHCF_3$
c) isolated yields

A probable mechanism for such reactions is suggested below.



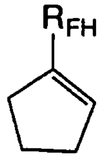
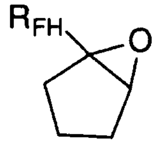
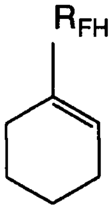
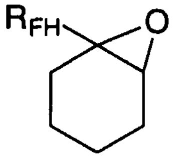
According to this mechanism anti - addition is anticipated[2]. However, the product mixture is complex as indicated by NMR, and it was not possible to deduce the absolute stereo chemistry of (**45**).

Additional objectives were to develop syntheses of dienes and aromatics containing the polyfluoroalkyl moiety and our initial approach to such compounds involved attempted dehydrobromination of (**45**), as well as (**46**), using bases[127, 128]. However, all reactions resulted in the elimination of bromine as compared to hydrogen bromide. Hence, a different approach to dienes and aromatics was pursued and success was achieved through dehydration of HFP-diol adducts, with thionyl chloride / pyridine as explained earlier[116]. This gave dienes and subsequent sulphur dehydrogenation[119, 120, 129] produced aromatics (see later).

6.5.2. Epoxidation

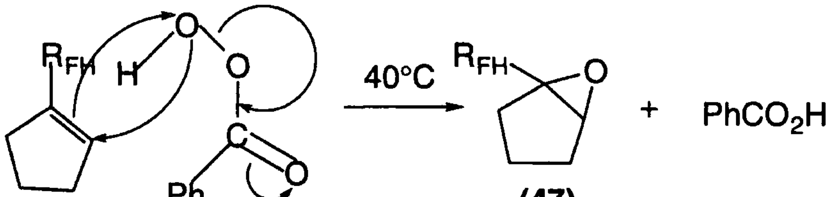
Compounds (**41**) and (**42**) were easily epoxidised using metachloroperbenzoic acid (M.C.P.B.A.)[130] (table 16) confirming that the C=C double bond of such fluoroalkenes is electrophilic in nature.

Table 16 :- Epoxidations^{ab} of alkene containing the hexafluoropropyl moiety directly attached to a C=C double bond

Starting Material	Products / Yields (%)^{c}
 **(41)**	 **(47)** 52%
 **(42)**	 **(48)** 46%

a) M.C.P.B.A. / 40°C / 7 days
b) $R_{FH} = CF_2CFHCF_3$
c) isolated yields

The process involves nucleophilic attack on oxygen as indicated below.



(41) **(47)**

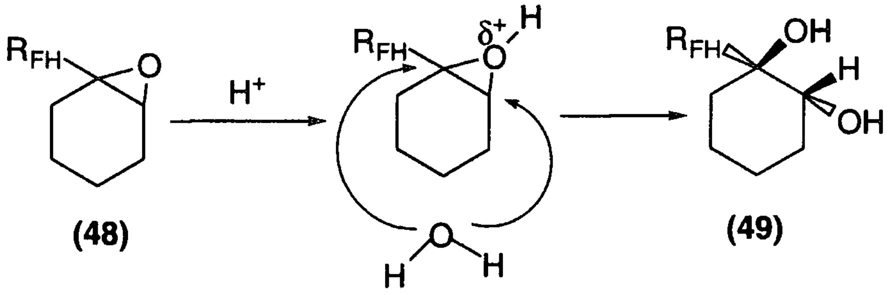
$R_{FH} = CF_2CFHCF_3$

Compound **(47)** contains three stereogenic centres but can only exist as four stereo isomers since the epoxide ring is locked in a cis conformation. Spectral data discussed later show pairs of signals representing the two diastereomeric forms of this compound.

A whole range of epoxide chemistry can now be developed on 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentene oxide **(47)** leading to novel products containing both hydrocarbon and fluorocarbon substituents. Furthermore, as has been previously mentioned, it has not been possible to introduce a polyfluoroalkyl group into a 1,2-diol using free radical processes as a consequence of the inductive deactivating effect of both oxygen atoms. The epoxides containing a polyfluoroalkyl group can be ring opened using acid[131], hence provide a route to 1,2-diols containing the hexafluoropropyl moiety.

6.6. Acid catalysed ring opening of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene oxide

An acid catalysed ring opening of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene oxide[131] (**48**) gave 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexane-1,2-diol (**49**) in high yield. A mechanism for such a process is suggested below.

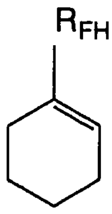
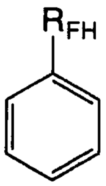
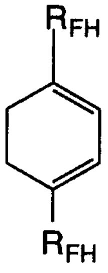
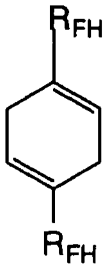
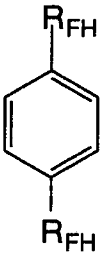


Compound (**49**) contains three stereogenic centres and could exist in eight stereoisomers. However, in the suggested mechanism, the protonated epoxide is opened as a consequence of backside attack by a water molecule from the opposite face of the epoxide ring, giving a trans diol. Hence, only four stereo isomers are now likely and spectral data discussed later showing pairs of signals for all ring carbons is consistent with a mixture containing the diastereoisomeric forms of this compound.

6.7. Synthesis of aromatic compounds containing the hexafluoropropyl moiety[129]

As previously mentioned[60], there is considerable interest in the development of methodology for inserting polyfluoroalkyl groups into aromatic rings. The present work shows a significant development in this field. Initial attempts to dehydrogenate 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene using Pd/C[129] as well as Pt/C[129] proved unsatisfactory, since in such reactions disproportionation occurred, yielding 1-(1,1,2,3,3,3-hexafluoropropyl)-benzene and (1,1,2,3,3,3-hexafluoropropyl)-cyclohexane. However, a reaction which involved heating a mixture of degassed 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene (**42**) and sulphur[119, 120, 129], yielded only 1-(1,1,2,3,3,3-hexafluoropropyl)-benzene (**50**) (table 17) in near quantitative yield, with no side products.

Table 17 :- Synthesis of aromatic compounds containing hexafluoropropyl moieties

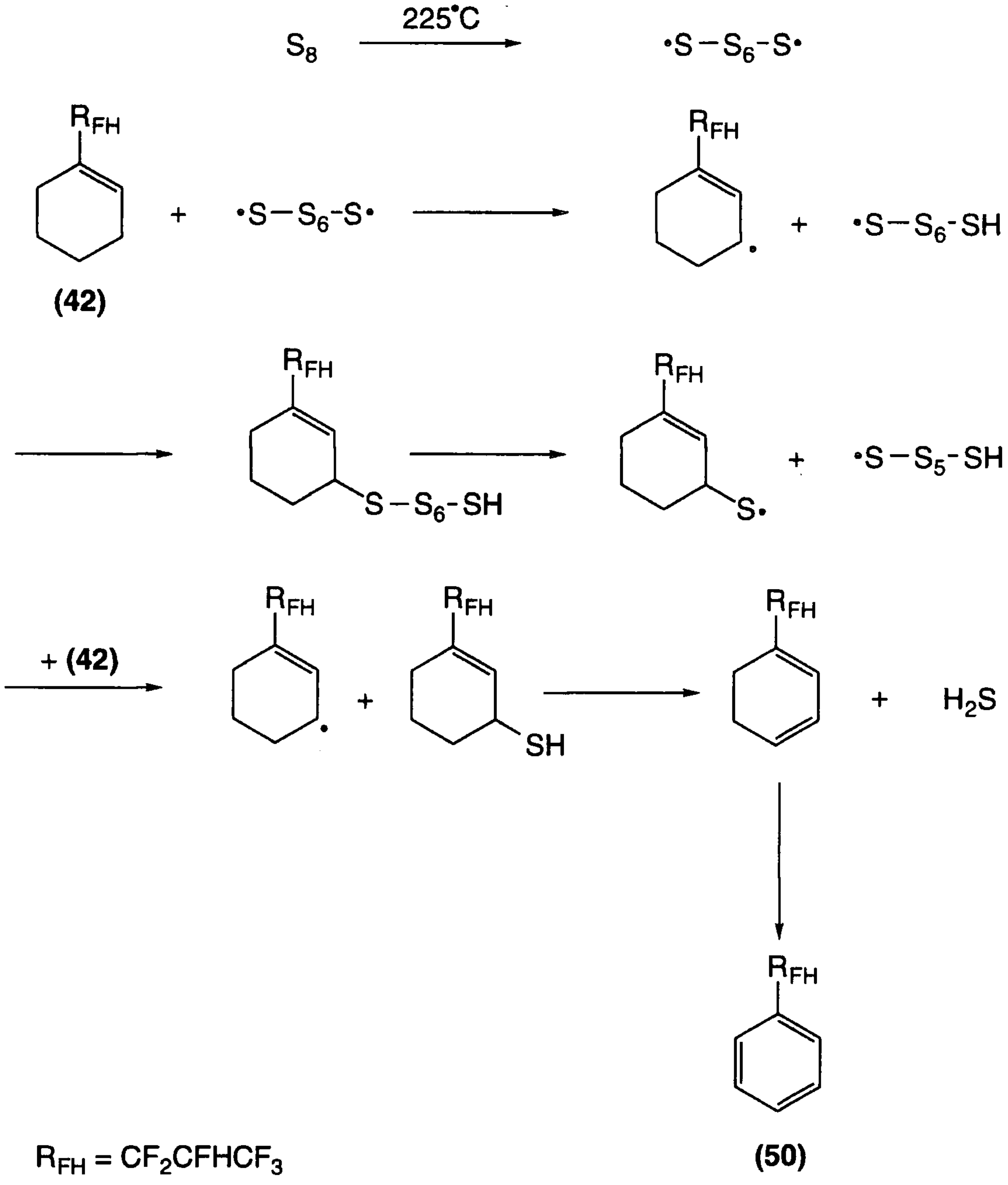
Starting Material	Products / Yields (%)[c]
 **(42)**	 **(50)** 88%
 **(43)**  **(44)**	 **(51)** 93%

a) S_8 / 225°C / 24H

b) RFH = CF_2CFHCF_3

c) isolated yields

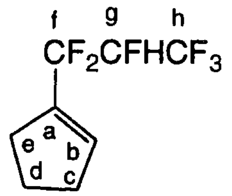
Furthermore a similar reaction of the mixture of compounds **(43)** and **(44)** yielded 1,4-di-(1,1,2,3,3,3-hexafluoropropyl)-benzene **(51)** in quantitative yield. A free radical mechanism[129, 132] for the above reactions is as shown in scheme 11.



Scheme 11 :- Free radical mechanism[129, 132] suggested for the dehydrogenation of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene (42) to (1,1,2,3,3,3-hexafluoropropyl)-benzene (50), using sulphur at 225°C

6.8. Characterisation of products

6.8.1. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclopentene (41)

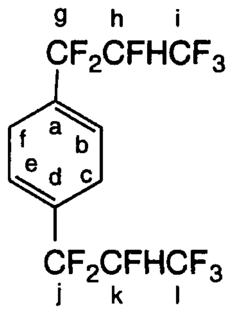


(41)

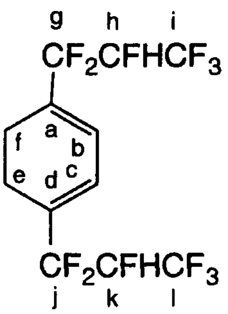
Evidence of dehydration was observed by examination of the ^{1}H NMR spectrum. Key signals included a multiplet at 6.2 ppm (int. = 1H) which is assigned[49] as arising from the vinylic hydrogen in compound **(41)**. Furthermore, a doublet of multiplets at 4.8ppm (int. = 1H) confirmed[49] that the hexafluoropropyl moiety remained intact during dehydration.

Two key signals in the ^{13}C NMR spectra confirmed that compound **(41)** has been produced. Firstly, a triplet at 135.2 ppm is assigned[49] as arising from **C(a)**, since the coupling constant (J 24 Hz) is characteristic of $^2J_{C\text{-}F}$ coupling with CF_2. Similarly a triplet at 135.8 ppm is assigned[49] as arising from **C(b)**, since the coupling constant (J 7.2) is characteristic of $^3J_{C\text{-}F}$ coupling with CF_2.

6.8.2. 1,4-Di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohex-1,4-diene (43) / (44)



(43)

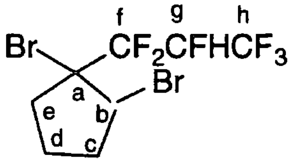


(44)

Dehydration of 1,4-di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexane-1,4-diol **(34)** to yield a mixture of dienes **(43+44)** was confirmed by examination of the ^{1}H and ^{13}C NMR spectra. From ^{1}H NMR spectra, key signals were singlets at 6.4 ppm (int. = 1H) as well as 6.6 ppm (int. = 1H) which are assigned[49] as arising from the vinylic hydrogens in compounds **(43)** and **(44)** respectively.

From ^{13}C NMR, triplets at 127.2 ppm as well as 132.6 ppm are assigned[49] as arising from **C(a)** and **C(d)** in both compounds **(43 + 44)**, on the basis of coupling constant values (J 23.3, J 22.5) characteristic of $^2J_{C\text{-}F}$ coupling with CF_2. Similarly, triplets at 125.7 ppm as well as 128.4 ppm are assigned[49] as arising from vinylic carbons (**44C(b)**, **44C(c)**, **43C(b)**, **43C(e)**), on the basis of coupling constants characteristic of $^3J_{C\text{-}F}$ coupling with CF_2.

6.8.3. 1-(1,1,2,3,3,3-Hexafluoropropyl)-1,2-dibromocyclopentane (45)

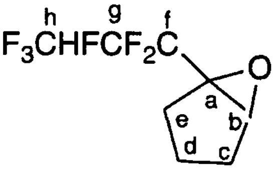


(45)

^{13}C NMR spectral data confirmed compound (**45**) has been formed. This compound contains three chiral centres at **C(a)**, **C(b)** and **C(g)** and therefore exists as eight stereo isomers. In the ^{13}C NMR spectra, pairs of signals are observed for all ring carbons arising from different diastereoisomeric forms of compound (**45**). However it is not possible to suggest whether this is indicative of an expected trans bromine product arising from ANTI addition to the fluoroalkene[2], or a mixture of cis and trans isomers. Furthermore, key signals confirming bromine addition to the C=C double bond include triplets at 74.8 ppm as well as 73.9 ppm, which are assigned[49] as arising from **C(a)** and the coupling constants (J 23.6, J 23.7 ppm) are characteristic of $^2J_{C\text{-}F}$ coupling with CF_2. Also, doublets of doublets as well as singlets at 52.8 ppm and 53.4 ppm respectively are assigned[49] as arising from **C(b)**, with the coupling constant values (J 2.3, J 6.3 Hz) showing that one diastereoisomer is in a more favoured conformation for $^3J_{C\text{-}F}$ through bond coupling with CF_2 than the other.

Evidence of C=C double bond bromination in compound (**45**) also came from a pair of doublets at 4.65 and 4.69 ppm in the ^1H NMR, assigned[49] as arising from **CH**, illustrating that this proton is found at a different chemical shift to that for the corresponding hydrogen in the starting material. The two separate signals arise from different diastereomeric forms of compound (**45**).

6.8.4. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclopentoxide (47)



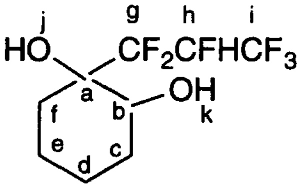
(47)

The epoxidation of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentene (**41**) was confirmed by ^1H NMR and ^{13}C NMR. From ^1H NMR, key signals include singlets at 3.8 ppm (int. = 1H) assigned[49] as arising from hydrogen attached to **C(b)**. Multiplets at

5.0 ppm (int. = 1H) assigned[49] as arising from CFH, confirm that the polyfluoroalkyl group was not affected during epoxidation.

Again from ^{13}C NMR spectra, pairs of signals are observed for ring carbons (C(**b**), C(**c**), C(**d**), C(**e**)) confirming that the epoxide exists in two diastereoisomers. Furthermore, compound (**47**) has three stereogenic centres at C(**a**),C(**b**) as well as C(**g**) and consequently the former carbon (C(**a**)) is observed as a complex multiplet. Remaining signals for ring carbon pairs show stronger through bond coupling with CF_2 for one particular ring conformation than the other. Confirmation that the polyfluoroalkyl group remained unaffected by epoxidation is also shown by ^{13}C NMR.

6.8.5. 1-(1,1,2,3,3,3-Hexafluoropropyl-)-cyclohexane-1,,2-diol (49)

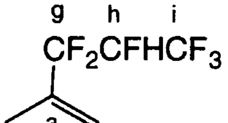


(49)

Compound (**49**) has three stereogenic centres (C(**a**), C(**b**), C(**h**)) and could exist as eight stereo isomers. However, the mechanism used earlier to explain the formation of this compound suggested only formation of a trans diol, and hence only four stereo isomers must exist.

Pairs of signals observed in the ^{13}C NMR spectrum for all ring carbons, are assigned[49] as arising from different diastereoisomers of this compound. Two key signals confirm the ring opening of the epoxide to give a diol. Firstly, triplets at 74.89 ppm as well as 75.11, are assigned [49] on the basis of chemical shift, as arising from C(**a**) indicating both diastereoisomers, and the coupling constants (J 22) values indicate $^2J_{C\text{-}F}$ coupling with CF_2. Secondly, singlets at 67.8 ppm as well as 69.5 ppm are assigned[49] on the basis of chemical shift to C(**b**), representing both diastereoisomers.

6.8.6. 1-(1,1,2,3,3,3-Hexafluoropropyl)-benzene (50)

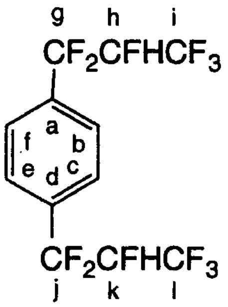


(50)

^1H NMR illustrated that 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene (**42**) was aromatised to 1-(1,1,2,3,3,3-hexafluoropropyl)-benzene (**50**). The key signals were multiplets at 7.6 ppm (area = 5H), which are assigned[49] as arising from all five aromatic ring hydrogens.

^{13}C NMR data further confirmed the structure of compound **(50)**. The triplet at 132.5 ppm is assigned[49] as arising from **C(a)**, since the coupling constant is characteristic of $^2J_{C-F}$ coupling with CF_2. Similarly, the triplet at 126.7 ppm is assigned[49] as arising from equivalent carbons **C(b)** and **C(f)**, since the coupling constant is characteristic of $^3J_{C-F}$ coupling with CF_2. The singlet at 129.8 ppm is assigned[49] as arising from equivalent carbons **C(c)** and **C(e)**. Finally, **C(d)** is observed[49] as a singlet at 132.4 ppm.

6.8.7. 1,4-Di-(1,1,2,3,3,3-hexafluoropropyl)-benzene (51)



(51)

Again, ^1H NMR and ^{13}C NMR confirmed that a mixture of 1,4-di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohex-1,3-diene **(43)** and 1,4-di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohex-1,4-diene **(44)** was converted to 1-4-di-(1,1,2,3,3,3-hexafluoropropyl)-benzene **(51)** using sulphur. From ^1H NMR, the key signal was a singlet at 7.9 ppm (int. = 4H), which is assigned[49] as arising from all four ring aromatic hydrogens.

Compound **(51)** contains two chiral centres and can therefore exist as four stereo isomers. From ^{13}C NMR, the triplet at 135.9 ppm is assigned[49] as arising from equivalent carbons **C(a)** and **C(d)**, since the coupling constant is characteristic of $^2J_{C-F}$ coupling with CF_2. Triplets at 126.8 ppm as well as 127.7 ppm are assigned[49] to equivalent carbons **C(b)**, **C(c)**, **C(e)** and **C(f)** since the coupling constant is characteristic of $^3J_{C-F}$ coupling with CF_2.

6.9. Summary and conclusions

1. Alcohols containing a polyfluoroalkyl group attached to the same carbon as an hydroxyl group are easily dehydrated using thionyl chloride and pyridine giving products in good yield.
2. The subsequent alkenes produced are surprisingly electrophilic in nature and react with bromine or peracids giving the corresponding dibromides as well as epoxides in good yield.
3. Acid catalysed ring opening of such epoxides occurs easily giving 1,2-diols containing a polyfluoroalkyl group, in high yield.
4. Dehydrogenation of alkenes containing one attached polyfluoroalkyl group is easily achieved using sulphur, producing aromatics in quantitative yield.

CHAPTER 4

REACTIONS INVOLVING THE USE OF A C-H BOND IN HYDROCARBONS AS A FUNCTIONAL GROUP FOR INSERTION OF FLUORO-ALKENES

7.1. Introduction

Basic chemistry explaining the factors influencing hydrocarbon addition to fluoroalkenes and a review of previous work in this field is shown in chapter 1.

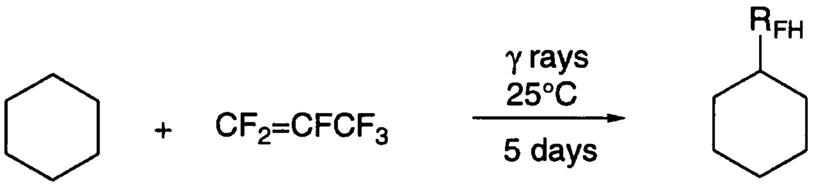
7.2. Our approach involving the use of C-H bonds in hydrocarbons for introducing fluoroalkenes and further reactions of adducts

The aim of this work is to use a C-H bond as a functional group by introducing hydrocarbons into fluoroalkenes, and then performing further reactions on the fluoroalkylated products. In particular, the selectivity of tertiary versus secondary C-H sites is investigated by reactions of hydrocarbons with hexafluoropropene. Also (1,1,2,3,3,3-hexafluoropropyl)-cyclohexane **(13)** is chlorinated[133-135], then dehydrochlorinated[136] creating an alkene with hydrocarbon and polyfluoroalkyl substituents. The chemistry of this alkene is investigated.

7.3. Reactions of non-substituted cyclic hydrocarbons with hexafluoropropene:-

7.3.1. Cyclohexane

A gamma source initiated reaction between cyclohexane and a deficiency of hexafluoropropene to give, as previously reported[18, 37, 39], (1,1,2,3,3,3-hexafluoropropyl)-cyclohexane **(13)** in good yield.



(13) 60%

$R_{FH} = CF_2CFHCF_3$

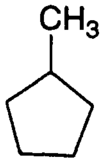
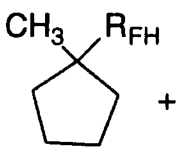
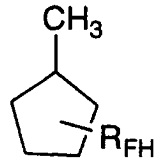
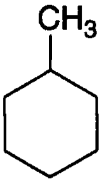
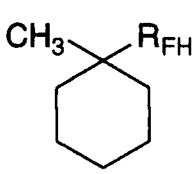
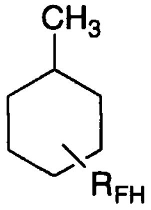
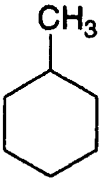
This reaction involved generating a secondary alkyl radical at any of six ring CH_2 sites.

7.4. Reactions of methyl substituted cyclic hydrocarbons with hexafluoropropene :-

7.4.1. Mono - methyl substituted cyclic hydrocarbons

Methylcyclohexane and methylcyclopentane contain one tertiary C-H site which is expected[2] to be more reactive towards hexafluoropropene addition than the remaining secondary C-H positions. As mentioned earlier, a tertiary radical is easier to generate[2], as well as being more nucleophilic than a secondary radial, and will therefore add in preference to an electron deficient alkene such as hexafluoropropene. However, the reaction between either methylcyclohexane or methylcyclopentane was found to give a complex final reaction mixture containing mono adducts formed by addition at secondary as well as tertiary C-H sites (table 18).

Table 18 :- Reactions of mono methyl cycloalkanes with hexafluoropropene
$R_{FH} = CF_2CFHCF_3$

Hydrocarbon	Cond^n	Conv^n of HFP (%)	Product (s) , yields (%)
	25°C^a 10d	35	 +  (52) (53) 9% ratio of mono adducts :- 52 : 40 : 8 and a trace of di-adducts.
	25°C^a 10d	15	  (55) (56) 6% ratio of mono adducts :- 49 : 25 : 8 : 5 : 5: 5 : 4 and a trace of di-adducts
	140°C^b 24h	52	Products as above. Ratio of mono adducts not available. N/Y

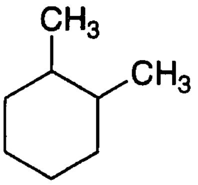
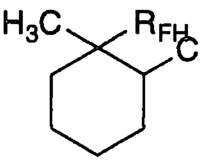
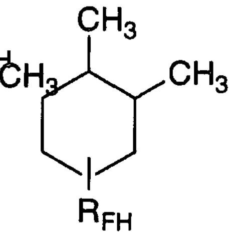
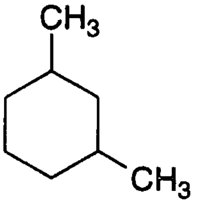
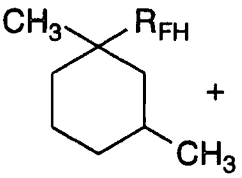
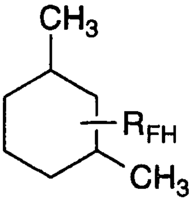
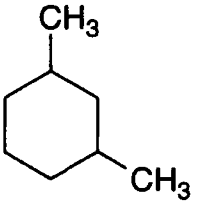
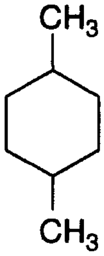
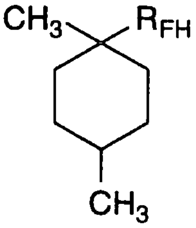
a) γ rays
b) D.T.B.P.
N/Y:- No yield recorded

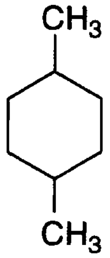
It can be concluded that in such systems, the one tertiary C-H site is not so much more reactive as to outweigh the statistical advantage (e.g. 10 secondary : 1 tertiary with methyl cyclohexane) of the secondary C-H positions. This differs from cyclohexanol addition to hexafluoropropene, in which the activating / deactivating effects of oxygen outweigh the statistical advantage of secondary C-H sites.

7.4.2. Di - methyl substituted cyclic hydrocarbons

The reactions of various dimethylcyclohexanes with hexafluoropropene is shown in table 19.

Table 19 :- Reactions of dimethylcyclohexanes with hexafluoropropene

Hydrocarbon	**Cond^n**	**Conv^n of HFP (%)**	**Products (s) (yield, %)** **R_{FH} = CF_2CFHCF_3**
	140°C^b 24h	63	 **(58)**  **(59)** 31% and a mixture of di-adducts.
	25°C^a 10d	12	 **(61)** +  **(62)** N/Y
	140°C^b 24h	93	Products as above 18.8% Ratio of mono adducts :- 54 : 18 : 8 : 8 : 5 : 5
	25°C^a 10d	30	 **(63)** 16%

	140°C[b] 24h	39	Major product as above. N/Y Ratio of mono-adducts 75 : 11 : 7 : 4 : 3 Ratio of di-adducts 53 : 22 : 14 : 3

a) γ rays
b) D.T.B.P.
N/Yindicates no yield recorded

As can be seen from table 19, the reaction of 1,4-dimethylcyclohexane with hexafluoropropene yielded only one major mono -adduct product, formed from addition at either tertiary C-H site. Conversely, the reactions of 1,3-dimethylcyclohexane or 1,2 dimethylcyclohexane with hexafluoropropene yielded mono adducts formed from addition at both tertiary as well as secondary C-H sites, and least selectivity was shown by the 1,2 dimethyl cyclic system.

Hence it can be concluded that the selectivity of 1,2-dimethylcyclohexane, 1,3-dimethylcyclohexane and 1,4-dimethylcyclohexane towards addition to hexafluoropropene at tertiary C-H sites is as follows :-

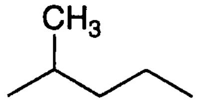
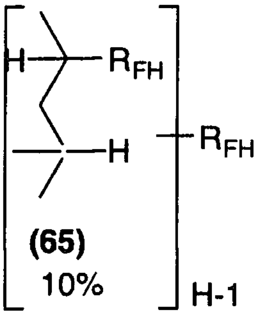
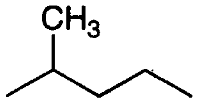
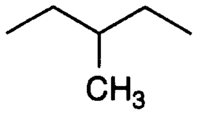
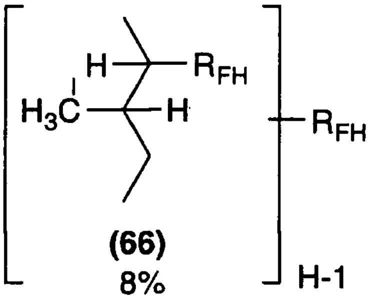
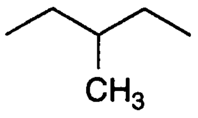
1,4-dimethylcyclohexane >> 1,3 dimethylcyclohexane >> 1,2-dimethylcyclohexane.

In all three dimethylcyclohexane systems the ratio of tertiary C-H sites to secondary C-H sites is 4 : 1, and hence the difference in selectivity must arise as a consequence of steric factors. Since least selectivity towards tertiary sites was shown by 1,2-dimethylcyclohexane, it is suggested that steric bulk of both methyl groups at adjacent carbon positions is hindering attack on hexafluoropropene, and consequently addition is also occurring at the less reactive (2° C-H site) and less hindered ring CH_2 positions. Furthermore, 1,4-dimethylcyclohexane showed by far the greatest selectivity, since steric effects of both methyl groups are at a minimum being at opposite ends of a ring system, and consequently allowing the greater reactivity of tertiary C-H sites to dominate. Addition of 1,3-dimethylcyclohexane to hexafluoropropene is affected by steric factors but the influence of such effects is not as strong as for 1,2-dimethylcyclohexane.

7.5. Reactions of acyclic hydrocarbons with hexafluoropropene

The addition of either 2-methylpentane or 3-methylpentane to hexafluoropropene yielded a di-hexafluoropropyl adduct (s) (table 20).

Table 20 :- Reactions of various acyclic hydrocarbons with hexafluoropropene $R_{FH} = CF_2CFHCF_3$

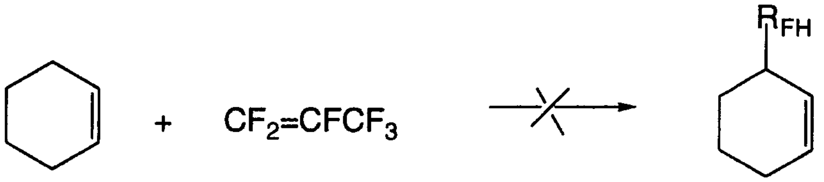
Hydrocarbon	Cond^n	Conv^n of HFP	Products^a
	25°C^c 10d	18^b	 (65) 10% H-1
	140°C^d 24h	34	Products as above. 4.1% ratio :- 26 : 25 : 15 : 14 : 9 : 4 : 4 :4.
	25°C^c 10d	10^b	 (66) 8% H-1 ratio of products :- 43 : 35 : 13 : 9.
	140°C 24h	39	Products as above. 4.7% ratio :- 33 : 19 : 17 : 14 : 9 : 3 : 3 : 3.

a) Ratios quoted by g.c..
b) Yields estimated by g.c..
c) γ rays
d) D.T.B.P.

Any such product with either of these two compounds will have four stereogenic centres, and can therefore exist as 16 stereoisomers. On the basis of radical reactivity[2], it is expected that addition has taken place at one tertiary site and a secondary position. However, the complexity of all spectra has made it impossible to identify the individual products.

7.6. Attempted reaction of cyclohexene with hexafluoropropene

Radicals of the allylic type are more stable, and less reactive than simple alkyl radicals, because of delocalisation of the unpaired electron over a pi orbital system[2].
A reaction involving heating cyclohexene and hexafluoropropene in a rocking autoclave for four days at 320°C, followed by fractional distillation gave very complex multicomponent mixtures, as previously reported[17].



$R_{FH} = CF_2CFHCF_3$

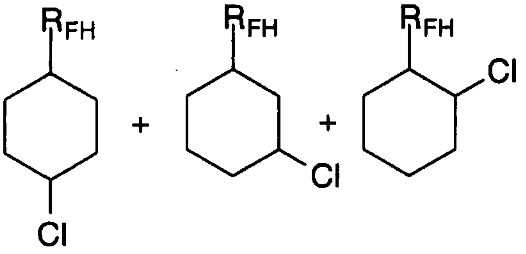
The desired product was not identified by g.l.c.-m.s. and this method was abandoned.

8.0. Functionalisation of (1,1,2,3,3,3-hexafluoropropyl)-cyclohexane (13)

8.1. Methodology for chlorination

8.1.1. Direct chlorination using chlorine gas

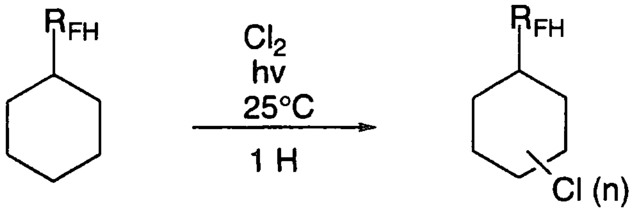
Chambers et al[137] showed previously, applying Hammonds[138] postulate, that if chlorination of hydrocarbons occurs via a transition state favoured by polar effects, it would involve attack of a chlorine atom at the least electrophilic C-H site. If such a transition state is formed in the reaction of compound (**13**) with chlorine, the product ratios of mono chloro derivatives would be (**67**) >> (**68**) >> (**69**).



(67) **(68)** **(69)**

$R_{FH} = CF_2CFHCF_3$

Chlorine gas[133] was bubbled through (1,1,2,3,3,3-hexafluoropropyl)-cyclohexane (**13**) and g.l.c.-m.s. analysis of the final reaction mixture showed six major peaks (7.2 : 5.4 : 3.9 : 2.6 : 1.2 : 1.0) all giving a highest mass ion equal to 232 (M^+ - HCl), and were identified as mono - chloro derivatives, illustrating this method of chlorination is not very selective.



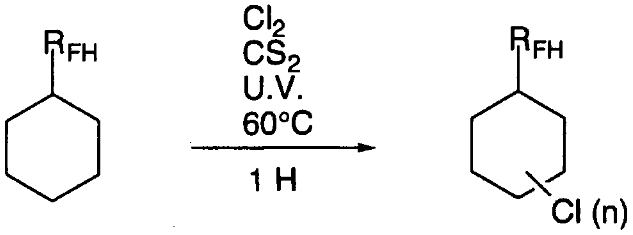
(13) (67-69)

$R_{FH} = CF_2CFHCF_3$
n = 1, 2, 3

Furthermore, the poor selectivity of this method was further confirmed by formation of dichloro derivatives, which are identified by seven major peaks (5.5 : 2.9 : 1.8 : 1.8 : 1.2 : 1.2 : 1.0) in g.l.c.-m.s.

8.1.2. Chlorine gas with carbon disulphide as solvent

It was reported[137] that the selectivity of direct chlorination can be improved by using carbon disulphide as a solvent. A mixture of chlorine gas, compound **(13)** and carbon disulphide, irradiated with U.V. light for one hour, yielded as shown by g.l.c.-m.s., mainly mono - chloro derivatives, with a smaller quantity of dichloro derivatives, and an overall 88% conversion of starting material.



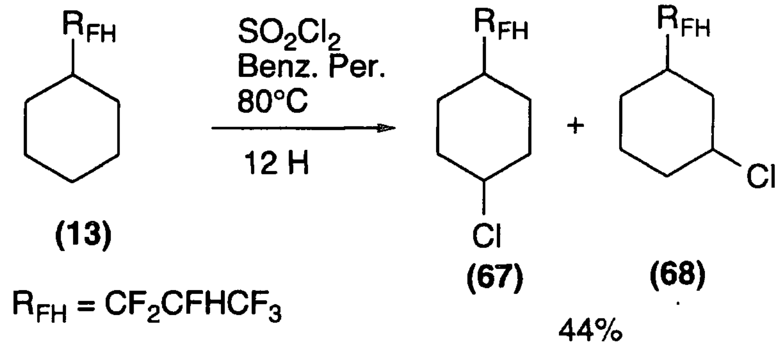
(13) (67-69)

$R_{FH} = CF_2CFHCF_3$
n = 1, 2

Hence the chlorine radical has been solvated by carbon disulphide, making chlorination more selective.

8.1.3. Sulphuryl chloride

A mixture of compound **(13)**, sulphuryl chloride[134, 135] and benzoyl peroxide, refluxed at 75°C for 12 hours, yielded a mixture of compounds **(67)** and **(68)**.

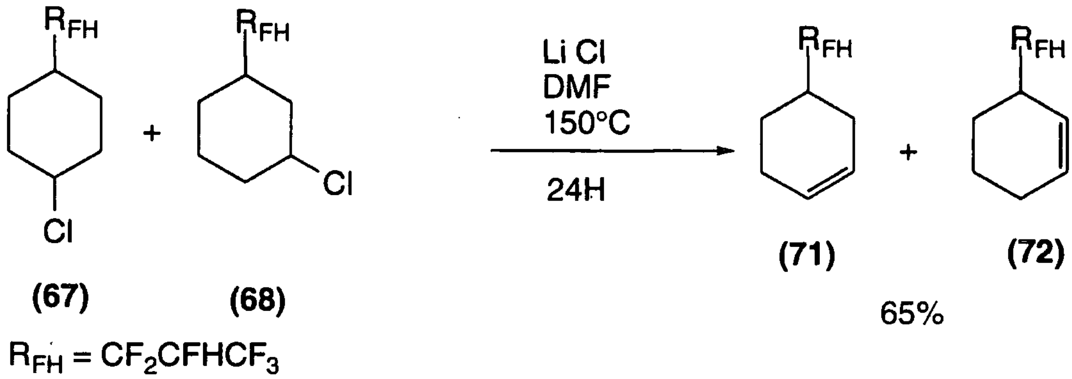


(13) **(67)** **(68)**

Subsequent dehydrochlorination[136] of this mixture yielded mainly compound **(71)**, proving that initial chlorination mainly occurred at the most electron rich C-H site i.e. compound **(67)** is the major product. It was thought that compound **(67)** would crystallise from a mixture containing **(67)** and **(68)**, since the former is more symmetrical. A neat solution of the mono-chloroderivative mixture was found to solidify at -72°C. This solution was cooled to a range of temperatures (-20°C, -40°C) but no selective crystallisation occurred.

8.2. Methodology for dehydrochlorination

A mixture of lithium chloride[136], DMF and compounds **(67+68)** refluxed at 150°C for 24 hours, yielded mainly compound **(71)** (ca. 80%) and a smaller quantity of **(72)** (ca. 20%) in good yield (65%).



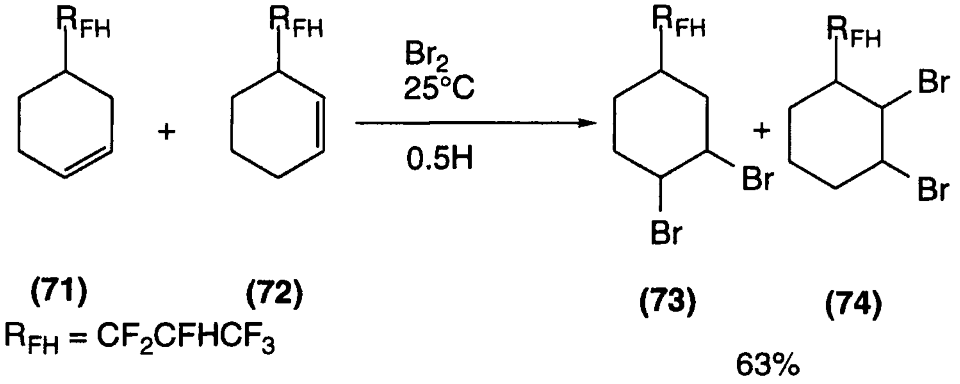
(67) **(68)** **(71)** **(72)**

However subsequent methodology discussed earlier[116] suggests that dehydrochlorination of the monochloro derivative mixture could be achieved in high yield by simply stirring with anhydrous pyridine for 24 hours.

8.3. Reactions of mixture of mainly 4-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene (71) and small quantity of 3-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene (72)

8.3.1. Bromination

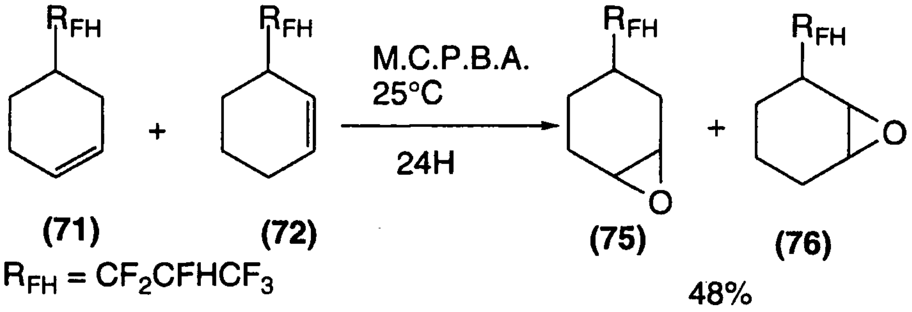
A mixture of mainly compound **(71)** as well as small quantity of **(72)** and bromine[126], stirred for 30 minutes at 0°C, yielded **(73)** (ca. 80%) as the major product.



The existence of four stereogenic centres in both compounds complicates spectra.

8.3.2. Epoxidation

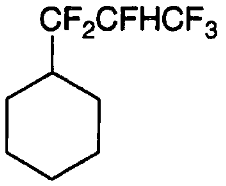
A mixture of mainly compound **(71)** and a small quantity of **(72)**, as well as M.C.P.B.A.[139], dissolved in sodium carbonate solution, was heated at 60°C for 5 hours, yielding **(75)** (ca. 80%) as the major product.



This confirms the double bond is electrophilic in nature, despite the presence of a polyfluoroalkyl group.

8.4. Characterisation of products

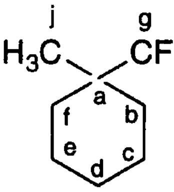
8.4.1. (1,1,2,3,3,3-Hexafluoropropyl)-cyclohexane (13)



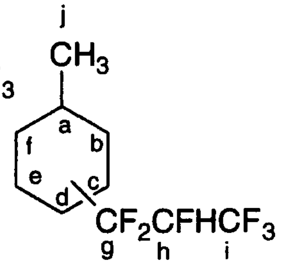
(13)

The addition of cyclohexane to hexafluoropropene giving compound **(13)**, was confirmed by comparing spectral data with that previously reported[18, 37, 39].

8.4.2. (1,1,2,3,3,3-Hexafluoropropyl)-methylcyclohexanes (55) / (56)



(55)



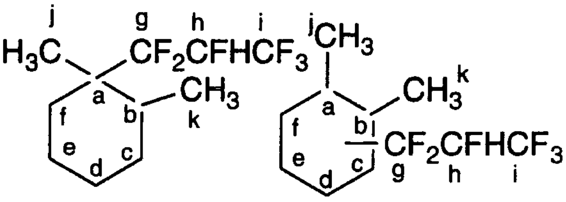
(56)

All spectra for compounds **(55)** and **(56)** are complicated. The hexafluoropropyl moiety's presence is confirmed[49] as previously by ^1H NMR, ^{19}F NMR and ^{13}C NMR.

The ^{19}F NMR also shows no evidence of hydrocarbon addition to the internal site of hexafluoropropene. Where has the hexafluoropropyl moiety attached to the ring? Generally, the complexity of ^1H NMR and ^{19}F NMR indicated multisite attack. This is further confirmed by g.l.c.-m.s..

^{13}C DEPT NMR spectra were the most revealing. Here, triplets at 48.4ppm as well as 49.5 ppm assigned[49] to C(**a**) in compound **(55)**, with coupling constants characteristic of $^2J_{C\text{-}F}$ coupling with CF_2, illustrate that some of the derived products have been formed by addition at the tertiary C-H site. However, triplets at 42.07 ppm assigned[49] to C(**c**) or C(**d**) or C(**e**) in compounds **(56)**, confirm multisite addition at secondary C-H sites. Furthermore, from ^1H NMR, multiplets at 3.5-3.7 ppm, assigned[49] as arising from C-H, and the presence of C-H bonds in the ^{13}C DEPT NMR, also show that hexafluoropropyl moieties have added at non-tertiary C-H sites as well as tertiary positions.

8.4.3. (1,1,2,3,3,3-Hexafluoropropyl)-1,2-dimethylcyclohexanes (58) / (59)



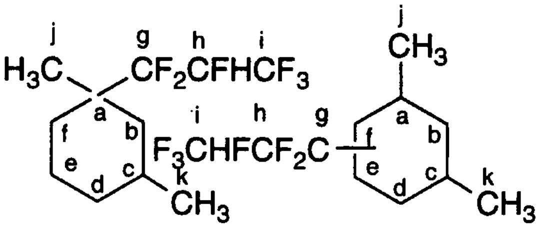
(58) **(59)**

A reaction between 1,2-dimethylcyclohexane and hexafluoropropene gave a mixture containing adducts **(58)** / **(59)** as confirmed by elemental analysis, ^{1}H NMR, ^{19}F NMR and ^{13}C NMR.

The structure of the polyfluoroalkyl group is confirmed by ^{1}H NMR and ^{19}F NMR as discussed for previous compounds. There was no evidence for addition of 1,2-dimethylcyclohexane to the fluoroolefin C-F site. Where has the hexafluoropropyl moiety added to 1,2-dimethylcyclohexane ? Again, generally, the complexity of ^{19}F NMR as well as^{1}H NMR and ^{13}C DEPT NMR indicated multi-site attack. This is further confirmed by g.l.c.-m.s..

However, ^{13}C DEPT NMR is most revealing. Here, triplets at 48.5 ppm as well as 49.8 ppm, are assigned[49] to **C(a)** in compound **(58),** and the coupling constant values (19.5 Hz) are characteristic of $^{2}J_{C\text{-}F}$ coupling with CF_2. This confirms that some tertiary C-H site addition has occurred. Furthermore, triplets at 42.29 ppm, assigned[49] to **C(d)** and **C(e)** in compounds **(59)**, illustrate addition at secondary C-H sites. Also, ^{13}C DEPT shows the presence of many C-H bonds in the region 32-42 ppm, again confirming addition of hexafluoropropene to secondary C-H sites.

8.4.4. (1,1,2,3,3,3-Hexafluoropropyl)-1,3-dimethylcyclohexanes (61) / (62)



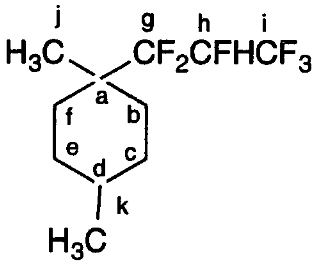
(61) **(62)**

A reaction between 1,3-dimethylcyclohexane and hexafluoropropene gave a mixture of monoadducts **(61)** / **(62)**, as confirmed by elemental analysis, ^{1}H NMR, ^{19}F NMR and ^{13}C DEPT NMR.

The same general comments mentioned for 1,2-dimethylcyclohexane addition to hexafluoropropene apply with 1,3-dimethylcyclohexane. However, ^{19}F NMR as well as ^{13}C NMR spectra are not as complex as for 1,2-dimethylcyclohexane, suggesting that this reaction was more selective, but some addition at non-tertiary C-H sites still occurs.

Again, ^{13}C DEPT NMR is most revealing where triplets at 48.0 ppm as well as 49.5 ppm, show[49] some polyfluoroalkyl addition to **C(a)** in compound **(61)**. As previously, triplets at 41.70 ppm assigned[49] to **C(e)** in compounds **(62)**, illustrate some addition of hexafluoropropene to secondary C-H sites.

8.4.5. 1-(1,1,2,3,3,3-Hexafluoropropyl)-1,4-dimethylcyclohexane (63)



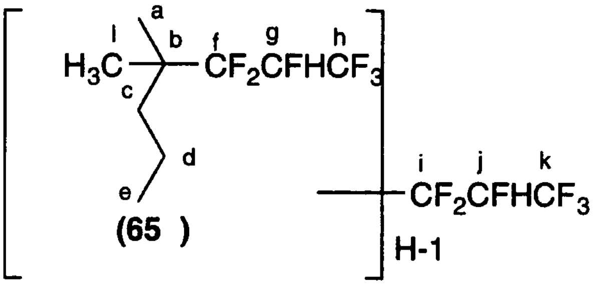
(63)

A reaction between 1,4-dimethylcyclohexane and hexafluoropropene yielding 1-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dimethylcyclohexane is confirmed by elemental analysis, ^{1}H NMR, ^{19}F NMR and ^{13}C NMR.

Again, ^{19}F NMR confirms[49] 1,4-dimethylcyclohexane addition exclusively at the CF_2 end of hexafluoropropene. However, all spectra are less complicated than for previous dimethylcyclohexanes indicating the greater selectivity of this reaction. In particular, formation of only one main product is confirmed[49] by a simple ^{19}F NMR spectrum, in which only one signal for each of theCF_3, CF_2 as well as CFH groups was observed.

Furthermore, a simple (non- complex) ^{13}C DEPT NMR spectrum shows the site selectivity of this reaction, where a triplet at 41.8 ppm is assigned[49] as arising from **C(a)**, and the coupling constant is characteristic of $^{2}J_{C\text{-}F}$ coupling with $\mathbf{CF_2}$.

8.4.6. Di-(1,1,2,3,3,3-hexafluoropropyl)-2-methylpentanes (65)

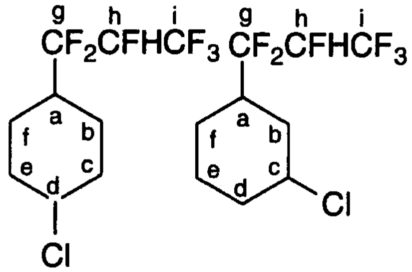


(65)

The reaction involving 2-methylpentane and hexafluoropropene creates di-HFP adducts as confirmed by elemental analysis, ^{1}H NMR, ^{19}F NMR and ^{13}C NMR data.

The spectra are extremely complicated and difficult to assign since any di-adduct formed will have four stereogenic centres and hence exist as 16 stereoisomers. In the ^{1}H NMR, multiplets (area = 2H) at 4.8-5.0ppm confirm[49] addition of two hexafluoropropyl groups to 2-methylpentane. The ^{19}F NMR and ^{13}C NMR spectra are too complex for drawing any firm conclusions.

8.4.7. A mixture of 1-(1,1,2,3,3,3-hexafluoropropyl)-4-chlorocyclohexane (67) and 1-(1,1,2,3,3,3-hexafluoropropyl)-3-chlorocyclohexane (68)



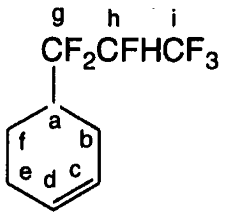
(67) **(68)**

Formation of compounds (**67**) and (**68**) is shown by elemental analysis, ^{1}H NMR, ^{13}C NMR and g.l.c.-m.s.. All spectra are complex and assignment is difficult.

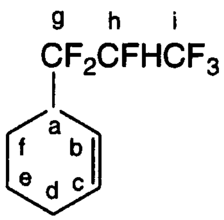
Chlorination is confirmed by the ^{1}H NMR spectrum, where multiplets at 4.55 ppm as well as 3.93 ppm, are assigned[49] as arising from hydrogen attached to the same carbon as chlorine, in compounds (**68**) and (**67**) respectively. In the ^{13}C NMR spectra key signals include multiplets at 47.8 ppm as well as 41.1 ppm, which are assigned[49] as arising from **C(c)** / **C(d)** in compounds (**68**) and (**67**) respectively.

Furthermore, in g.l.c.-m.s., a highest mass ion equal to 232 (int. 3.9%) corresponds to loss of HCl from the molecular ion.

8.4.8. A mixture mainly containing 4-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene (71) and a small quantity of 3-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene (72)



(71)



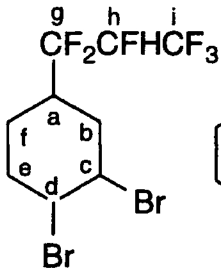
(72)

That formation of compounds (**71**) and (**72**) was achieved is shown by ^{1}H NMR, ^{19}F NMR and g.l.c.-m.s..

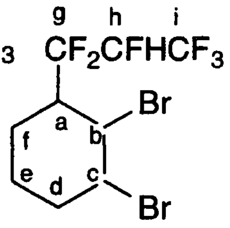
^{1}H NMR spectra show multiplets at 5.68 ppm (int. 2H), which are assigned[49] as arising from both vinylic hydrogens in compounds (**71**) and (**72**).

Furthermore, the ^{19}F NMR spectrum show one major signal for each of the CF_3, CF_2 and CFH, suggesting the final reaction mixture is mostly probably almost entirely compound **(71)** since the starting mixture is mainly **(67)** with a little **(68)** as explained earlier. G.l.c.-m.s.. shows one major peak and a minor peak with masses equal to 232, assigned as molecular ions, further suggesting that the final mixture is mainly compound **(71)**.

8.4.9. A mixture containing mainly 1-(1,1,2,3,3,3-hexafluoropropyl)-3,4-dibromocyclohexane (73) and a small quantity of 1-(1,1,2,3,3,3-hexafluoropropyl)-2,3-dibromocyclohexane (74)



(73)



(74)

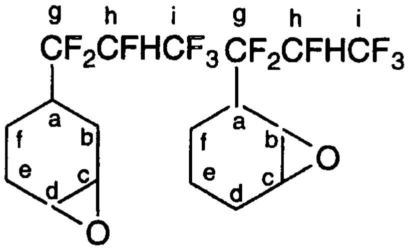
A mixture of compounds (73) and (74) is shown by ^{1}H NMR, ^{19}F NMR and g.l.c.-m.s..

The ^{19}F NMR spectrum is simple, showing one main peak for each of the CF_3, CF_2 and CFH, illustrating the final reaction mixture is probably mainly compound **(73)** since the starting material is most likely to be mainly compound **(71)**.

The ^{1}H NMR spectrum shows multiplets at 4.5-4.9 ppm (int. = 4H), which are assigned[49] as arising mainly from hydrogens attached to **C(a)**, **C(c)**, **C(d)** and **C(h)** in compound **(73)**.

G.l.c.-m.s. spectra show major ions with mass equal to 231 (intensity 100%), assigned[49] as loss of HBr from the molecular ion.

8.4.10. A mixture mainly containing 4-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexeneoxide (75) and a small quantity of 3-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexeneoxide (76)



(75) **(76)**

Confirmation of an epoxide mixture is shown by ^{1}H NMR and g.l.c.-m.s..

The ^{1}H NMR spectrum shows singlets at 3.3 ppm as well as 3.2 ppm, which are assigned[49] as arising mainly from hydrogens within the epoxide ring in compounds (75).

G.l.c.-m.s. shows highest mass ions equal to 248, which is assigned[49] as arising from compounds **(75)** and **(76)**. Furthermore, two major peaks are assigned to cis / trans forms of compound **(75)** since the starting material is mainly most probably compound **(71)**.

8.5. Summary and conclusions

1. 1,4-Dimethylcyclohexane reacts with hexafluoropropene forming a major mono - adduct, arising from tertiary C-H site addition.
2. 1,3- and 1,2-Dimethylcyclohexane react with hexafluoropropene to give mono adducts in a complex final reaction mixture, in which addition is at secondary as well as tertiary C-H sites, reflecting that steric effects of both methyl groups are influencing the position of attack of the hydrocarbon on the fluoro-alkene.
3. Methylcyclohexane and methylcyclopentane react with hexafluoropropene to give complex mono-adduct mixtures in which addition is occurring at secondary as well as tertiary C-H sites. In this case, the statistical advantage of secondary C-H sites is competing effectively with the extra stability of a tertiary C-H site.
4. The chlorination / dehydrochlorination of (1,1,2,3,3,3-hexafluoropropyl)-cyclohexane gives a mixture containing mainly 4-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene. This product following epoxidation and bromination of the C=C double bond, is found to be electrophilic in nature.

INSTRUMENTATION

Distillation

Fractional distillation of lower boiling point mixtures (up to 200°C/1mmHg) was carried out using a Fischer Spahltrohr MMS 255 small concentric tube apparatus. Higher boiling materials were distilled using a Buchi kugelrohr GKR-51 apparatus. Boiling points were recorded during distillation.

Elemental Analysis

Carbon, hydrogen and nitrogen elemental analyses were obtained using a Perkin-Elmer 240 Elemental Analyser or a Carlo Erba Stumentazione 1106 Elemental Analyser. Analysis for halogens were performed as described in the literature[140].

GLC Analysis

Gas Liquid Chromatography (GLC) analysis was carried out on a Hewlett Packard 5890A gas chromatograph with a 25m cross-linked methyl silicone capillary column. Preparative GLC was performed on a Varian Aerograph Model 920 (catharometer detector) gas chromatograph.

IR Spectra

IR spectra were recorded on Perkin-Elmer 457 or 577 Grating Spectrophotometer using conventional techniques.

Mass Spectra

Mass spectra were recorded on a VG 7070E spectrometer. G.l.c.-m.s. were recorded on the VG 7070E spectrometer linked to a Hewlett Packard 5790A gas chromatograph fitted with a 25m cross-linked methyl silicone capillary column. FAB spectra were run on the VG 7070E spectrometer using xenon.

NMR Spectra

^{1}H NMR spectra were recorded on a Hitachi Perkin-Elmer R-24B (60 MHz), a Bruker AC250 (250.13 MHz), a Varian VXR400S (399.952 MHz) and a Bruker AMX500 (500.135 MHz) NMR spectrometer.

^{13}C NMR spectra were recorded on a Varian VXR400S (100.577 MHz).

^{19}F NMR spectra were recorded on a Varian EM3601 (56.45 MHz), a Bruker AC250 (235.34 MHz) and a Varian VXR400S (376.289) NMR spectrometer.

Coupling constants are given in Hz.

Reagents and Solvents

Unless otherwise stated, reagents were used as supplied by the manufacturers.

CHAPTER 5
EXPERIMENTAL TO CHAPTER 2

9.1. General procedure for gamma ray initiated reactions

Solid and liquid reagents were introduced into a pyrex Carius tube (ca. 70 ml) together with dried Analar acetone (10g), and degassed twice by freeze-thawing. Hexafluoropropene was then introduced into the cooled (liquid air) Carius tube using standard vacuum line techniques, the tube then being sealed, and placed in a metal sleeve. After regaining room temperature, the Carius tube was irradiated with γ rays from a ^{60}Co source (85 krad hr^{-1}) for usually ten days. Subsequently, the tube was cooled (liquid air) and opened. Any remaining hexafluoropropene was recovered as the tube returned to room temperature. The residue was fractionally distilled under vacuum yielding pure samples of polyfluoroalkylated products.

9.2. Reactions of hexafluoropropene with:-

9.2.1. Cyclopentanol

A Carius tube charged with cyclopentanol (12.8g, 149 mmol) and hexafluoropropene (28.3g, 189 mmol) dissolved in acetone (10g) was irradiated with gamma rays for ten days. Hexafluoropropene (0.8g, 97.1% conversion) was recovered, and, following fractional distillation, yielded 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentanol **(20)** (27.5g, 78%), as a colourless liquid; b.p. 49.5°C/8mmHg; (Found: C, 41.0; H, 4.5; F, 48.3. $C_8H_{10}F_60$ requires C, 40.7; H, 4.2; F, 48.3%); I.R.. spectrum 1; N.M.R. spectra 1; Mass spectrum 1; and di-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentanols **(21)** as a mixture of isomers (11.0g) which could not be separated but were identified by g.l.c.-m.s.; Mass spectrum 2 .

9.2.2. Cyclohexanol

A Carius tube charged with cyclohexanol (13.7g, 137 mmol) and hexafluoropropene (29.3g, 195 mmol) dissolved in acetone (10g) was irradiated with gamma rays for ten days. Hexafluoropropene (0.7g, 97.6% conversion) was recovered, and, following fractional distillation, yielded 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexanol **(22)** (26.5g, 77.9%), as a colourless liquid; b.p. 64.5°C/8mmHg; (Found: C, 43.0; H, 5.0; F, 45.6. $C_9H_{12}F_60$ requires C, 43.2; H, 4.8, F, 45.6%); I.R. spectrum 6; N.M.R. spectra 22; Mass spectrum 5; and di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexanols **(23)** as a mixture of isomers (7.0g) which could not be separated but were identified by g.l.c.-m.s.; Mass spectrum 6.

9.2.3. Cycloheptanol

A Carius tube charged with cycloheptanol (10.8g, 95 mmol) and hexafluoropropene (17.8g, 119 mmol) dissolved in acetone (10g) was irradiated with gamma rays for ten days. Hexafluoropropene (0.5g, 96.6% conversion) was recovered, and following fractional distillation, yielded 1-(1,1,2,3,3,3-hexafluoropropyl)-cycloheptanol (**24**) (20.1g, 80.1%) as a colourless liquid; b.p. 76.4°C/9mmHg; (Found: C, 45.5; H, 5.4. $C_{10}H_{14}F_6O$ requires C, 45.5; H, 5.3%); I.R. spectrum 7; N.M.R. spectra 3; Mass spectrum 7.

9.2.4. Cyclooctanol

A Carius tube charged with cyclooctanol (11.7g, 91 mmol) and hexafluoropropene (16.3g, 109 mmol) dissolved in acetone (10g) was irradiated with gamma rays for ten days. Hexafluoropropene (0.8g, 95.0% conversion) was recovered, leaving a colourless liquid, which contained (1,1,2,3,3,3-hexafluoropropyl)-cyclooctanols (**25**) and di-(1,1,2,3,3,3-hexafluoropropyl)-cyclooctanols (**26**) as a mixture of isomers (11.0g) which could not be separated but were identified by g.l.c.-m.s.; Mass spectra 8, 9.

9.2.5. 4-Methylcyclohexanol

A Carius tube charged with 4-methycyclohexanol (15.7g, 137 mmol) and hexafluoropropene (22.6g, 151 mmol) dissolved in acetone (10g) was irradiated with gamma rays for seven days. No volatile material was recovered (100% conversion of hexafluoropropene). The resulting colourless liquid was fractionally distilled yielding 1-(1,1,2,3,3,3-hexafluoropropyl)-4-methylcyclohexanol (**29**) (26.5g, 77.9%) as a mixture of diastereoisomers; b.p. 60.0°C/8mmHg; (Found: C, 45.5; H, 5.4. $C_{10}H_{14}F_6O$ requires C, 45.5; H, 5.3%); I.R. spectrum 8; N.M.R. spectra 4; Mass spectrum 10; and di-(1,1,2,3,3,3-hexafluoropropyl)-4-methylcyclohexanols (**30**) as a mixture of isomers which could not be separated but were identified by g.l.c.-m.s.; Mass spectrum 11.

9.2.6. 3-Methylcyclohexanol

A Carius tube charged with 3-methylcyclohexanol (10.3g, 90 mmol) and hexafluoropropene (21.3g, 142 mmol) dissolved in acetone (10g) was irradiated with gamma rays for ten days. Hexafluoropropene (1.2g, 94.0% conversion) was recovered, leaving a colourless liquid which, after fractional distillation, yielded 1-(1,1,2,3,3,3-hexafluoropropyl)-3-methylcyclohexanol (**27**) (19.2g, 80.7%) as a mixture of diastereoisomers; b.p. 61.0°C/8mmHg; (Found: C, 45.3; H, 5.2. $C_{10}H_{14}F_6O$ requires C, 45.5; H, 5.3%); I.R. spectrum 9; N.M.R. spectra 5; Mass spectrum 12; and di-(1,1,2,3,3,3-hexafluoropropyl)-3-methylcyclohexanols (**28**) as a mixture of isomers which could not be separated but were identified by g.l.c.-m.s.; Mass spectrum 13.

9.2.7. 1,2-Cyclohexanediol

A Carius tube charged with 1,2-cyclohexanediol (9.1g, 79 mmol) and hexafluoropropene (26.0g, 173 mmol) dissolved in acetone (10g) was irradiated with gamma rays for ten days. Hexafluoropropene (26.0g, 0% conversion) and starting materials were recovered unchanged.

9.2.8. 1,3-Cyclopentanediol

A Carius tube charged with 1,3-cyclopentanediol (5.0g, 49 mmol) and hexafluoropropene (15.4g, 103 mmol) dissolved in acetone (10g) was irradiated with gamma rays for ten days. Hexafluoropropene (2.4g, 84.4% conversion) was recovered, leaving a colourless liquid which, after fractional distillation, yielded a white solid, 1,3-di-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentane-1,3-diol **(31)** (14.0g, 71.1%), as a mixture of diastereoisomers; b.p. 95.3°C/5mmHg; (Found: M^- 401.038561. $C_{11}H_9F_{12}O_2$ requires M^- 401.041094.); I.R. spectrum 10; N.M.R. spectra 6; Mass spectrum 14.

9.2.9. 1,3-Cyclohexanediol

A Carius tube charged with 1,3-cyclohexanediol (8.3g, 72 mmol) and hexafluoropropene (25.8g, 172 mmol) dissolved in acetone (10g) was irradiated with gamma rays for ten days. Hexafluoropropene (7.8g, 70.0% conversion) was recovered leaving the product in acetone. Solvent removal, followed by column chromatography on silica using 9 :1 ether and hexane as elutant yielded a white solid, 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexane-1,3-diol **(32)** (8.0g, 71.1%), as a mixture of diastereoisomers; b.p. 95.3°C/5mmHg; (Found: C, 40.5; H, 4.5; F, 42.9. $C_9H_{12}F_6O_2$ requires C, 40.6; H, 4.5, F, 42.9%); I.R. spectrum 11; N.M.R. spectra 7; Mass spectrum 15; and 1,3-di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexane-1,3-diol **(33)** (16.6g, 55.5%) as a white solid; m.p. 56°C; (Found: C, 34.3; H, 2.6. $C_{12}H_{12}F_{12}O_2$ requires C, 34.6; H, 2.9%); I.R. spectrum 12; N.M.R. spectra 8; Mass spectrum 16.

9.2.10. 1,4-Cyclohexanediol

A Carius tube charged with 1,4-cyclohexanediol (8.0g, 69 mmol) and hexafluoropropene (24.8g, 165 mmol) dissolved in acetone (10g) was irradiated with gamma rays for ten days. Hexafluoropropene (2.0g, 92% conversion) was recovered leaving the product partially miscible in acetone. Solvent removal, followed by drying in a desiccator, yielded a white solid, 1,4-di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexane-1,4-diol **(34)** (27.7g, 96.9%), as a mixture of diastereoisomers; m.p.

118°C; (Found: C, 34.7; H, 2.9; F, 54.6. $C_{12}H_{12}F_{12}O_2$ requires C, 34.6; H, 2.9, F, 54.8%); I.R. spectrum 13; N.M.R. spectra 9; Mass spectrum 17.

9.2.11. 1,4-Cyclooctanediol

A Carius tube charged with 1,4-cyclooctanediol (5.0g, 35 mmol) and hexafluoropropene (12.0g, 80 mmol) dissolved in acetone (10g) was irradiated with gamma rays for ten days. Hexafluoropropene (12.0g, 0% conversion) and starting materials were recovered unchanged.

9.2.12. 1,5-Cyclooctanediol

A Carius tube charged with 1,5-cyclooctanediol (9.2g, 64 mmol) and hexafluoropropene (19.1g, 127 mmol) dissolved in acetone (10g), was irradiated with gamma rays for ten days. Hexafluoropropene (12.7g, 34% conversion) was removed leaving a white solid suspended in acetone. G.l.c.-m.s. analysis suggested the formation of tri-hexafluoropropyl adducts **(35)** ; Mass spectrum 18.

9.2.13. 2,4-Pentanediol

A Carius tube charged with 2,4-pentanediol (7.9g, 75 mmol) and hexafluoropropene (23.8g, 159 mmol) dissolved in acetone (10g) was irradiated with gamma rays for ten days. Hexafluoropropene (3.8g, 84% conversion) was recovered, and, following fractional distillation, yielded 2,4-di-(1,1,2,3,3,3-hexafluoropropyl)-pentane-2,4-diol **(36)** (25.5g, 84%) as a colourless liquid; b.p. 105.9°C/4mmHg; (Found: C, 33.0; H, 3.1; M^- 403.057466. $C_{11}H_{12}F_{12}O_2$ requires C, 32.7; H, 3.0%; M^- 403.056744); I.R. spectrum 14; N.M.R. spectra 10; Mass spectrum 19.

9.2.14. 2,5-Hexanediol

A Carius tube charged with 2,5-hexanediol (9.1g, 77 mmol) and hexafluoropropene (25.4g, 169 mmol) dissolved in acetone (10g), was irradiated with gamma rays for ten days. Hexafluoropropene (8.0g, 68.5% conversion) was recovered, and following fractional distillation, yielded 2,5-di-(1,1,2,3,3,3-hexafluoropropyl)-hexane-2,5-diol **(37)** (16.5g, 51.4%), as a colourless liquid; b.p. 90.2°C/3mmHg; (Found: M^- 417.070250. $C_{12}H_{13}F_{12}O_2$ requires M^- 417.072394.); I.R. spectrum 15; N.M.R. spectra 11; Mass spectrum 20.

9.2.15. Competition between 2,4-pentanediol and 2,5-hexanediol

A Carius tube charged with 2,4-pentanediol (9.7g, 93 mmol), 2,5-hexanediol (11.0g, 93 mmol) and hexafluoropropene (1.4g, 9.3 mmol) dissolved in acetone (10g) was irradiated with gamma rays for ten days. Hexafluoropropene (0.4g, 71.4% conversion) was recovered. G.l.c. analysis showed that the proportion of 2,4-pentanediol in the mixture had dropped from 43.2% to 39.0%, while 2,5-hexanediol had changed from 56.8% to 48.8%, illustrating little difference in the reaction rate of each diol; G.c. spectrum 21.

9.3. General procedure for peroxide initiated reactions

Peroxide initiated reactions were performed in nickel autoclaves (ca. 125 ml, fitted with bursting discs, maximum working pressure 220 atm) into which any solid and liquid reagents were charged. The autoclave was then sealed using a copper gasket and, as before, degassed twice by freeze-thawing. Hexafluoropropene was introduced into the cooled (liquid air) autoclave as before and the valve closed. The autoclave was then heated, whilst rocking, in a purpose built cell for 20 hours. Subsequently, the autoclave was cooled (liquid air) and opened. Any remaining hexafluoropropene was recovered as it returned to room temperature and the residue was fractionally distilled under vacuum , yielding pure samples of polyfluoroalkylated products.

9.4. Reaction of hexafluoropropene with:-

9.4.1. Cyclopentanol

A mixture of cyclopentanol (9.1g, 106 mmol), hexafluoropropene (17.7g, 118 mmol) and di-tert.-butyl peroxide (1.6g, 10 mmol) was reacted in a rocking autoclave at 140°C for 24 hours. Removal of excess hexafluoropropene (0.4g, 97.7% conversion), followed by fractional distillation, yielded 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentanol **(20)** (20.2g, 80.8%); Mass spectrum 3; and a mixture of di-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentanols **(21)** (5.9g, 14.4%); Mass spectrum 4.

9.4.2. 2,4-Pentanediol

A mixture of 2,4-pentanediol (7.9g, 76 mmol), hexafluoropropene (26.3g, 175 mmol) and di-tert.-butyl peroxide (1.7g, 11 mmol) was heated in a rocking autoclave at 140°C for 24 hours. Excess hexafluoropropene (13.1g, 50.2% conversion) was removed, and g.l.c.-m.s. analysis of the final mixture confirmed formation of only 2,4-di-(1,1,2,3,3,3-hexafluoropropyl)-pentane-2,4-diol **(36)**; Mass spectrum 23.

CHAPTER 6
EXPERIMENTAL TO CHAPTER 3

10.1. General procedure for synthesis of alkenes and dienes[116]

A mixture containing an alcohol or diol, a large excess of thionyl chloride and anhydrous pyridine was stirred at room temperature for 24 hours. The resultant black liquid was poured down a condenser into a stirred mixture of ice and dichloromethane and allowed to reach room temperature. Following separation of the organic layer, the aqueous layer was extracted twice more with dichloromethane (2 x 150ml). All organic extracts were combined and dried ($MgSO_4$). Solvent was removed by atmospheric distillation at 50°C, and the resultant yellow liquid was purified by vacuum transfer, to give pure samples of polyfluoroalkylated alkenes and dienes, as colourless, clear liquids.

10.2. Synthesis of :-

10.2.1. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclopentene (41)

A mixture containing 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentanol **(20)** (24.9g, 110 mmol), thionyl chloride (100.4g, 840 mmol) and dry pyridine (110 ml) gave 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentene **(41)** (14.0g, 60.9%); b.p. 161°C; (Found: C, 44.3; H, 3.7. $C_8H_8F_6$ requires C, 44.0; H, 3.7%); I.R. spectrum 16; N.M.R. spectra 12; Mass spectrum 24.

10.2.2. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene (42)

A mixture containing 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexanol **(22)** (4.7g, 19 mmol), thionyl chloride (20ml) and dry pyridine (15ml) gave 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene **(42)** (14.0g, 60.9%); b.p. 161°C; (Found: C, 47.0; H, 4.5; F, 49.4. $C_9H_{10}F_6$ requires C, 46.6; H, 4.3; F, 49.1%); I.R. spectrum 17; N.M.R. spectra 13; Mass spectrum 25.

10.2.3. A mixture of 1,4-di-(1,1,2,3,3,3-hexafluoropropyl)-1,3-cyclohexadiene (43) and 1,4-di-(1,1,2,3,3,3-hexafluoropropyl)-1,4-cyclohexadiene (44)

A mixture containing 1,4-di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexan-1,4-diol **(34)** (6.9g, 17 mmol), thionyl chloride (40.4g, 340 mmol) and dry pyridine (32.4g, 410 mmol) gave a mixture of 1,4-di-(1,1,2,3,3,3-hexafluoropropyl)-1,3-cyclohexadiene **(43)** and 1,4-di-(1,1,2,3,3,3-hexafluoropropyl)-1,4-cyclohexadiene **(44)** (60 : 40) (2.7g, 42%); b.p. 147°C; (Found: M^+, 380.0434000. $C_{12}H_8F_{12}$ requires M^+, 380.1783600); I.R. spectrum 18; N.M.R. spectra 14; Mass spectrum 26.

10.3. General procedure for bromination of perfluoroalkylated alkenes[126]

Bromine was added dropwise to a polyfluoroalkylated alkene cooled to 0°C until this mixture was permanently brown, and the resultant solution was stirred at room temperature for a further 30 minutes. The mixture was washed with dilute sodium metabisulphite solution (2 x 50 ml), extracted with dichloromethane (3 x 25 ml) and all extracts combined, then dried ($MgSO_4$). Dichloromethane was removed by atmospheric distillation at 50°C to yield a crude product mixture which, after fractional distillation using the Spahltrohr apparatus, gave pure colourless liquids of polyfluoroalkylated dibromides.

10.4. Synthesis of :-

10.4.1. 1-(1,1,2,3,3,3-Hexafluoropropyl)-1,2-dibromocyclopentane (45)

Bromine (7.9g, 44 mmol) and 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentene **(41)** (3.5g, 16 m mol) gave pure 1-(1,1,2,3,3,3-hexafluoropropyl)-1,2-dibromocyclopentane **(45)** (4.8g, 80%), as a mixture of diastereoisomers; b.p. 43.4°C /4mmHg; (Found: C, 25.0; H, 2.0. $C_8H_8F_6Br_2$ requires C, 25.4; H, 2.0%); I.R. spectrum 19; N.M.R. spectra 15; Mass spectrum 27.

10.4.2. 1-(1,1,2,3,3,3-Hexafluoropropyl)-1,2-dibromocyclohexane (46)

Bromine (9.8g, 61 m mol) and 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene **(42)** (7.0g, 30 m mol) gave pure 1-(1,1,2,3,3,3-hexafluoropropyl)-1,2-dibromocyclohexane **(46)** (8.3g, 70.3%), as a mixture of diastereoisomers; b.p. 90.2°C/7mmHg; (Found: C, 27.6; H, 2.4. $C_9H_{10}F_6Br_2$ requires C, 27.6; H, 2.6%); I.R. spectrum 20; N.M.R. spectra 16; Mass spectrum 28.

10.5. General procedure for epoxidation of perfluoroalkylated alkenes[130]

Metachloroperbenzoic acid (M.C.P.B.A.) was added over a period of ten minutes to a cooled (ice bath) homogeneous mixture of polyfluoroalkylated alkene dissolved in dichloromethane. The mixture was refluxed at 40°C for 7 days. On cooling, activated potassium fluoride (dried in an oven at 250°C) was added to the mixture, and the resultant suspension vigorously stirred at room temperature for 2 hours. Potassium fluoride and precipitated M.C.P.B.A. salts were removed by filtration, and solvent removed from the resultant solution by distillation at 50°C, to give a yellow liquid. This final liquid was purified by vacuum transfer, yielding a colourless polyfluoroalkylated epoxide product.

10.6. Synthesis of :-

10.6.1. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclopentene oxide (47)

M.C.P.B.A. (3.9g, 25.5 mmol) and 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentene **(41)** (4.0g, 18 mmol) in dichloromethane (50ml) gave pure 1-(1,1,2,3,3,3-hexafluoropropyl)cyclopentene oxide **(47)** (2.9g, 52%); b.p. 148°C; (Found: C, 40.9; H, 3.5; F, 49.0. $C_8H_8F_6O$ requires C, 41.0; H, 3.4; F, 48.7%); I.R. spectrum 21; N.M.R. spectra 17; Mass spectrum29.

10.6.2. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene oxide (48)

M.C.P.B.A. (12.1g, 70.0 mmol) and 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene **(42)** (7.5g, 32 mmol) in dichloromethane (100ml) gave pure 1-(1,1,2,3,3,3-hexafluoropropyl)cyclohexene oxide **(48)** (3.6g, 45.6%); b.p. 170°C; (Found: C, 43.6; H, 4.0. $C_9H_{10}F_6O$ requires C, 43.5; H, 4.0%); I.R. spectrum 22; N.M.R. spectra 18; Mass spectrum 30.

10.7. Other epoxidation reactions

10.7.1. M.C.P.B.A. in an aqueous system[139]

M.C.P.B.A. (4.0g, mol) was added over a period of ten minutes to a cooled stirred heterogeneous mixture of 1-(1,1,2,3,3,3-hexafluoropropyl)cyclopentene **(41)** (2.5g, 12 mol) in sodium hydrogen carbonate solution (30ml, 0.1M), and this solution was stirred at 40°C for 24 hours. On cooling, the organic layer was extracted with dichloromethane (2 x 25ml), washed with 10% sodium hydroxide (2 x 25ml), saturated brine (2 x 25ml) and dried ($MgSO_4$). Solvent was removed by distillation, yielding a pale yellow liquid of 1-(1,1,2,3,3,3-hexafluoropropyl)cyclopentene oxide **(47)** (0.6g, 21.4%) as confirmed by g.l.c.-m.s.; Mass spectrum 31.

10.7.2. Sodium hypochlorite[141]

a) Sodium hypochlorite 5% (13 ml) was added to a stirred solution of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentene **(41)** (1.1g, 5.2 mmol) dissolved in dioxane (20 ml). The resultant yellow solution turned pale yellow after 5 minutes, and was stirred for a further 30 minutes. The reaction mixture was then poured into water, extracted with dichloromethane (3 x 25 ml), and all organic fractions washed and dried ($MgSO_4$). Solvent was removed from the resultant solution leaving a pale yellow liquid which, following g.l.c.-m.s. analysis, was found to be unreacted starting materials; Mass spectrum 32.

b) A mixture of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentene **(41)** (1.0g, 4.8 mmol), anhydrous pyridine (10 ml) and sodium hypochlorite solution (5%) (13 ml) was stirred at room temperature for 30 minutes. The resultant solution was poured into water (25 ml), extracted with dichloromethane (3 x 25 ml) and all organic extracts combined and dried ($MgSO_4$). Dichloromethane was removed by distillation, and g.l.c.-m.s. analysis showed the resultant liquid was starting materials; Mass spectrum 33.

10.8. Other attempted reactions of perfluoroalkylated alkenes :-

10.8.1. Attempted bromohydrin formation[142-144]

A mixture of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentene **(41)** (1.1g, 5.2 mmol), N-bromosuccinimide (NBS) 1.2g, 6.7 mmol) in dichloromethane (20ml) was stirred at room temperature until the NBS disappeared. The organic layer was separated, and the aqueous layer extracted with dichloromethane (2 x 25 ml). The organic extracts were combined, then washed with a solution of sodium metabisulphite (1 x 25 ml) and dried ($MgSO_4$). Dichloromethane was removed by distillation, and g.l.c.-m.s. analysis showed the final product mixture (10.5g) contained some bromohydrin compounds; Mass spectrum 34.

10.9. Synthesis of 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexane-1,2-diol[131] (49)

A mixture of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene oxide **(48)** (2.5g, 10 mmol) and dilute sulphuric acid (100 ml) was refluxed at 95°C for 24 hours. The resultant liquid was cooled to room temperature and extracted with dichloromethane (3 x 25 ml). The organic extracts were washed with saturated sodium hydrogen carbonate solution (2 x 50 ml), water (2 x 50 ml) and saturated sodium chloride solution (2 x 50 ml), then dried ($MgSO_4$). Solvent was removed under vacuum to yield 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexane-1,2-diol **(49)** (2.3g, 86%); m.p. 73°C; (Found: C, 40.4; H, 4.5. $C_9H_{12}F_6O_2$ requires C, 40.6; H, 4.5%); I.R. spectrum 23; N.M.R. spectra 19; Mass spectrum35.

11.0. General procedure for synthesis of Polyfluoroalkylated Aromatics[119, 120]

A quartz Carius tube (ca. 20 ml) was charged with a polyfluoroalkylated alkene or diene and sulphur, degassed and sealed under vacuum. The tube was heated at 225°C for 24 hours, cooled and opened. Hydrogen sulphide was allowed to evaporate through a scrubber, and the remaining liquid was purified by transfer under vacuum to give pure samples of the aromatic systems as colourless, clear liquids.

11.1. Synthesis of :-

11.1.1. 1-(1,1,2,3,3,3-Hexafluoropropyl)-benzene (50)

1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene (**42**) (0.8g, 3.5 mmol) and sulphur (0.3g, 10 mmol) gave 1-(1,1,2,3,3,3-hexafluoropropyl)-benzene (**50**) (0.7g, 88%); b.p. 134°C; (Found: C, 47.1; H, 2.7. $C_9H_6F_6$ requires C, 47.4; H, 2.6%); I.R. spectrum 24; N.M.R. spectra 20; Mass spectrum 36.

11.1.2. 1,4-Di-(1,1,2,3,3,3-hexafluoropropyl)-benzene (51)

A mixture of 1,4-di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohex-1,3-diene (**43**), 1,4-di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohex-1,4-diene (**44**) (1.3g, 3.4 mmol) and sulphur (0.24g, 7.5 mmol) gave 1,4-di-(1,1,2,3,3,3-hexafluoropropyl)-benzene (**51**) (0.7g, 88%); b.p. 188°C; (Found: C, 37.8; H, 1.4. $C_{12}H_6F_{12}$ requires C, 38.1; H, 1.6%); I.R. spectrum 25; N.M.R. spectra 21; Mass spectrum 37.

CHAPTER 7
EXPERIMENTAL TO CHAPTER 4

12.1. General procedure for gamma ray initiated reactions

The same general procedure for γ ray initiated free radical additions of alcohols to hexafluoropropene was used in reactions involving hydrocarbons with this fluoroalkene (Chapter 5).

12.2. Reactions of hexafluoropropene with:-

12.2.1. Methylcyclopentane

A Carius tube charged with methylcyclopentane (8.4g, 100 mmol) and hexafluoropropene (10.5g, 70 mmol) dissolved in acetone (10g) was irradiated with gamma rays for ten days. Hexafluoropropene (6.9g, 35% conversion) was recovered, and, following fractional distillation, yielded a mixture of (1,1,2,3,3,3,-hexafluoropropyl)-cyclopentanes **(52)** /**(53)** (2.1g, 9%) as a colourless liquid; b.p. 22.9°C/6mmHg; (Found: C, 46.2; H, 5.2; F, 48.7. $C_9H_{12}F_6$ requires C, 46.2; H, 5.1; F, 48.7%); I.R. spectrum 27; N.M.R. spectra 23; Mass spectrum 38; and di-(1,1,2,3,3,3-hexafluoropropyl)-methylcyclopentanes **(54)**, (0.4g, 1.0%) as a colourless liquid, containing mixtures of isomers which could not be separated but were identified by g.l.c.-m.s..; Mass spectrum 39.

12.2.2. Methylcyclohexane

A Carius tube charged with methylcyclohexane (5.8g, 60 mmol) and hexafluoropropene (9.2g, 60 mmol) dissolved in acetone (10g) was irradiated with gamma rays for ten days. Hexafluoropropene (8.8g, 15% conversion) was recovered, and, following fractional distillation, yielded a mixture of (1,1,2,3,3,3,-hexafluoropropyl)-cyclohexanes **(55)** / **(56)** (0.6g, 6%) as a colourless liquid; b.p. 41.0°C/8mm; (Found: C, 48.8; H, 5.8; F, 46.0. $C_{10}H_{14}F_6$ requires C, 48.4; H, 5.6; F, 46.0%); I.R. spectrum 28; N.M.R. spectra 24; Mass spectrum 40; and di-(1,1,2,3,3,3-hexafluoropropyl)-methylcyclohexanes **(57)** as a colourless liquid (0.1g, 0.4%), containing mixtures of isomers which could not be separated but were identified by g.l.c.-m.s.; b.p. 46.2°C/8mmHg; Mass spectrum 41.

12.2.3. 1,3-Dimethylcyclohexane

A Carius tube charged with 1,3-dimethylcyclohexane (7.6g, 68 mmol) and hexafluoropropene (10.2g, 68 mmol) dissolved in acetone (10g) was irradiated with gamma rays for ten days. Hexafluoropropene (9.0g, 12% conversion) was recovered, leaving a colourless liquid (4.1g), which contained, as shown by g.l.c.-m.s., starting material and a mixture of (1,1,2,3,3,3-hexafluoropropyl)-1,3-dimethylcyclohexanes **(61)** / **(62)** (17%); Mass spectrum 46.

12.2.4. 1,4-Dimethylcyclohexane

A Carius tube charged with 1,4-dimethylcyclohexane (5.4g, 48 mmol) and hexafluoropropene (7.2g, 48 mmol) dissolved in acetone (10g) was irradiated with gamma rays for ten days. Hexafluoropropene (5.0g, 30% conversion) was recovered, and, following fractional distillation, yielded mainly 1-(1,1,2,3,3,3,-hexafluoropropyl)-1,4-dimethylcyclohexane **(63)** (2.0g, 16%) as a colourless liquid; b.p. 59.0°C / 6mmHg; (Found: C, 50.1; H, 6.2. $C_{11}H_{16}F_6$ requires C, 50.4; H, 6.1%); I.R. spectrum 29; N.M.R. spectra 27; Mass spectrum 48; and di-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dimethylcyclohexanes **(64)** (0.2g, 0.8%) as a colourless liquid, containing mixtures of isomers which could not be separated but were identified by g.l.c.-m.s.; Mass spectrum 49.

12.2.5. 2-Methylpentane

A Carius tube charged with 2-methylpentane (10.2g, 120 mmol) and hexafluoropropene (12.5g, 83 mmol) dissolved in acetone (10g) was irradiated with gamma rays for ten days. Hexafluoropropene (10.4g, 18% conversion) was recovered, leaving a colourless liquid (4.1g), which contained, as shown by g.l.c.-m.s., a mixture of di-(1,1,2,3,3,3-hexafluoropropyl)-2-methylpentanes **(65)** (approx. 10% by g.c.); Mass spectrum 52.

12.2.6. 3-Methylpentane

A Carius tube charged with 3-methylpentane (9.5g, 110 mmol) and hexafluoropropene (11.6g, 77 mmol) dissolved in acetone (10g) was irradiated with gamma rays for ten days. Hexafluoropropene (11.2g, 10% conversion) was recovered, leaving a colourless liquid (2.1g), which contained, as shown by g.l.c.-m.s., a mixture of di-(1,1,2,3,3,3-hexafluoropropyl)-3-methylpentanes **(66)** (approx. 8% by g.c.); Mass spectrum 54.

12.2.7. Cyclohexane[18, 37, 39]

A Carius tube charged with cyclohexane (8.4g, 100 mmol) and hexafluoropropene (13.8g, 90 mmol) dissolved in acetone (10g) was irradiated with gamma rays for ten days. Hexafluoropropene (5.0g, 30% conversion) was recovered, and, following fractional distillation, yielded (1,1,2,3,3,3-hexafluoropropyl)-

cyclohexane **(13)** (13.8g, 59%) as a colourless liquid; b.p. 155°C; (Found: C, 46.3; H, 4.6; F, 49.1. $C_9H_{12}F_6$ requires C, 46.2; H, 5.1; F, 48.7%); I.R. spectrum 17; N.M.R. spectra 22; Mass spectrum 56.

12.2.8. 1-Methyl-4-chlorocyclohexane

A Carius tube charged with 1-methyl-4-chlorocyclohexane (1.5g, 11 mmol) and hexafluoropropene (1.7g, 11 mmol) dissolved in acetone (10g) was irradiated with gamma rays for ten days. Hexafluoropropene (1.7g, 0% conversion) was recovered, and hence no reaction had occurred.

12.3. General procedure for di-tertiary butyl peroxide initiated reactions

The same general procedure used in free radical additions of alcohols to hexafluoropropene initiated by D.T.B.P. was used in the following reactions between hydrocarbons and hexafluoropropene (Chapter 5).

12.4. Reactions of hexafluoropropene with:-

12.4.1. Methylcyclohexane

A mixture of methylcyclohexane (4.7g, 48 mmol), hexafluoropropene (1.7g, 11 mmol) and di-tert.-butyl peroxide (0.05g, 0.33 mmol) was reacted in a rotating oil bath at 140°C for 24 hours. Removal of excess hexafluoropropene (0.8g, 52% conversion), yielded, as shown by g.l.c.-m.s., methylcyclohexane, (1,1,2,3,3,3-hexafluoropropyl)methylcyclohexanes **(55)** /**(56)** and di-(1,1,2,3,3,3-hexafluoropropyl)-methylcyclohexanes **(57)** as a brown liquid; Mass spectra 42, 43 respectively.

12.4.2. 1,2-Dimethylcyclohexane

A mixture of 1,2-dimethylcyclohexane (22.4g, 200 mmol), hexafluoropropene (20.1g, 133 mmol) and di-tert.-butyl peroxide (1.5g) was reacted in a rocking autoclave at 140°C for 24 hours. Removal of excess hexafluoropropene (0.4g, 97.7% conversion), followed by fractional distillation, yielded mixtures containing (1,1,2,3,3,3-hexafluoropropyl)-1,2-dimethylcyclohexanes **(58)** / **(59)** (16.0g, 30.5%) as a colourless liquid; b.p. 59.0°C/8mmHg; (Found: C, 50.6; H, 6.4. $C_{11}H_{16}F_6$ requires C, 50.4; H, 6.1%); I.R. spectrum 2; N.M.R. spectra 25; Mass spectrum 44; and di-(1,1,2,3,3,3-hexafluoropropyl)-1,2-dimethylcyclohexanes **(60)** (13.2g, 16.0%), which could not be separated but were identified by g.l.c.-m.s.; Mass spectrum 45.

12.4.3. 1,3-Dimethylcyclohexane

A mixture of 1,3-dimethylcyclohexane (16.7g, 150 mmol), hexafluoropropene (17.6g, 117 mmol) and di-tert.-butyl peroxide (1.5g, 5%) was reacted in a rocking autoclave at 140°C for 24 hours. Removal of excess hexafluoropropene (1.2g, 93% conversion), followed by fractional distillation, yielded a mixture containing (1,1,2,3,3,3-hexafluoropropyl)-1,3-dimethylcyclohexanes **(61)** / **(62)** (7.4g, 18.8%), as colourless liquids; b.p. 67.2-67.8°C/10mmHg; (Found: C, 49.3; H, 6.5; F, 43.6. $C_{11}H_{16}F_6$ requires C, 50.4; H, 6.1; F, 43.5%); I.R. spectrum 3; N.M.R. spectra 26; Mass spectra 47.

12.4.4. 1,4-Dimethylcyclohexane

A Carius tube charged with 1,4-dimethylcyclohexane (1.4g, 12 mmol), hexafluoropropene (0.9g, 6 mmol) and di-tert.-butyl peroxide (0.2g) was heated in a rotating oil bath at 140°C for 24 hours. Removal of excess hexafluoropropene (0.6g, 39% conversion) yielded, as shown by g.l.c.-m.s., 1,4-dimethylcyclohexane (81%), 1-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dimethylcyclohexane **(63)** , and di-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dimethylcyclohexanes **(64)** as a brown liquid; Mass spectra 50, 51 respectively.

12.4.5. 2-Methylpentane

A mixture of 2-methylpentane (13.1g, 152 mmol), hexafluoropropene (15.2g, 101 mmol) and di-tert.-butyl peroxide (1.1g, 8 mmol) was heated in a rocking autoclave at 140°C for 24 hours. Removal of excess hexafluoropropene (10.0g, 34% conversion), followed by fractional distillation, yielded a mixture of di-(1,1,2,3,3,3-hexafluoropropyl)-2-methylpentane **(65)** (1.5g, 4.1%); b.p. 69.3-70.8°C/10mmHg; (Found: F, 59.0. $C_{12}H_{14}F_{12}$ requires F, 59.1%); I.R. spectrum 4; N.M.R. spectra 28; Mass spectrum 53.

12.4.6. 3-Methylpentane

A mixture of 3-methylpentane (14.0g, 162 mmol), hexafluoropropene (16.2g, 108 mmol) and di-tert.-butyl peroxide (1.2g, 8 mmol) was heated in a rocking autoclave at 140°C for 24 hours. Removal of excess hexafluoropropene (10.0g, 38% conversion), followed by fractional distillation, yielded a mixture of di-(1,1,2,3,3,3-hexafluoropropyl)-3-methylpentanes **(66)** (1.8g, 4.7%); b.p. 67.0-71.0°C/6mmHg; (Found:- F, 58.4. $C_{12}H_{14}F_{12}$ requires F, 59.1%); I.R. spectrum 5; N.M.R. spectra 29; Mass spectrum 55.

12.4.7. Cyclohexene[17]

A mixture of cyclohexene (18.4g, 225 mmol) and hexafluoropropene (11.3g, 75 mmol) was heated in a rocking autoclave at 320°C for 4 days. Removal of hexafluoropropene (3.7g, 67% conversion), followed by fractional distillation, yielded multicomponent mixtures (b.p. 34°C/4mmHg - 94°C/4mmHg), and 3-(1,1,2,3,3,3-hexafluoropropyl-cyclohexene was not observed; Mass spectrum too complicated for printing.

12.4.8. 1-Methyl-4-chlorocyclohexane

A Carius tube containing a mixture of 1-methyl-4-chlorocyclohexane (1.2g, 9 mmol), hexafluoropropene (1.1g, 7.3 mmol) and di-tert-butyl peroxide (0.2g) was heated in a rocking autoclave at 140°C for 48 hours. Hexafluoropropene (0.8g, 24% conversion) was recovered, leaving a yellow liquid, which contained as shown by g.l.c.-m.s., 1,4-dimethylcyclohexane (89%), (1,1,2,3,3,3-hexafluoropropyl)-1-methyl-4-chlorocyclohexanes **(70)** (3%), and unidentified material (8%); Mass spectrum 62.

13.0. Attempted chlorinations of (1,1,2,3,3,3-hexafluoropropyl)-cyclohexane (13)

13.1. Chlorine gas[133]

Chlorine gas was slowly passed through neat (1,1,2,3,3,3-hexafluoropropyl)-cyclohexane **(13)** (12.0g, 52 mmol) and the reaction monitored by g.c.. This reaction was non selective forming many (1,1,2,3,3,3-hexafluoropropyl)-chlorocyclohexanes **(67)**, **(68)**, **(69)**; G.c. spectrum 57.

13.2. Chlorine gas with carbon disulphide[137] as a solvent

A quartz Carius tube charged with (1,1,2,3,3,3-hexafluoropropyl)-cyclohexane **(13)** (1.4g, 5.9 mmol), chlorine gas (0.5g, 7.1 mmol) and carbon disulphide (3.4g, 44 mmol) was irradiated with U.V. light for 1 hour. Volatiles were recovered, leaving a colourless liquid, which contained, as shown by g.l.c.-m.s., a mixture of (1,1,2,3,3,3-hexafluoropropyl)chlorocyclohexanes **(67)**, **(68)**, **(69)**; Mass spectra 58.

13.3. Sulphuryl chloride[134, 135]

A flask charged with (1,1,2,3,3,3-hexafluoropropyl)-cyclohexane **(13)** (93.6g, 400 mmol), sulphuryl chloride (68.0g, 500 mmol) and benzoyl peroxide (4.0g, 16 mmol) was heated at 70°C for 6 hours. The resultant black liquid was fractionally distilled, yielding a mixture of 1-(1,1,2,3,3,3-hexafluoropropyl)-3-chlorocyclohexane **(68)** and 1-(1,1,2,3,3,3-hexafluoropropyl)-4-chlorocyclohexane **(67)** (47.0g, 44%); b.p. 74.2°C - 80.3°C/6mmHg; (Found: C, 40.2; H, 4.1. $C_9H_{11}F_6Cl$ requires C, 40.2; H, 4.1%); I.R. spectrum 30; N.M.R. spectra 30; Mass spectrum 59.

14.0. Reactions of 1-(1,1,2,3,3,3-hexafluoropropyl)-3-chloro-cyclohexane **(68)** and 1-(1,1,2,3,3,3-hexafluoropropyl)-4-chlorocyclohexane **(67)** with:-

14.0.1. (1,8-Diazabicycloundec-7-ene) D.B.U.[145]

i) A mixture of compounds **(67)** / **(68)** (2.7g, 10 mol), D.B.U. (1.5g, 10 mmol) and thiophenol (1.1g, 10 mmol) dissolved in toluene (30ml) was stirred at room temperature for 12 hours. The precipitate formed was filtered, washed with water (2 x 25 ml) and dried ($MgSO_4$). Toluene was transferred under vacuum from the resultant liquid, and g.l.c.-m.s. analysis showed this reaction had resulted in recovery of starting materials.

ii) A mixture of compounds **(67)** / **(68)** (2.7g, 10 mol), D.B.U. (1.5g, 10 mmol) and thiophenol (1.1g, 10 mmol) dissolved in acetonitrile (30 ml) was refluxed for 12 hours. The resultant liquid was poured into water (50 ml), and the organic layer separated and dried ($MgSO_4$). Acetonitrile was transferred under vacuum from this liquid, leaving a brown solid, which following T.L.C., on silica and hexane as the elutant, contained two main components (R_F 0.63, R_F 0.80). A 150 ml silica packed column, using hexane as the elutant, was used to separate 0.5g of this brown solid. Four fractions contained the same two components (R_F 0.63, R_F 0.80), and a single fraction contained one component (R_F 0.74). Following solvent removal, the above fractions were analysed by g.l.c.-m.s., and it was not possible to identify the unexpected products; Mass spectrum 60.

14.0.2. Lithium chloride[136]

i) A flask charged with dried lithium chloride (11.9g, 280 mmol), anhydrous D.M.F. (47 ml) and a mixture of 1-(1,1,2,3,3,3-hexafluoropropyl)-4-chlorocyclohexane **(67)** and 1-(1,1,2,3,3,3-hexafluoropropyl)-3-chlorocyclohexane **(68)** (50.4g, 188 mmol), was refluxed at 150°C for 23 hours. Volatile material (47.2g) was transferred under vacuum from the resultant mixture leaving a green residue. The volatiles were washed with water, dried ($MgSO_4$), and fractionally distilled, yielding 4-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene **(71)** (32.8g, 65%) as the major product; b.p. 48°C/10mmHg; (Found: C, 47.0; H, 4.3. $C_9H_{10}F_6$ requires C, 46.6; H, 4.3%); I.R. spectrum 31; N.M.R. spectra 31; Mass spectrum 63.

ii) A flask charged with dried lithium chloride (3.2g, 75 mmol), anhydrous D.M.F. (12.5 ml) and a mixture of 1-(1,1,2,3,3,3-hexafluoropropyl)-4-chlorocyclohexane (**67**) and 1-(1,1,2,3,3,3-hexafluoropropyl)-3-chlorocyclohexane (**68**) (13.4g, 50 mmol), was refluxed at 150°C for 23 hours. Volatile material (17.6g) was transferred under vacuum from the resultant mixture leaving a brown residue. D.M.F. was removed by flash chromatography on silica using hexane as a solvent. Fractional distillation of the final reaction mixture yielded as shown by g.l.c.-m.s., 4-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene (**71**) as the major product; Mass spectrum 64.

14.1. Reactions of mainly 4-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene (71) with :-

14.1.1. Bromine[126]

Bromine (2.9g, 18 mmol) was added dropwise to a mixture containing mainly 4-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene (**71**) (3.5g, 15 mmol) at 0°C, and the resultant liquid was stirred at room temperature for 30 minutes. The resultant organic liquid was worked up as in the general procedure (experimental for chapter 6), to give pure 1-(1,1,2,3,3,3-hexafluoropropyl)-3,4-dibromo-cyclohexane (**73**) (3.7g, 63%) as the major product; b.p. 58.0°C/1mmHg; (Found: C, 28.0; H, 2.5. $C_9H_{10}F_6Br_2$ requires C, 27.6; H, 2.6%); I.R. spectrum 32; N.M.R. spectra 32; Mass spectrum 65.

14.1.2. Meta-chloro-perbenzoic acid (M.C.P.B.A.)[139]

M.C.P.B.A. (1.0g, 5.5 mmol) was added in about 10 minutes to a stirred heterogeneous mixture of sodium hydrogen carbonate (0.3M, 30 ml) as well as mainly 4-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene (**71**) (1.2g, 5 mmol) at 0°C, and the resultant suspension heated (60°C) for 5 hours. The resultant pale yellow liquid was extracted with ether, washed with 10% sodium hydroxide (2 x 10 ml), saturated brine (2 x 5 ml) and dried ($MgSO_4$). Following ether removal, fractional distillation, gave a colourless liquid of 4-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene oxide (**75**) (1.3g, 48%) as the major product; b.p. 69.4°C/6mmHg; (Found: C, 44.1; H, 4.2. $C_9H_{10}F_6O$ requires C, 43.6; H, 4.0%); I.R.spectrum 33; N.M.R. spectra 33; Mass spectrum 66.

APPENDICES AND REFERENCES

APPENDIX 1
NMR SPECTRA DATA

Appendix One
NMR Spectra Data

1. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclopentanol **(20)**
2. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexanol **(22)**
3. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cycloheptanol **(24)**
4. 1-(1,1,2,3,3,3-Hexafluoropropyl)-4-methylcyclohexanol **(29)**
5. 1-(1,1,2,3,3,3-Hexafluoropropyl)-3-methylcyclohexanol **(27)**
6. 1,3-Di-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentan-1,3-diol **(31)**
7. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexan-1,3-diol **(32)**
8. 1,3-Di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexan-1,3-diol **(33)**
9. 1,4-Di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexan-1,4-diol **(34)**
10. 2,4-Di-(1,1,2,3,3,3-hexafluoropropyl)-pentan-2,4-diol **(36)**
11. 2,5-Di-(1,1,2,3,3,3-hexafluoropropyl)-hexan-2,5-diol **(37)**
12. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclopentene **(41)**
13. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene **(42)**
14. 1,4-Di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexa-1,3-diene **(44)** and 1,4-di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexa-1,4-diene **(43)**
15. 1-(1,1,2,3,3,3-Hexafluoropropyl)-1,2-dibromocyclopentane **(45)**
16. 1-(1,1,2,3,3,3-Hexafluoropropyl)-1,2-dibromocyclohexane **(46)**
17. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclopentene oxide **(47)**
18. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene oxide **(48)**
19. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexan-1,2-diol **(49)**
20. 1-(1,1,2,3,3,3-Hexafluoropropyl)-benzene **(50)**
21. 1,4-Di-(1,1,2,3,3,3-hexafluoropropyl)-benzene **(51)**
22. (1,1,2,3,3,3-Hexafluoropropyl)-cyclohexane **(13)**
23. (1,1,2,3,3,3-Hexafluoropropyl)-methylcyclopentanes **(52)** / **(53)**
24. (1,1,2,3,3,3-Hexafluoropropyl)-methylcyclohexanes **(55)** / **(56)**
25. (1,1,2,3,3,3-Hexafluoropropyl)-1,2-dimethylcyclohexanes **(58)** / **(59)**
26. (1,1,2,3,3,3-Hexafluoropropyl)-1,3-dimethylcyclohexanes **(61)** / **(62)**
27. 1-(1,1,2,3,3,3-Hexafluoropropyl)-1,4-dimethylcyclohexane **(63)**
28. Di-(1,1,2,3,3,3-hexafluoropropyl)-2-methylpentanes **(65)**
29. Di-(1,1,2,3,3,3-hexafluoropropyl)-3-methylpentanes **(66)**
30. A mixture of 1-(1,1,2,3,3,3-hexafluoropropyl)-3-chlorocyclohexane **(68)** and 1-(1,1,2,3,3,3-hexafluoropropyl)-4-chlorocyclohexane **(67)**
31. 4-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene **(71)**
32. 1-(1,1,2,3,3,3-Hexafluoropropyl)-3,4-dibromocyclohexane **(73)**
33. 4-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene oxide **(75)**

Spectra were run in either deutrochloroform or deutroacetone.

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

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

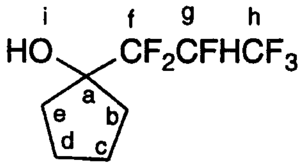
$$(\delta_1 - \delta_3) = (\delta_2 - \delta_4) = (\Delta V^2 + J^2)^{1/2}$$

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

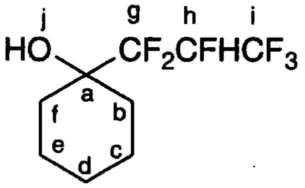
1. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclopentanol (20)



(20)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H				
1.5 - 2.0	m		8	b, c, d, e
2.50	s		1	i
5.23	dm	^2J 44.0	1	g
^{19}F				
-74.5	s		3	h
-121.39 / -127.14	AB	J_{AB} 275	2	f
-210.0	dm	^2J 42.4	1	g
^{13}C				
23.64	s			c, d
24.75	d	^4J 1.8		c, d
34.70	t	^3J 4.6		b, e
35.61	t	^3J 1.8		b, e
81.70	t	^2J 34.2		a
82.20	dm			g
119.05	d, d, d	^1J 261.7 ^1J 246.6 ^2J 24		f
121.86	q, d	^1J 282 ^2J 26		

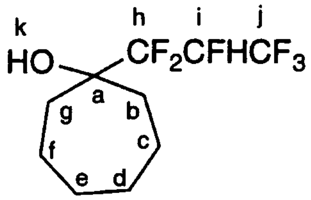
2. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexanol (22)



(22)

Chemical Shift (ppm)	Multiplicity	Coupling Constant	Relative Intensity	Assignment
^{1}H				
1.2 - 1.9	m		10	b, c, d, e, f
2.30	s		1	j
5.23	dm	^{2}J 43.6	1	h
^{19}F				
-74.43	s		3	i
-126.87 / -128.87	AB	J_{AB} 276	2	g
-207.71	d	^{2}J 40.2	1	h
^{13}C				
20.35	s			c, e
20.49	s			c, e
25.06	s			d
29.04	m			b, f
29.21	dt	^{4}J 37 ^{3}J 3.8		b, f
74.22	t	^{2}J 24.4		a
82.90	dm	^{1}J 196.1		h
118.10	d, d, d	^{1}J 264.5 ^{1}J 249.5 ^{2}J 21.4		g
121.30	qd	^{1}J 282.6 ^{2}J 26.4		i

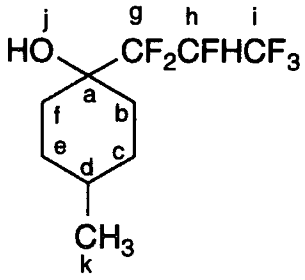
3. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cycloheptanol (24)



(24)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
1.4 - 2.1	m		12	b, c, d, e, f, g
3.16	s		1	k
5.63	dm	^2J 44.0	1	i
^{19}F				
-74.79	m		3	j
-122.6 / -127.1	AB	J_{AB} 270.9	2	h
-207.0	dm	^2J 41.4	1	i
^{13}C				
21.96	s			c, f
22.24	d	^4J 1.1		c, f
29.95	s			d, e
30.11	s			d, e
33.96	t	^3J 5.3		b, g
34.64	s			b, g
77.01	td	^2J 22.8 ^3J 9.9		a
83.57	dm	^1J 193.1		i
119.91	d, d, d	^1J 264.5 ^1J 251.5 ^2J 20.2		h
122.26	qd	^1J 282.6 ^2J 26.3		j

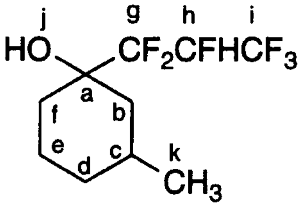
4. 1-(1,1,2,3,3,3-Hexafluoropropyl)-4-methylcyclohexanol (29)



(29)

Chemical Shift	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
0.94	m		3	k
1.3 - 2.1	m		9	b, c, d, e, f
2.76	s		1	j
5.26	dm	^{2}J 44.0	1	h
^{19}F				
-74.50	m		3	i
-126.31 / -128.65	AB	J_{AB} 274.7	2	g
-207.63	dm	^{2}J 37.6	1	h
^{13}C				
21.99	s			k
22.21	s			k
29.19	s			c, e
29.28	s			c, e
29.67	s			b, f
29.72	t	^{3}J 3.4		b, f
32.03	s			d
32.12	s			d
74.08	t	^{2}J 24.4		a
83.16	dm	^{1}J 195.1		h
118.55	d, d, d	^{1}J 264.5 ^{1}J 250.4 ^{2}J 21.3		g
121.6	qd	^{1}J 282.6 ^{2}J 26.0		i

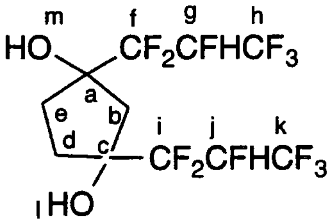
5. 1-(1,1,2,3,3,3-Hexafluoropropyl)-3-methylcyclohexanol (27)



(27)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H				
1.35	m		12	a, b, c, d, e, f, k
2.15	s		1	j
5.24	dm	^2J 48	1	h
^{19}F				
-74.38	m		3	i
-126.72 / -128.73	AB	J_{AB} 274.7	2	g
-207.48	t	^3J 14.1	1	h
^{13}C				
20.62	s			d
20.63	s			d
22.35	s			k
22.42	s			k
27.16	s			c
27.36	s			c
28.86	t	^3J 2.5		b
29.19	t	^3J 4.0		b
34.12	s			e
34.14	s			e
37.55	d	^3J 3.4		f
37.90	t	^3J 3.8		f
75.11	td	^2J 23.9 ^3J 9.2		a
83.1	dm	^1J 195.1		h
118.22	d, d, d	^1J 264.5 ^1J 250.5 ^2J 21.3		g
121.52	qd	^1J 282.6 ^2J 26.4		i

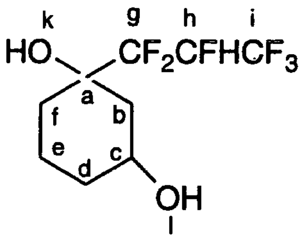
6. 1,3-Di-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentane-1,3-diol (31)



(31)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H				
2.0 - 2.6	m		6	b, d, e
3.13	m		2	l, m
5.78	dm	^2J 44.0	2	g, j
^{19}F				
-74.71	m		6	h, k
-124.27	m		4	f, i
-211.3	m		2	g, j
^{13}C				
33.04	m			d, e
33.49	m			d, e
34.02	m			d, e
34.37	m			d, e
42.76	m			b
44.88	m			b
83.18	m			a, c
83.95	dm	^1J 191.1		g, j
119.31	m			f, i
122.39	qd	^1J 282.6 ^2J 26.0		h, k

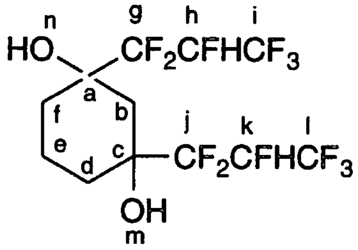
7. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexane-1,3-diol (32)



(32)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H				
1.6 - 2.1	m		8	b, d, e, f
2.93	s		2	j, k
3.88	m		1	c
5.71	dm		1	h
^{19}F				
-74.72	m		3	i
-126.53/ -128.26	AB	J_{AB} 270.9	2	g
-126.27 / -128.39	AB	J_{AB} 270.9		g
-208.4	m		1	h
^{13}C				
19.55	s			d
19.67	s			d
28.52	s			e
28.56	s			e
35.75	s			f
35.85	s			f
38.4	t	^3J 4.2		b
39.7	t	^3J 4.2		b
66.23	s			c
66.35	s			c
75.81	m	^2J 24.5		a
83.4	dm	^1J 180.0		h
119.1	d, d, d	^1J 249.5 ^2J 21.0		g
122.5	qd	^1J 282.6 ^2J 26.4		i

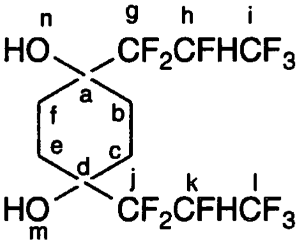
8. 1,3-Di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexane-1,3-diol (33)



(33)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H				
1.6 - 2.2	m		8	b, d, e, f
5.6 - 6.0	m		2	h, k
^{19}F				
-74.72	m		6	i, l
-126.96	m		4	g, j
-208.96	m		2	h, k
^{13}C				
15.62	s			e
15.65	s			e
28.10	t	^3J 3.4		b
28.29	m			b
31.43	s			d, f
32.68	s			d, f
75.36	m			a, c
83.36	dm	^1J 192.7		h, k
118.47	d, d, d	^2J 21.3		g, j
122.38	qd	^1J 281.6 ^2J 26.4		i, l

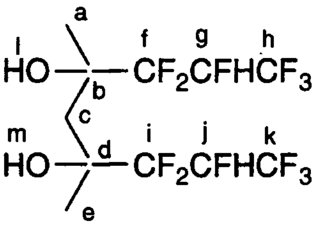
9. 1,4-Di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexane-1,4-diol (34)



(34)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H				
1.7 - 2.2	m		8	b, c, e, f
5.02	s		2	m, n
5.77	dm	^2J 36	2	h, k
^{19}F				
-74.74	m		6	i, l
-126.44 / -128.38	AB	J_{AB} 270.9	4	g, j
-208.52	dm	^2J 41.4	2	h, k
^{13}C				
23.86	m			b, c, e, f
25.10	m			b, c, e, f
72.5	t			a, d
73.15	t	^2J 23.6		a, d
83.68	dm	^1J 193.0		h, k
119.54	d, d, d	^1J 264.53 ^1J 250.45 ^2J 26.0		g, j
122.56	qd	^1J 282.6 ^2J 26.4		i, l

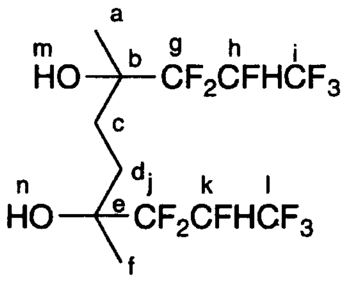
10. 2,4-Di-(1,1,2,3,3,3-hexafluoropropyl)-2,4-pentanediol (36)



(36)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
1.5 - 1.8	m		8	a, c, e
3.15	d		2	l, m
5.76	m		2	g, j
^{19}F				
-74.79	m		6	h, k
-124.35 / -126.31	AB	J_{AB} 270.9	4	f, i
-207.1	m		1	g or j
-207.6	m		1	g or j
^{13}C				
19.25	m			a, e
20.32	m			a, e
34.71	m			c
35.40	m			c
75.50	m			b, d
83.53	dm	^{1}J 196.2		g, j
119.53	d, d, d	^{1}J 266.5 ^{1}J 253.5		f, i
122.56	qd	^{1}J 281.6 ^{2}J 26.3		h, k

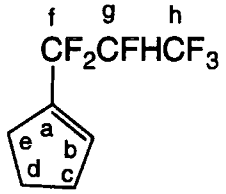
11. 2,5-Di-(1,1,2,3,3,3-hexafluoropropyl)-hexane-2,5-diol (37)



(37)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
1.2 - 2.1	m		10	a, c, d, f
4.96	m		2	h, k
5.73	m		2	h, k
^{19}F				
-73.68	s		6	i, l
-124.22 / -126.52	AB	J_{AB} 270.9	4	g, j
-206.84	d	^2J 36	2	h, k
^{13}C				
19.02	m			a, f
20.14	s			a, f
28.02	d	^3J 16.8		c, d
28.65	d	^3J 20.2		c, d
74.69	m			b, e
83.87	dm	^1J 184.1		h, k
120.52	m			g, j
122.53	qd	^1J 281.9 ^2J 26.2		i, l

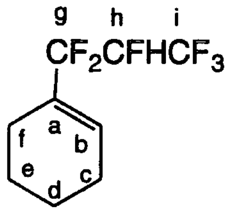
12. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclopentene (41)



(41)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
2.00	pent	^3J 7.6	2	d
2.50	m		4	c, e
4.82	dm	^2J 44	1	g
6.22	m		1	a
^{19}F				
-74.85	s		3	h
-104.56 / -109.72	AB	J_{AB} 273.5	2	f
-210.14	m		1	g
^{13}C				
23.23	s			d
30.83	s			c or e
32.68	s			c or e
86.37	dm	^1J 197.1		g
115.65	td	^1J 246.4 ^2J 24		f
120.74	qd	^1J 282.0 ^2J 25.5		h
135.16	t	^2J 24.0		a
135.83	t	^3J 7.2		b

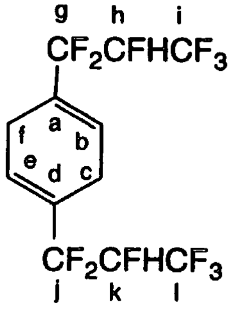
13. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene (42)



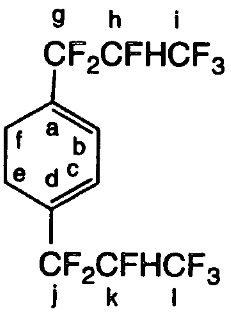
(42)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
1.66	m		4	d, e
2.12	m		4	c, f
4.79	dm	^{2}J 42.3	1	h
6.24	m		1	b
^{19}F				
-74.55	m		3	i
-108.86 / -113.48	AB	J_{AB} 262.5	2	g
-210.43	dm	^{2}J 44	1	h
^{13}C				
21.38	s			d
21.82	s			e
22.98	m			c
24.73	s			f
86.09	dm	^{1}J 198.2		h
116.23	td	^{1}J 248.4 ^{2}J 23.2		g
120.82	qd	^{1}J 281.6 ^{2}J 26.0		i
129.42	t	^{2}J 21.7		a
131.23	t	^{3}J 8.8		b

14. 1,4-Di-(1,1,2,3,3,3-hexafluoropropyl)-1,3-cyclohexadiene (44) and 1,4-di-(1,1,2,3,3,3-hexafluoropropyl)-1,4-cyclohexadiene (43)



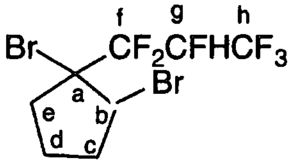
(43)



(44)

Chemical Shift (ppm)	Multipicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
2.50	s		2	(44) e or f (43) c or f
3.08	s		2	(44) e or f (43) c or f
5.73	dm		2	(43 + 44) h, k
6.43	s		1	(44) b or c (43) b or e
6.62	s		1	(44) b or c (43) b or e
^{19}F				
-74.86	m		3	i, l
-110.75 / -114.45	AB	J_{AB} 251.7	2	g, j
-110.87 / -114.96	AB	J_{AB} 263.4		g, j
-212.71	dm	^{2}J 51	1	h, k
^{13}C				
21.35	s			(44) e or f (43) c or f
24.86	s			(44) e or f (43) c or f
86.12	dm	^{1}J 185.5		h, k
117.51	td	^{1}J 250.5		g, j
122.00	qd	^{1}J 282.6 ^{2}J 23.6		i, l
125.74	t	^{3}J 10.0		(44) b or c (43) b or e
127.22	t	^{2}J 23.34		a, d
128.36	t	^{3}J 8.9		(44) b or c (43) b or e
132.63	t	^{2}J 22.5		a, d

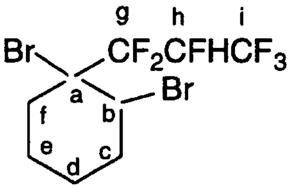
15. 1-(1,1,2,3,3,3-Hexafluoropropyl)-1,2-dibromocyclopentane (45)



(45)

Chemical Shift (ppm)	Multiplicity	Coupling Constant	Relative Intensity	Assignment
^1H				
2.0 - 3.1	m		6	c, d, e
4.65	d	^4J 4.8	1	b
4.69	d	^4J 5.2		b
5.64	dm	^2J 44	1	g
^{19}F				
-74.33	s		3	h
-100.57 / -112.89	AB	J_{AB} 273	2	f
-209.06	d	^2J 35.5	1	g
-209.44	d	^2J 41.2		g
^{13}C				
18.41	s			d
20.22	d	^4J 1.2		d
32.96	d	^3J 1.5		e
33.69	t	^3J 2.3		e
35.95	s			c
37.23	s			c
52.83	dd	^3J 6.3 ^3J 2.3		b
53.40	s			b
73.86	t	^2J 23.6		a
74.83	t	^2J 23.7		a
85.24	m			g
116.55	d, d, d	^1J 267.6 ^1J 246.5 ^2J 27.1		f
120.74	qd	^1J 286.7 ^2J 25.8		h

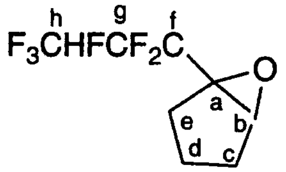
16. 1-(1,1,2,3,3,3-Hexafluoropropyl)-1,2-dibromocyclohexane **(46)**



(46)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H				
1.5 - 2.8	m		8	c, d, e, f
4.65	m		1	b
5.71	dm	^2J 54.6	1	h
^{19}F				
-74.05	s		3	i
-107.46 / -111.82	AB	J_{AB} 274.6	2	g
-206.69	d	^2J 41.7	1	h
-207.23	d	^2J 41.7		h
^{13}C				
19.21	s			d
20.90	s			e
21.48	s			e
26.43	s			c
27.75	d	^4J 2.0		c
32.32	s			f
32.40	s			f
48.56	d	^3J 4.5		b
48.95	dd	^3J 5.7 ^4J 1.5		b
70.50	t			a
72.56	t			a
84.84	dm	^1J 182.3		h
116.10	d, d, d	^1J 269.6 ^1J 250.5 ^2J 23.7		g
120.77	qd	^1J 283.0 ^2J 26.0		i

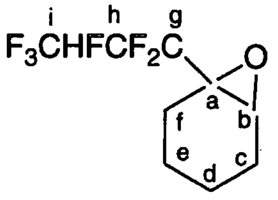
17. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclopentene oxide (47)



(47)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
1.4 - 2.2	m		6	c, d, e
3.75	s		1	b
4.95	m		1	g
^{19}F				
-74.45	s		3	h
-74.62	s			h
-112.10/ -118.45	AB	J_{AB} 288.3	2	f
-115.47 / -122.07	AB	J_{AB} 275.4		f
-211.31	m		1	g
^{13}C				
18.44	s			d
19.26	s			d
24.38	s			e
25.29	t	^{3}J 3.0		e
26.37	s			c
26.82	d	^{4}J 0.8		c
60.82	m			b
61.67	d	^{3}J 6.1		b
65.34	m			a
84.60	m			g
115.46	m			f
120.65	qd	^{1}J 282.6 ^{2}J 25.1		h

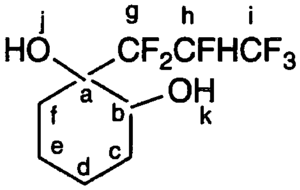
18. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene oxide (48)



(48)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H				
1.1 - 1.5	m		4	e, d
1.6 - 2.1	m		4	f, c
3.43	m		1	b
3.48	m			b
4.94	m		1	h
^{19}F				
-74.29	m		3	i
-74.50	m			i
-118.13 / -121.88	AB	J_{AB} 278.5	2	g
-121.04 / -123.79	AB	J_{AB} 274.7		g
-210.61	dm	^2J 33.9	1	h
-211.11	dm	^2J 38.4		h
^{13}C				
18.49	s			d
19.23	s			e
19.32	s			e
21.96	s			c
22.90	m			c
23.62	s			f
23.73	d	^3J 1.2		f
54.45	m			b
55.30	m			b
57.83	t	^2J 29.8		a
58.27	t	^2J 29.8		a
84.35	m			h
115.85	d, d, d	^1J 256.5 ^1J 251.5		g
120.64	qd	^1J 282.6 ^2J 25.5		i

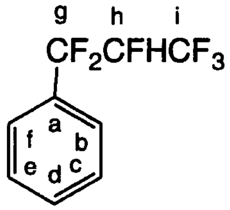
19. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexane-1,2-diol (49)



(49)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
1.4 - 2.4	m		10	c, d, e, f, j, k
3.90	m		1	b
5.40	m		1	h
^{19}F				
-73.84	m		3	i
-73.92	m			i
-119.21 / -121.76	AB	J_{AB} 277.0	2	g
-208.89	m		1	h
^{13}C				
18.57	s			d
19.28	s			d
19.79	s			e
19.87	s			e
25.00	s			c
26.37	s			c
28.80	s			f
29.20	s			f
67.82	s			b
69.51	s			b
74.89	t	^{2}J 22.0		a
75.11	t	^{2}J 22.0		a
83.84	dm	^{1}J 195.1		h
119.02	d, d, d	^{1}J 264.3 ^{1}J 253.5 ^{2}J 22.9		g
121.09	qd	^{1}J 282.6 ^{2}J 25.5		i

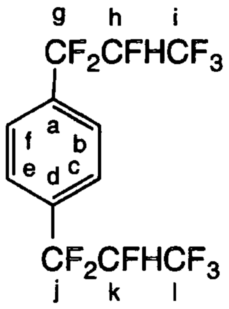
20. 1-(1,1,2,3,3,3-Hexafluoropropyl)-benzene (50)



(50)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
5.87	dm	^{2}J 37.6	1	h
7.60	m		5	b, c, d, e, f
^{19}F				
-74.50	m		3	i
-106.33 / -109.92	AB	J_{AB} 267.2	2	g
-211.49	dm	^{2}J 41.4	1	h
^{13}C				
87.26	dm	^{1}J 194.1		h
117.96	td	^{1}J 248.4 ^{2}J 23.6		g
121.94	qd	^{1}J 281.6 ^{2}J 26.0		i
126.65	t	^{3}J 6.4		b, f
129.76	s			c, e
132.44	s			d
132.49	t	^{2}J 24.2		a

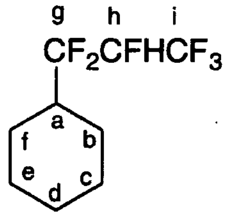
21. 1,4-Di-(1,1,2,3,3,3-hexafluoropropyl)-benzene (51)



(51)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H				
5.96	dm	^2J 44	2	h, k
7.91	s		4	b, c, e, f
^{19}F				
-74.59	m		6	i, l
-106.46 / -110.75	AB	J_{AB} 267.5	4	g, j
-211.75	dm	^2J 41.4	2	h, k
^{13}C				
87.25	dm	^1J 195.1		h, k
117.61	td	^1J 249.4 ^2J 23.7		g, j
121.94	qd	^1J 281.6 ^2J 26.2		i, l
126.77	t	^3J 6.5		b, c, e, f
127.68	t	^3J 6.4		b, c, e, f
135.86	t	^2J 24.8		a, d

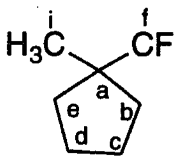
22. (1,1,2,3,3,3-Hexafluoropropyl)-cyclohexane (13)



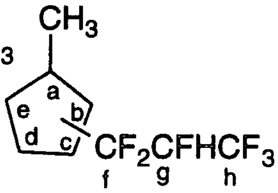
(13)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
1.55	m		11	b, c, d, e, f
4.84	dm	^{2}J 44	1	h
^{19}F				
-74.45	s		3	i
-118.68	m		2	g
-212.02	dm	2J 35.3	1	h

23. (1,1,2,3,3,3-Hexafluoropropyl)-methylcyclopentanes (52) / (53)



(52)

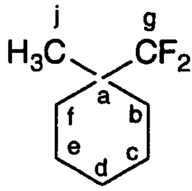


(53)

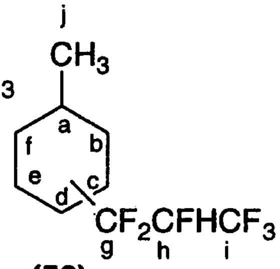
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
0.9 - 2.2	m		11	**(52)** b, c, d, e, i **(53)** b, c, d, e, i
4.6 - 5.0	m		1	**(52)** g **(53)** g
^{19}F				
-74.55	m		3	**(52)** or **(53)** h
-74.77	m			**(52)** or **(53)** h
-114.37 / -123.50	AB	J_{AB} 270.9	2	**(52)** or **(53)** f
-207.97	d	^{2}J 43.7	1	**(52)** or **(53)** g
-210.80	m			**(52)** or **(53)** g
-211.50	m			**(52)** or **(53)** g
^{13}C				
22.74	m			**(52)** i
25.11	s			**(52)** c, d
26.02	d	^{4}J 1.5		**(52)** c, d
34.47	dd	^{3}J 8.1 ^{3}J 4.6		**(52)** b, e
34.68	dd	^{3}J 8.1 ^{3}J 4.9		**(52)** b, e
49.56	dd	^{2}J 44.3 ^{2}J 21.8		**(52)** a
50.16	dd	^{2}J 26.2 ^{2}J 21.3		**(52)** a
85.70	dm	^{1}J 196.1		**(52)** g
121.68	ddd	^{1}J 258.5 ^{1}J 244.4 ^{2}J 23.6		**(52)** f
121.74	qd	^{1}J 282.6 ^{2}J 25.6		**(52)** h

Note :- For interpretation of ^{13}C NMR spectra, only signals assigned to compound **(52)** are shown in the table. However, many other signals are observed in this spectrum, confirming the final reaction mixture is complex.

24. (1,1,2,3,3,3-Hexafluoropropyl)-methylcyclohexanes (55) / (56)



(55)

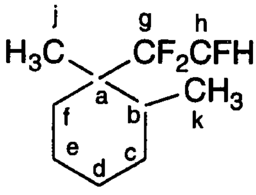


(56)

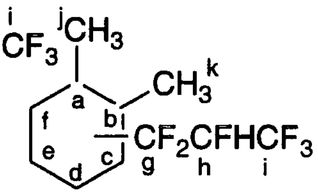
Chemical Shift (ppm)	Multipicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
0.7 - 2.1	m		13	(55) b, c, d, e, f, j (56) b, c, d, e, f, j
3.5 - 3.7	m		1	(56) c, d, e
4.7 - 5.0	m		1	(55) h (56) h
^{19}F				
-74.33	m		3	(55) or (56) i
-74.57	m			(55) or (56) i
-74.72	m			(55) or (56) i
-118.36	m		2	(55) or (56) g
-120.24, -127.40	AB	J_{AB} 270.9		(55) or (56) g
-206.62	d	^{3}J 12.0	1	(55) or (56) h
-211.60	m			(55) or (56) h
-212.26	d	^{2}J 44.4		(55) or (56) h
^{13}C				
21.94	d	^{3}J 4.9		(55) j
25.56	m			(55) c, e
25.72	s			(55) c, e
26.10	s			(55) d
34.41	m			(55) b, f
34.93	s			(55) b, f
42.07	t	^{2}J 20.9		(56) c or d or e
48.38	t	^{2}J 20.2		(55) a
49.49	t	^{2}J 20.2		(55) a
85.22	dm	^{1}J 195.3		(55) h
121.17	d, d, d	^{1}J 261.5 ^{1}J 247.4 ^{2}J 21.8		(55) g
121.72	q,d	^{1}J 281.6 ^{2}J 26.0		(55) i

Note :- From ^{13}C NMR spectra, many other peaks are observed than those quoted in the table, illustrating this reaction is not very selective, and all products formed contain isomers

25. (1,1,2,3,3,3-Hexafluoropropyl)-1,2-dimethylcyclohexanes (58) / (59)



(58)

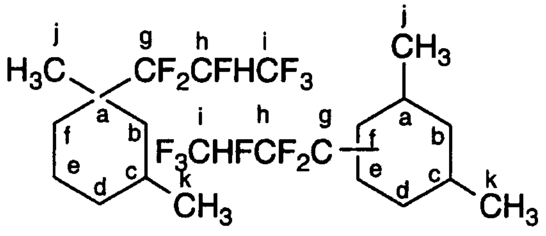


(59)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
0.9 - 2.1	m		15	**(58)** b, c, d, e, f, j, k **(59)** b, c, d, e, f, j, k
4.8 - 5.0	m		1	**(58)** h **(59)** h
^{19}F				
-74.19	m			**(58)** or **(59)** i
-74.38	m		3	**(58)** or **(59)** i
-74.62	m			**(58)** or **(59)** i
-108 / -120	m		2	**(58)** or **(59)** g
-204.61	dm	^{2}J 35.0		**(58)** or **(59)** h
-207.14	dm	^{2}J 42.9		**(58)** or **(59)** h
-211.31	dm	^{2}J 44.0	1	**(58)** or **(59)** h
-212.15	m			**(58)** or **(59)** h
^{13}C				
10.0 - 40.0	m			**(58)** b, c, d, e, f, j, k **(59)** b, c, d, e, f, j, k
42.29	t	^{2}J 21.0		**(59)** d or e
48.49	t	^{2}J 19.5		**(58)** a
49.82	t	^{2}J 195		**(58)** a
85.37	dm	^{1}J 194.1		**(58)** h **(59)** h
116.0-126.0	m			**(58)** g, i **(59)** g, i

Note :- All spectra are complex illustrating isomer mixtures of different products.

26. (1,1,2,3,3,3-Hexafluoropropyl)-1,3-dimethylcyclohexanes (61) / (62)

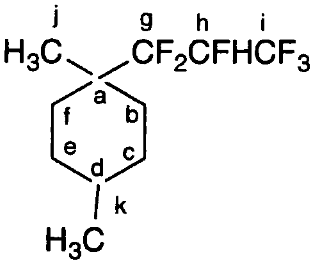


(61) **(62)**

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
0.6 - 2.2	m		15	**(61)** b, c, d, e, f, j, k **(62)** b, c, d, e, f, j, k
4.76	dm	^2J 17.2	1	**(62)** h
4.93	dm	^2J 44.0		**(61)** h
^{19}F				
-74.70	m		3	**(61)** or **(62)** i
-74.54	m			**(61)** or **(62)** i
-120.27 / -127.51	AB	J_{AB} 270.9	2	**(61)** or **(62)** g
-206.45	m		1	**(61)** or **(62)** h
-210.22	dm	^2J 45.2		**(61)** or **(62)** h
-211.52	dm	^2J 42.5		**(61)** or **(62)** h
-212.01	dm	^2J 44.03		**(61)** or **(62)** h
-212.36	dm	^2J 44.78		**(61)** or **(62)** h
^{13}C				
17.08	dd	^5J 4.0 ^5J 1.9		**(61)** j, k
21.13	s			**(61)** d
21.30	s			**(61)** d
29.13	m			**(61)** f
32.00	s			**(61)** c
32.18	s			**(61)** c
34.78	s			**(61)** e
38.30	m			**(61)** b
41.70	t	^2J 20.0		**(62)** e
48.00	t			**(61)** a
49.50	t			**(61)** a
84.62	dm			**(61)** h
120.79	m			**(61)** g
121.64	qd	^1J 283.6 ^2J 26.7		**(61)** i

^{13}C NMR data listed above is mainly assigned as arising from compound **(61)**. However, many other signals are present than shown above, which would be assigned to compounds **(62)**.

27. 1-(1,1,2,3,3,3-Hexafluoropropyl)-1,4-dimethylcyclohexane (63)

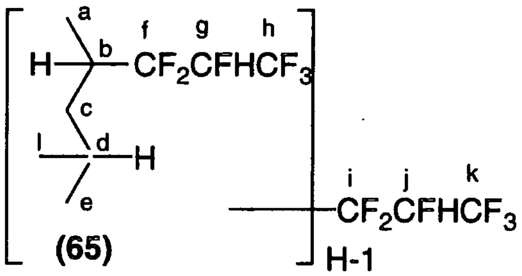


(63)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H				
0.8 - 1.8	m		15	b, c, d, e, f, j, k
4.90	m		1	h
^{19}F				
-74.41	m		3	i
-120.08 / -127.28	AB	J_{AB} 270.6	2	g
-206.49	d	^2J 43.3	1	h
^{13}C				
16.49	dd	^3J 8.1 ^3J 3.8		j
22.44	s			k
29.92	m			b, f
30.10	s			c, e
32.86	s			d
41.76	t	^2J 19.8		a
84.74	dm	^1J 197.1		h
121.30	ddd	^1J 261.5 ^1J 247.4 ^2J 21.7		g
121.97	qd	^1J 282.6 ^2J 26.0		i

Note :- The relative simplicity of both ^{13}C and ^{19}F NMR spectra illustrates formation of only one major product i.e. compound (**63**).

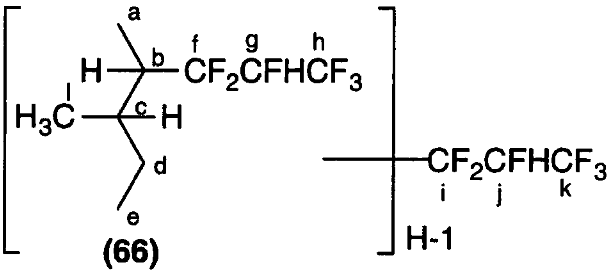
28. Di-(1,1,,2,3,3,3-hexafluoropropyl)-2-methylpentanes (65)



(65)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
1.0 - 2.4	m		12	a, b, c, e, l
4.8 - 5.0	m		2	g, j
^{19}F				
-73.85	m		3	h, k
-73.99	m			h, k
-74.10	m			h, k
-74.43	m			h, k
-104.0 / -124.2	m		2	f, i
-205.89	t	^{2}J 57.57	1	g, j
-206.26	dm	^{2}J 44.0		g, j
-208.60	dm	^{2}J 44.0		g, j
-210.19	dm	^{2}J 44.0		g, j
-210.54	dm	^{2}J 44.0		g, j
-211.74	m			g, j
^{13}C				
15.0 - 42.0	m			a, b, c, d, e, l
84.44	dm	^{1}J 194.2		g, j
116.5 - 125.0	m			f, h, i, k

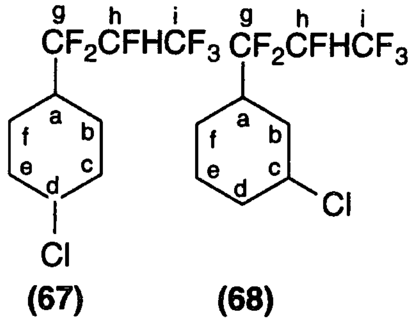
29. Di-(1,1,2,3,3,3-hexafluoropropyl)-3-methylpentanes (66)



(66)

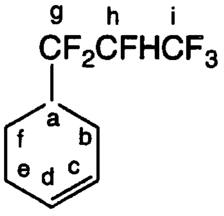
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
0.8-2.2	m		12	a, b, c, d, e, l
4.85	m		2	g, j
^{19}F				
-73.90	m		3	h, k
-74.03	m			h, k
-74.57	m			h, k
-75.50	m			h, k
-106.0 / -119.4	m		2	f, i
-206.55	m		1	g, j
-210.32	dm	^{2}J 45.2		g, j
^{13}C				
8.0 - 73.0	m			a, b, c, d, e, l
82.0 - 88.0	m			g, j
116.0 - 126.0	m			f, h, i, k

30. A mixture of 1-(1,1,2,3,3,3-hexafluoropropyl)-3-chlorocyclohexane **(68)** and 1-(1,1,2,3,3,3-hexafluoropropyl)-4-chlorocyclohexane **(67)**

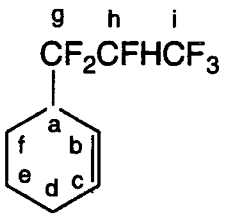


Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H				
1.1 - 2.7	m		10	**(67)** a, b, c, d, e, f **(68)** a, b, c, d, e, f
3.93	m		1	**(67)** c
4.55	m		1	**(68)** c
4.78	dm	^2J 43.6	1	**(67)** h **(68)** h
^{13}C				
17.94 - 36.49	m			**(67)** b, d, e, f **(68)** b, c, e, f
41.13	m			**(67)** d
47.81	m			**(68)** c
57.31	m			**(67)** a **(68)** a
84.81	dm	^1J 160.0		**(67)** h **(68)** h
117.0 - 125.0	m			**(67)** g, i **(68)** g, i

31. A mixture mainly containing 4-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene (71) and a small quantity of 3-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene (72)



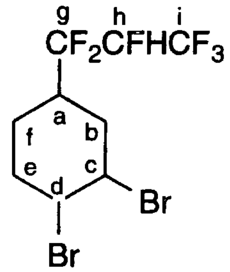
(71)



(72)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H				
1.5 - 2.5	m		7	**(71)** a, b, e, f **(72)** a, d, e, f
4.84	m		1	**(71)** h **(72)** h
5.6 - 6.2	m		1	**(71)** c, d **(72)** b, c
^{19}F				
-73.89 (small)	m		3	**(72)** i
-74.67 (small)				**(72)** i
-74.55 (large)				**(71)** i
-117.82 / -120 .02 major signal	AB	J_{AB} 263.6	2	**(71)** g
-211.77 major signal	m		1	**(71)** h

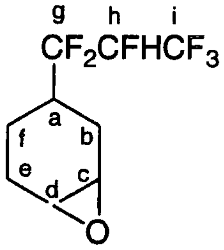
32. A mixture containing 1-(1,1,2,3,3,3-hexafluoropropyl)-3,4-dibromocyclohexane (73) as the major product



(73)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
1.5 - 2.7	m		6	b, e, f
4.5 - 4.9	m		4	a, c, d, h
^{19}F				
-74.57 major signal	s		3	i
-117.25 major signal	d	^{1}J 285.0	2	g
-210.66 major signal	s		1	h

33. A mixture containing 4-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexene oxide (75) as the major product



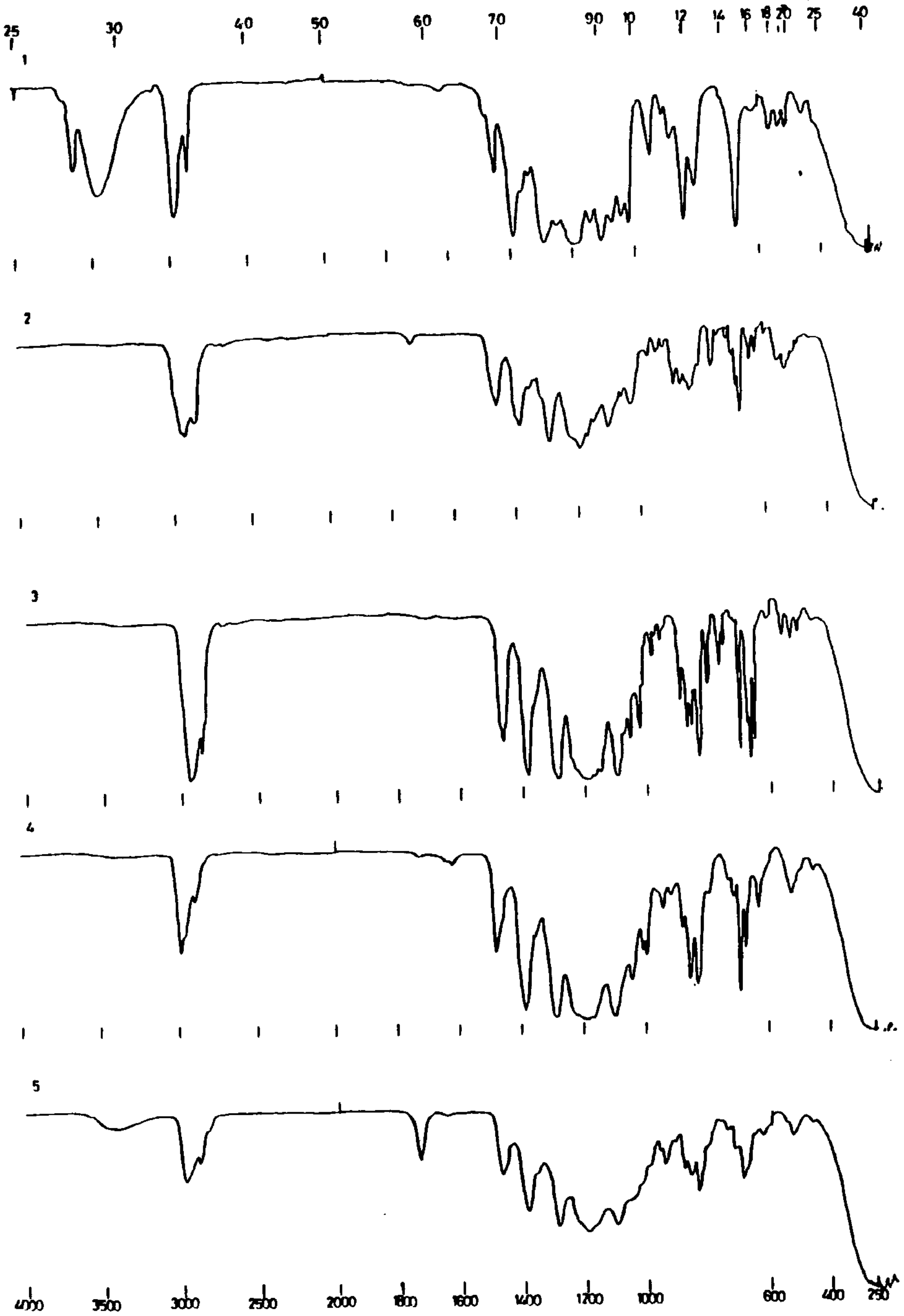
(75)

Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^1H				
1.0 - 2.5	m		7	a, b, e, f
3.22	s		1	d
3.31	s		1	c
4.80	m		1	h
^{19}F				
-73.92	s			i
minor signal				
-74.56	s		3	i
major signal				
-118.55	m		2	g
one major signal				
-211.02	d	^2J 42.4		h
-211.46	d	^2J 40.7	1	h
-211.94	d	^2J 40.9		h

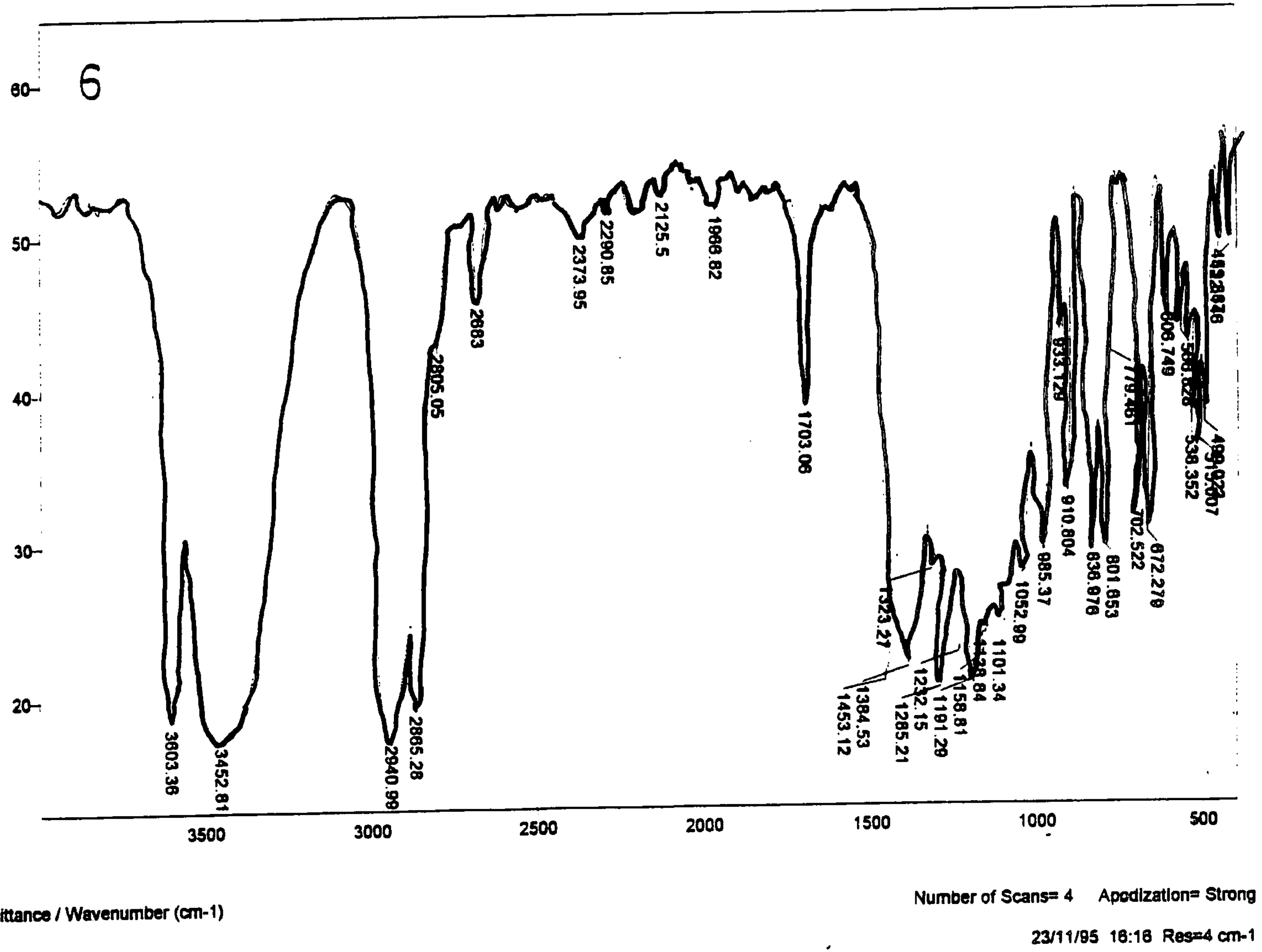
APPENDIX 2
IR SPECTRA

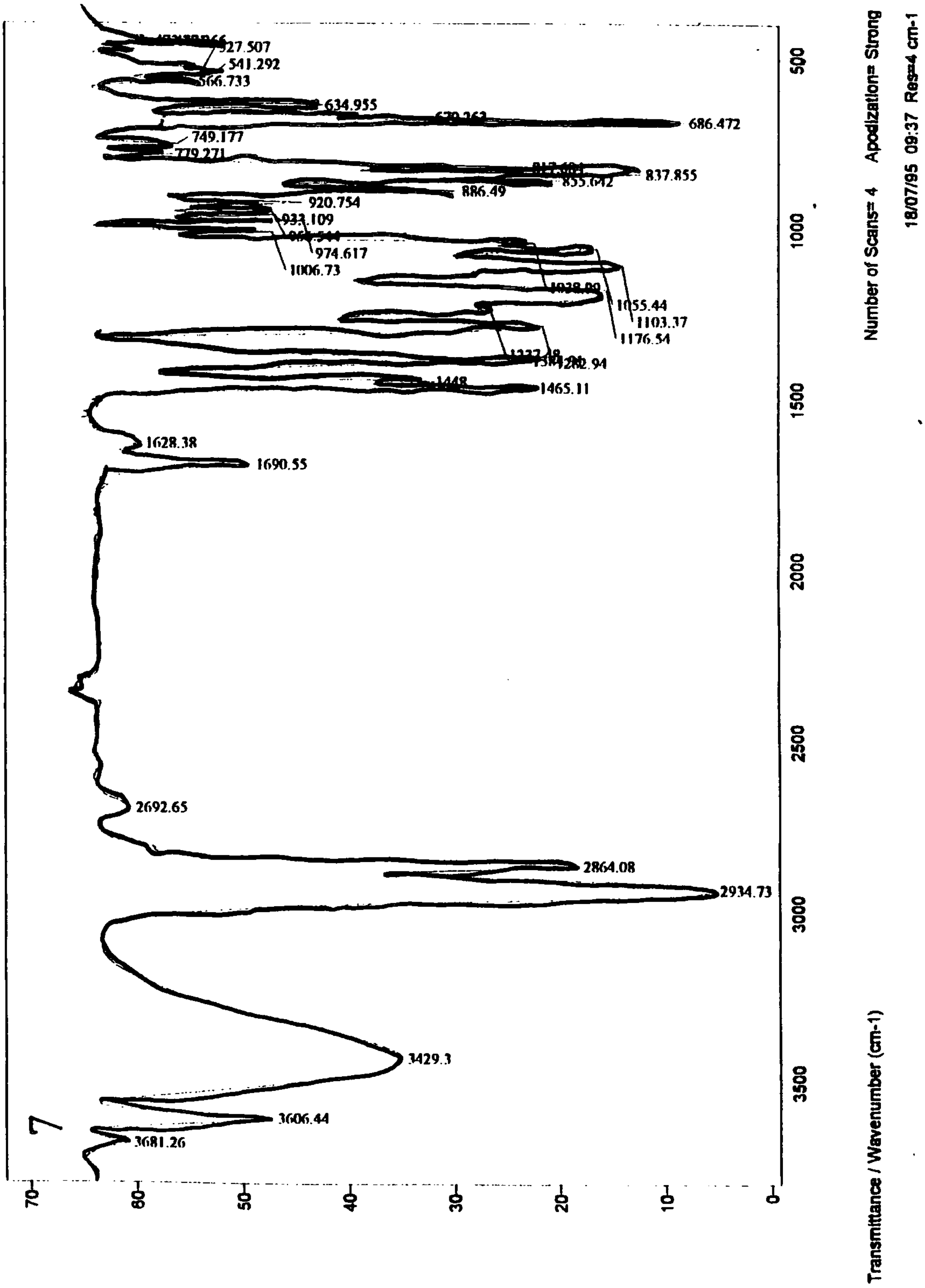
Appendix Two
IR spectra

1. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclopentanol **(20)**
2. (1,1,2,3,3,3-Hexafluoropropyl)-1,2-dimethylcyclohexanes **(58)** / **(59)**
3. (1,1,2,3,3,3-Hexafluoropropyl)-1,3-dimethylcyclohexanes **(61)** / **(62)**
4. (1,1,2,3,3,3-Hexafluoropropyl)-2-methylpentanes **(65)**
5. (1,1,2,3,3,3-Hexafluoropropyl)-3-methylpentanes **(66)**
6. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexanol **(22)**
7. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cycloheptanol **(24)**
8. 1-(1,1,2,3,3,3-Hexafluoropropyl)-4-methylcyclohexanol **(29)**
9. 1-(1,1,2,3,3,3-Hexafluoropropyl)-3-methylcyclohexanol **(27)**
10. 1,3-di-(1,1,2,3,3,3-Hexafluoropropyl)-cyclopentan-1,3-diol **(31)**
11. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexan-1,3-diol **(32)**
12. 1,3-Di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexan-1,3-diol **(33)**
13. 1,4-Di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexan-1,4-diol **(34)**
14. 2,4-Di-(1,1,2,3,3,3-hexafluoropropyl)-pentan-2,4-diol **(36)**
15. 2,5-Di-(1,1,2,3,3,3-hexafluoropropyl)-hexane-2,5-diol **(37)**
16. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclopentene **(41)**
17. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene **(42)**
18. 1,4-Di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexa-1,3-diene (44) and 1,4-di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexa-1,4-diene (43)
19. 1-(1,1,2,3,3,3-Hexafluoropropyl)-1,2-dibromocyclopentane **(45)**
20. 1-(1,1,2,3,3,3-hexafluoropropyl)-1,2-dibromocyclohexane **(46)**
21. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclopentene oxide **(47)**
22. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene oxide **(48)**
23. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexan-1,2-diol **(49)**
24. 1-(1,1,2,3,3,3-Hexafluoropropyl)-benzene **(50)**
25. 1,4-Di-(1,1,2,3,3,3-hexafluoropropyl)-benzene **(51)**
26. (1,1,2,3,3,3-Hexafluoropropyl)-cyclohexane **(13)**
27. (1,1,2,3,3,3-Hexafluoropropyl)-methylcyclopentanes **(52)** / **(53)**
28. (1,1,2,3,3,3-Hexafluoropropyl)-methylcyclohexanes **(55)** / **(56)**
29. 1-(1,1,2,3,3,3-Hexafluoropropyl)-1,4-dimethylcyclohexane **(63)**
30. A mixture of 1-(1,1,2,3,3,3-hexafluoropropyl)-3-chlorocyclohexane **(68)** and 1-(1,1,2,3,3,3-hexafluoropropyl)-4-chlorocyclohexane **(67)**
31. 4-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene **(71)**
32. 1-(1,1,2,3,3,3-Hexafluoropropyl)-3,4-dibromocyclohexane **(73)**
33. 4-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene oxide **(75)**

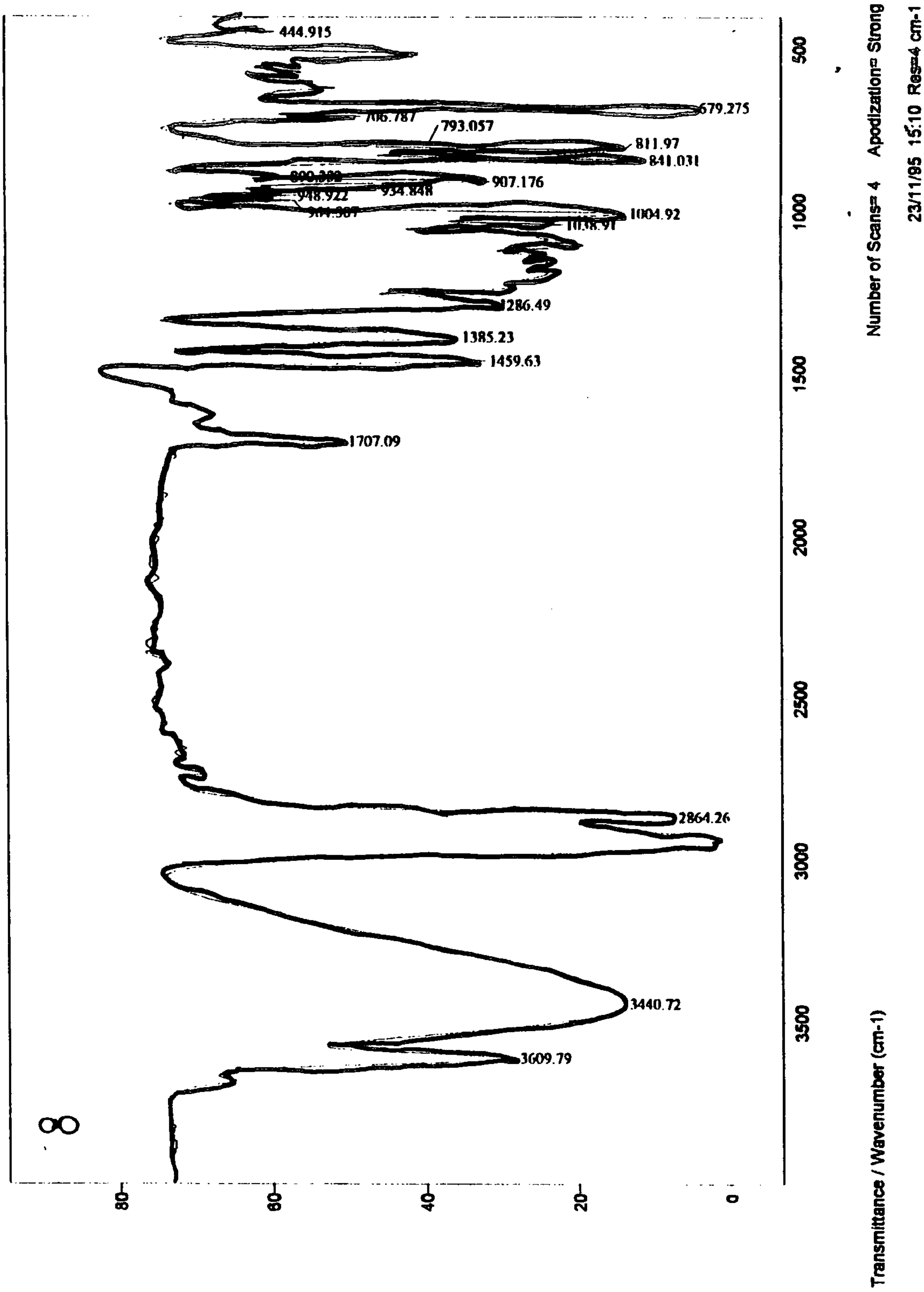

25
30
40
50
60
70
90
10
12
14
16
18
20
25
40
1
2
3
4
5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
600
400
250

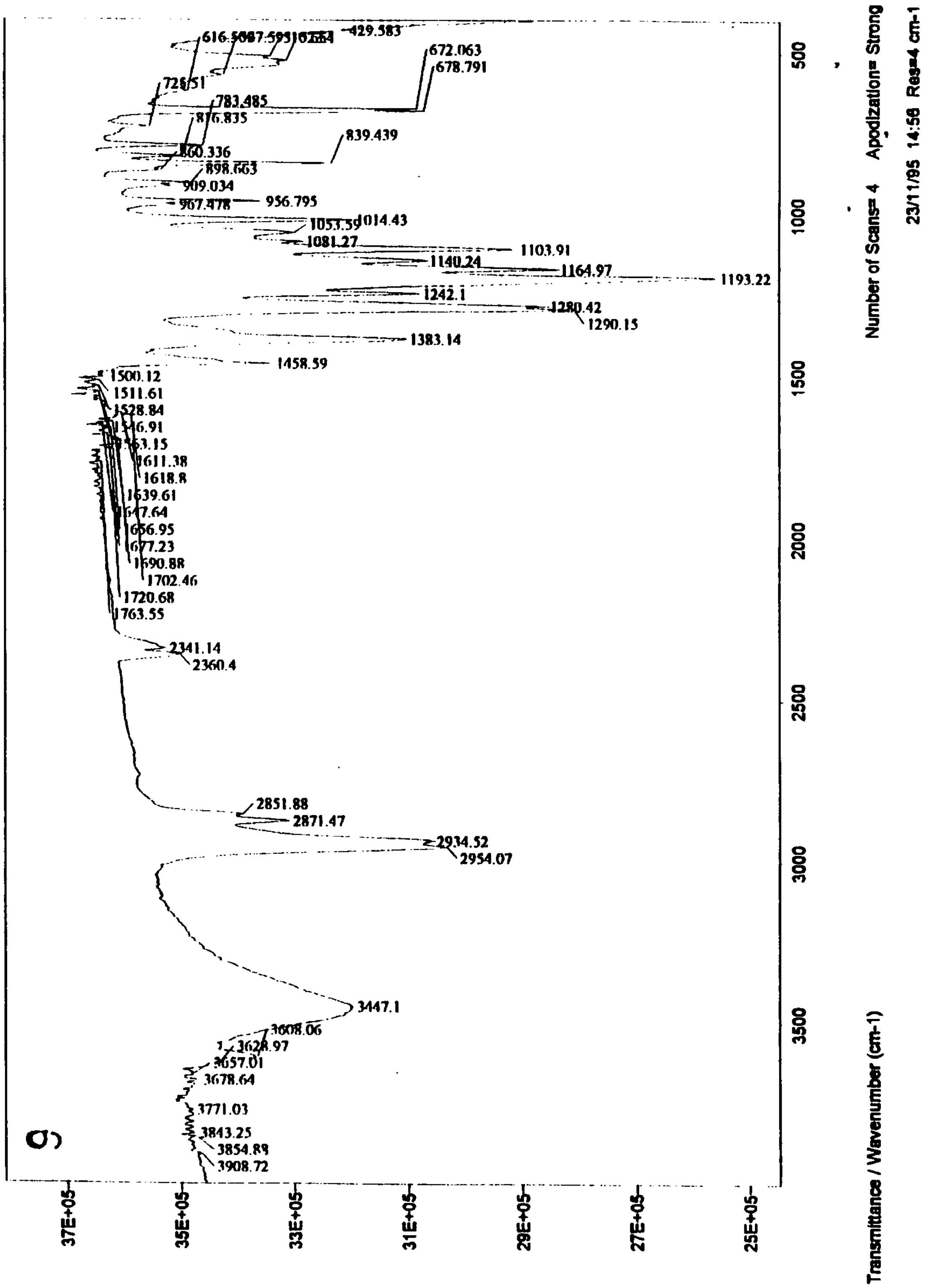
6

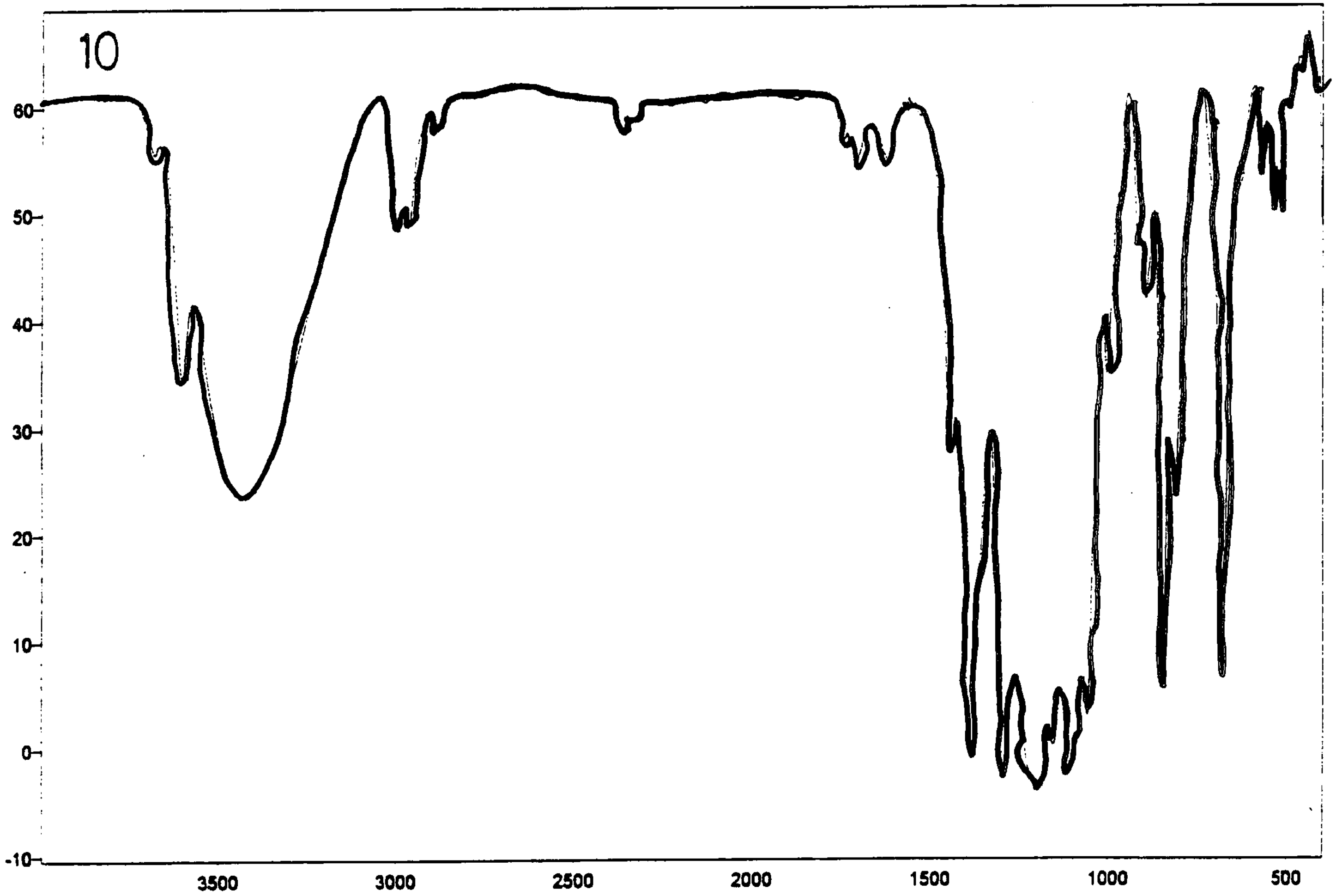

60
50
40
30
20
3603.36
3452.81
2940.99
2865.28
2805.05
2683
2373.95
2290.85
2125.5
1968.82
1703.06
1453.12
1384.53
1323.27
1285.21
1232.15
1191.29
1158.81
1138.84
1101.34
1052.99
985.37
933.129
910.804
836.976
801.853
779.461
702.522
672.279
606.749
566.828
538.352
519.607
499.023
482.876
3500
3000
2500
2000
1500
1000
500
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong
23/11/95 16:16 Res=4 cm-1


527.507
541.292
566.733
634.955
686.472
749.177
779.271
837.855
855.642
886.49
920.754
933.109
974.617
1006.73
1055.44
1103.37
1176.54
1282.94
1448
1465.11
1628.38
1690.55
2692.65
2864.08
2934.73
3429.3
3606.44
3681.26
500
1000
1500
2000
2500
3000
3500
70
60
50
40
30
20
10
0
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong
18/07/95 09:37 Res=4 cm-1

7


8
444.915
679.275
706.787
793.057
811.97
841.031
907.176
934.848
948.922
1004.92
1038.91
1286.49
1385.23
1459.63
1707.09
2864.26
3440.72
3609.79
80
60
40
20
0
500
1000
1500
2000
2500
3000
3500
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong
23/11/95 15:10 Res=4 cm-1

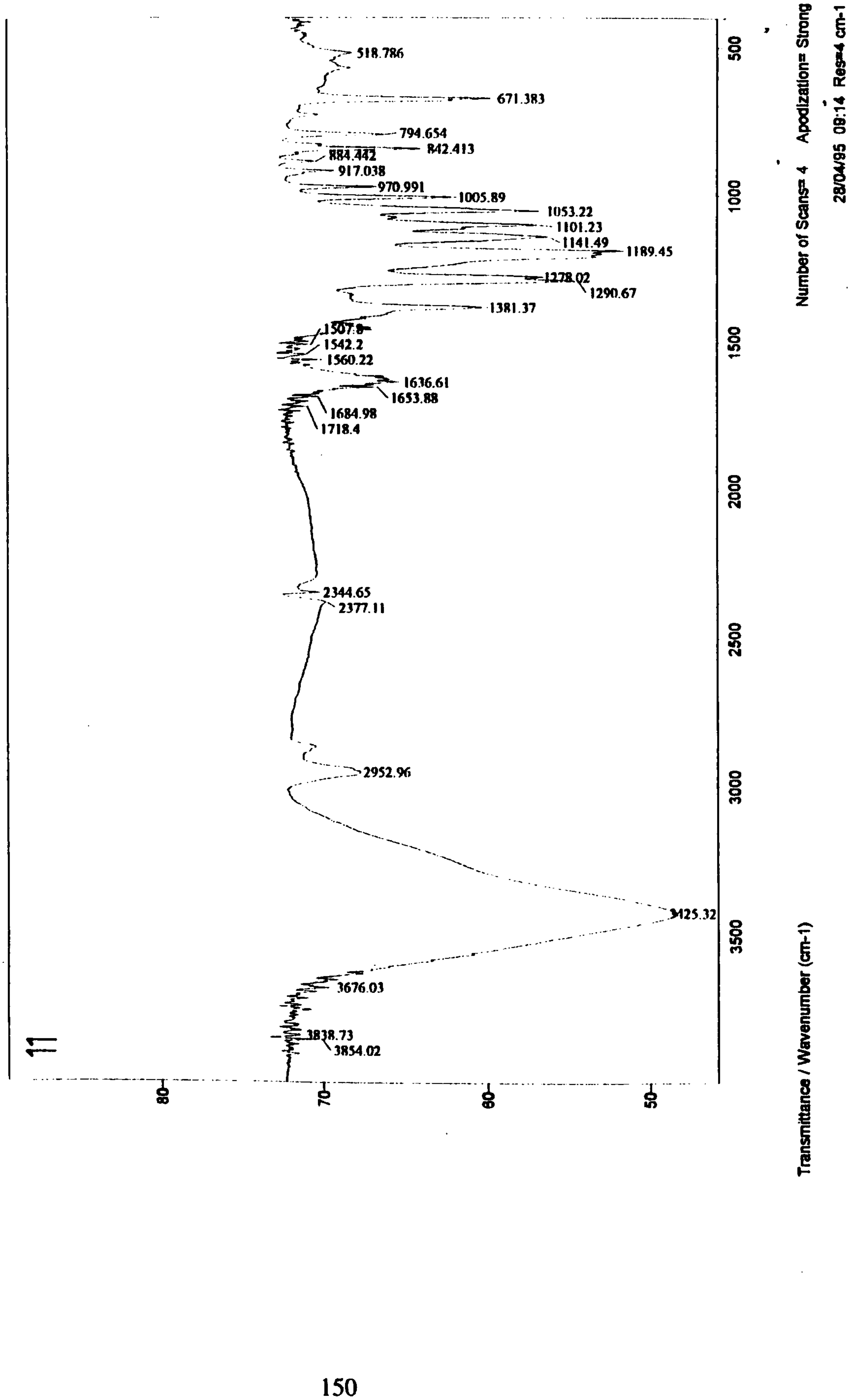

a)
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong
23/11/95 14:58 Res=4 cm-1
37E+05
35E+05
33E+05
31E+05
29E+05
27E+05
25E+05
500
1000
1500
2000
2500
3000
3500
429.583
616.5
672.063
678.791
728.51
783.485
816.835
839.439
860.336
898.663
909.034
967.478
956.795
1014.43
1053.59
1081.27
1103.91
1140.24
1164.97
1193.22
1242.1
1280.42
1290.15
1383.14
1458.59
1500.12
1511.61
1528.84
1546.91
1563.15
1611.38
1618.8
1639.61
1647.64
1656.95
1677.23
1690.88
1702.46
1720.68
1763.55
2341.14
2360.4
2851.88
2871.47
2934.52
2954.07
3447.1
3608.06
3628.97
3657.01
3678.64
3771.03
3843.25
3854.89
3908.72

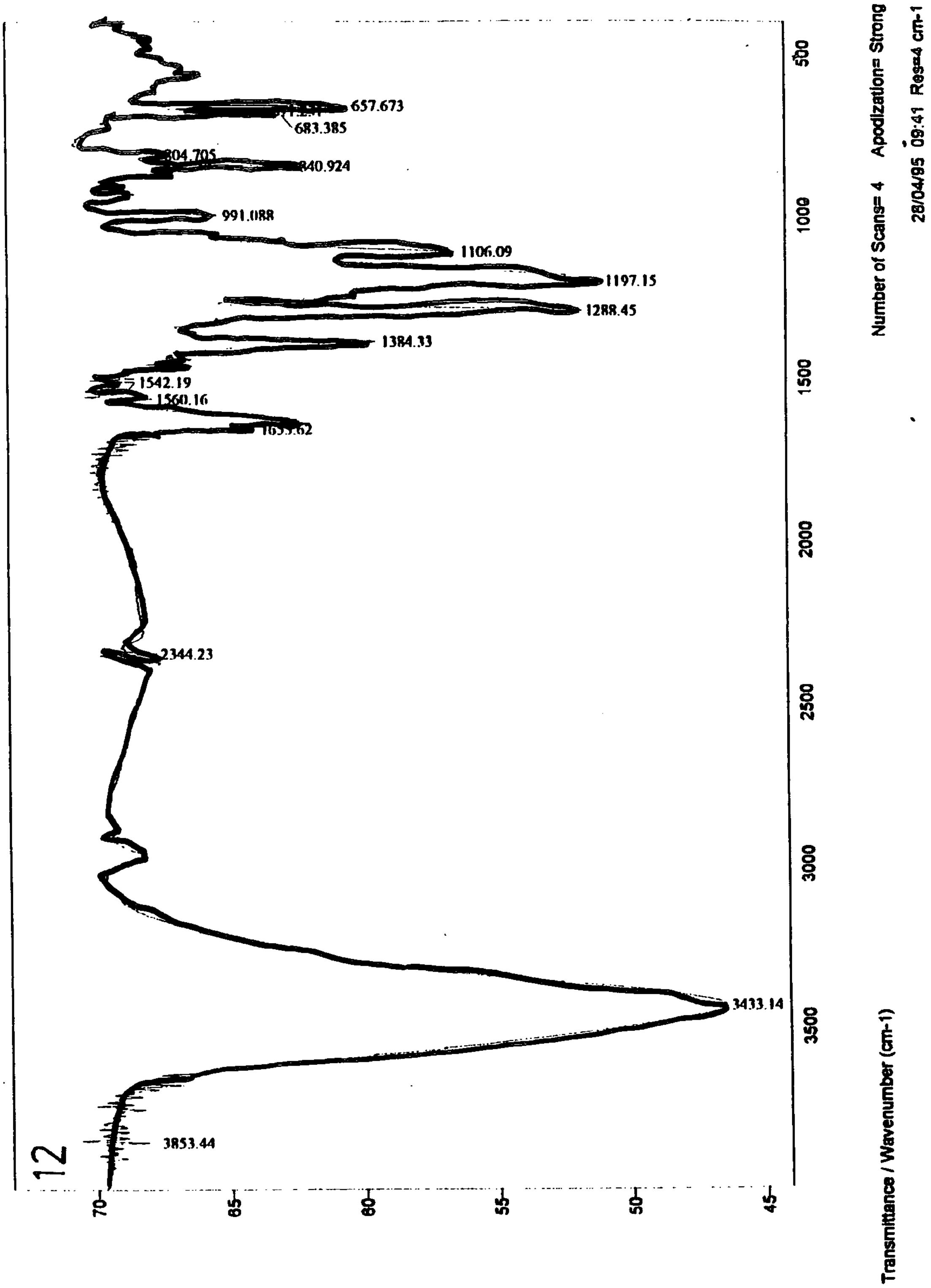


Transmittance / Wavenumber (cm-1)

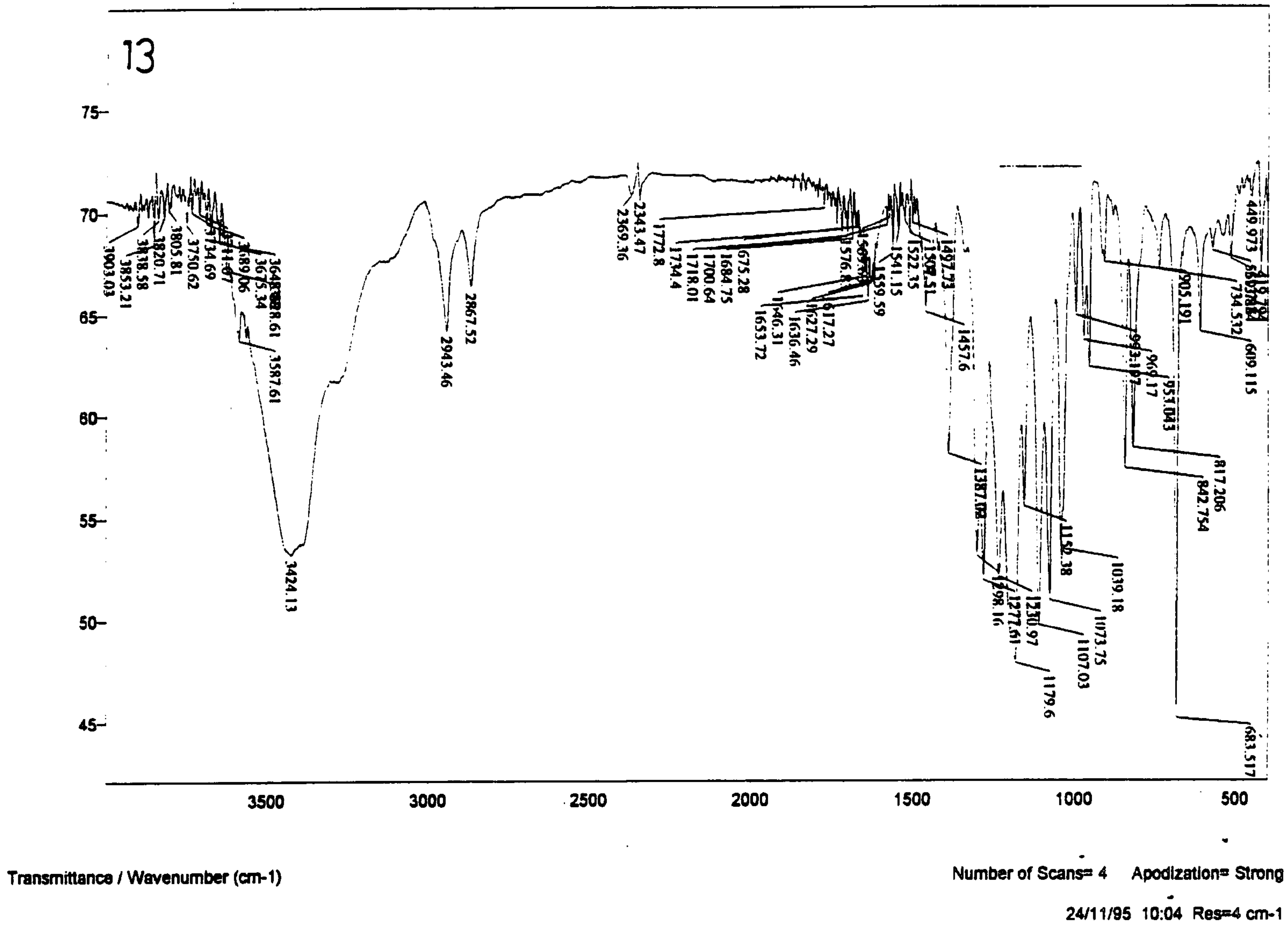
Number of Scans= 4 Apodization= Strong

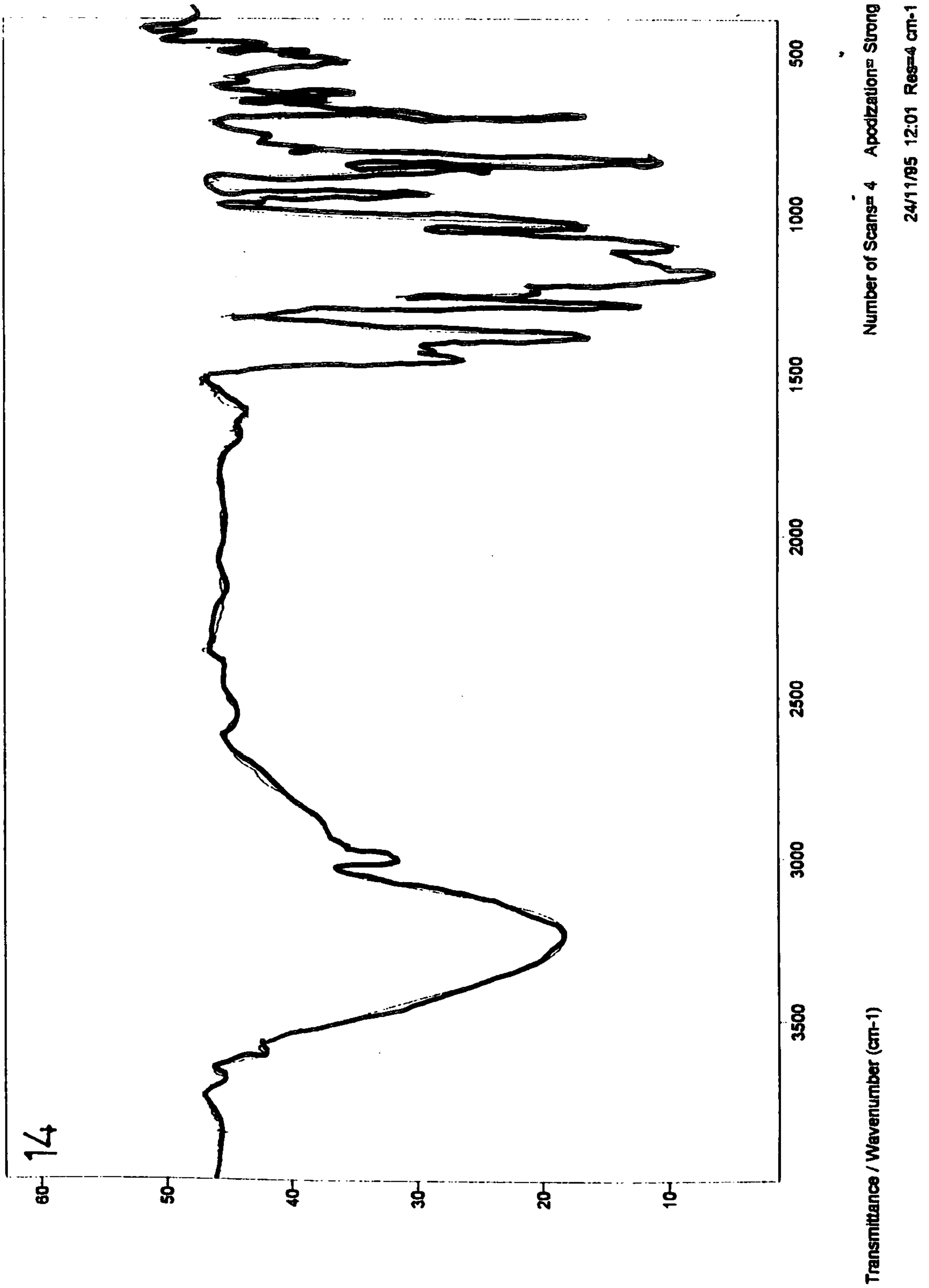
24/11/95 11:32 Res=4 cm-1

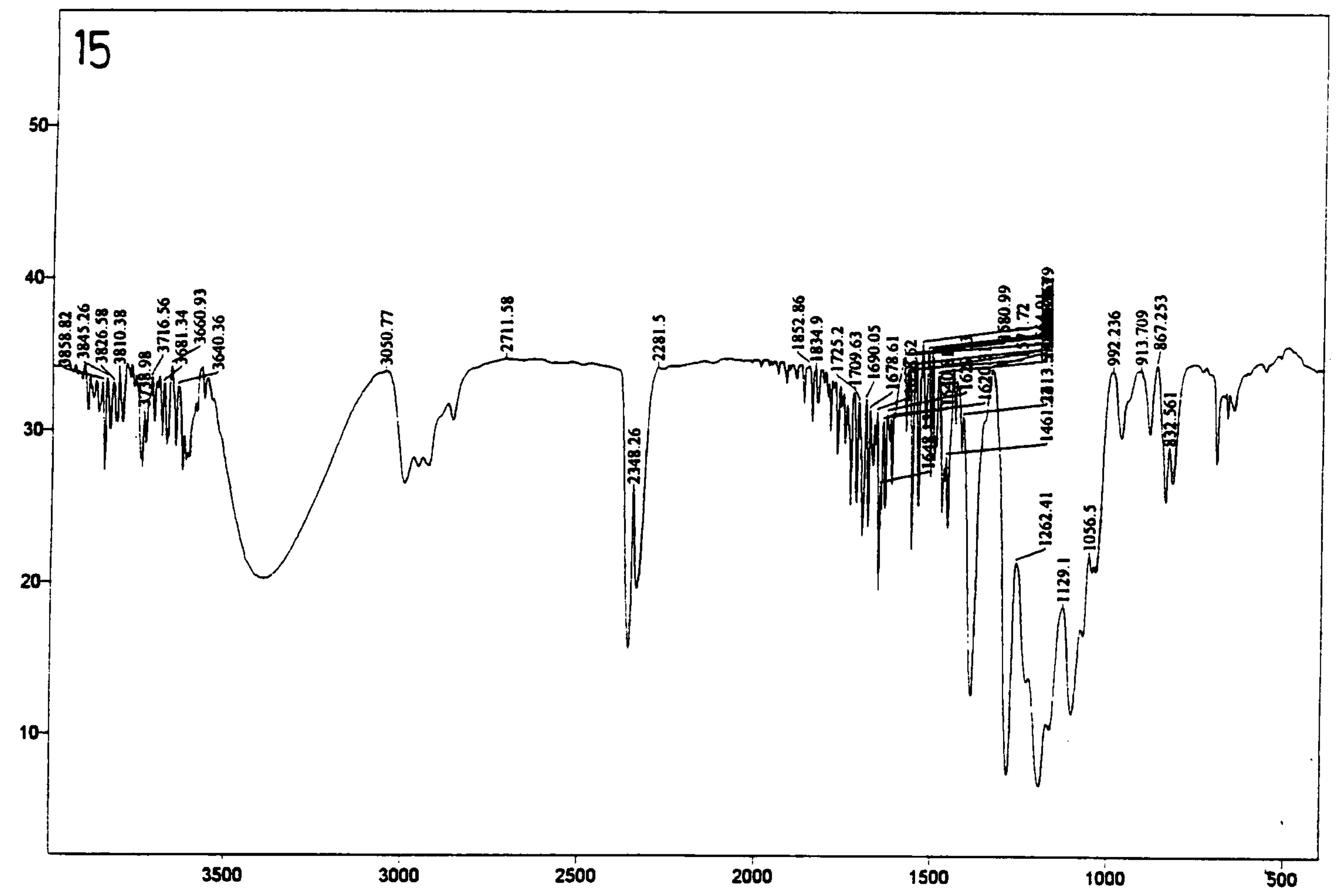

11
518.786
671.383
794.654
842.413
884.442
917.038
970.991
1005.89
1053.22
1101.23
1141.49
1189.45
1278.02
1290.67
1381.37
1507.8
1542.2
1560.22
1636.61
1653.88
1684.98
1718.4
2344.65
2377.11
2952.96
3425.32
3676.03
3838.73
3854.02
80
70
60
50
500
1000
1500
2000
2500
3000
3500
Number of Scans= 4 Apodization= Strong
28/04/95 08:14 Res=4 cm-1
Transmittance / Wavenumber (cm-1)


12
3853.44
3433.14
2344.23
1653.62
1560.16
1542.19
1384.33
1288.45
1197.15
1106.09
991.088
840.924
804.705
683.385
657.673
70
65
60
55
50
45
3500
3000
2500
2000
1500
1000
500
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong
28/04/95 09:41 Res=4 cm-1

13


75
70
65
60
55
50
45
3500
3000
2500
2000
1500
1000
500
3903.03
3853.21
3838.58
3820.71
3805.81
3750.62
3734.69
3711.07
3689.06
3675.34
3587.61
3424.13
2943.46
2867.52
2369.36
2343.47
1772.8
1734.4
1718.01
1700.64
1684.75
1675.28
1653.72
1646.31
1636.46
1627.29
1617.27
1576.8
1559.59
1541.15
1522.35
1497.73
1457.6
1387.02
1298.16
1277.61
1230.97
1179.6
1152.38
1107.03
1073.75
1039.18
993.107
969.17
953.043
905.191
842.754
817.206
734.532
683.517
609.115
449.973
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong
24/11/95 10:04 Res=4 cm-1

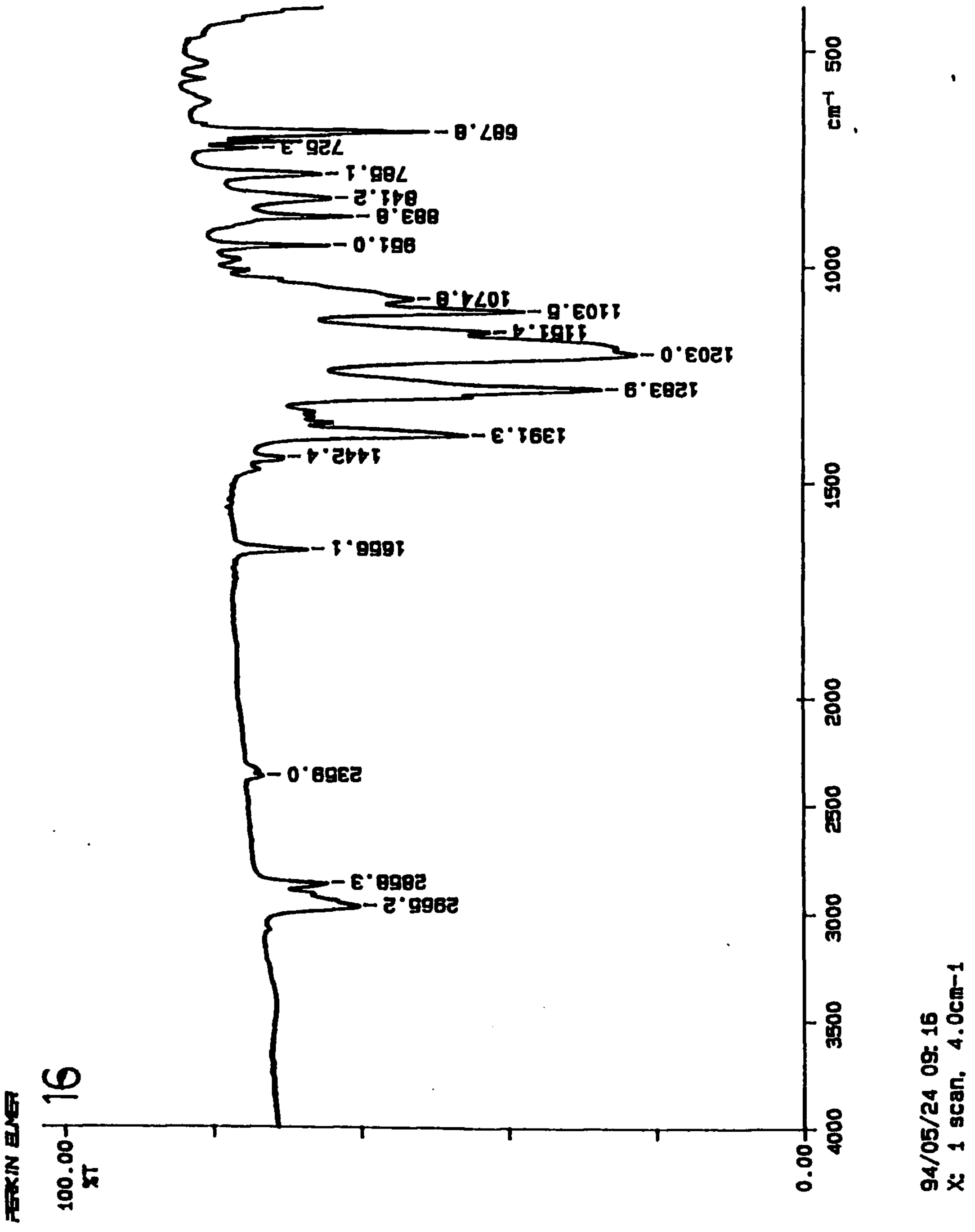

14
60
50
40
30
20
10
3500
3000
2500
2000
1500
1000
500
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong
24/11/95 12:01 Res=4 cm-1

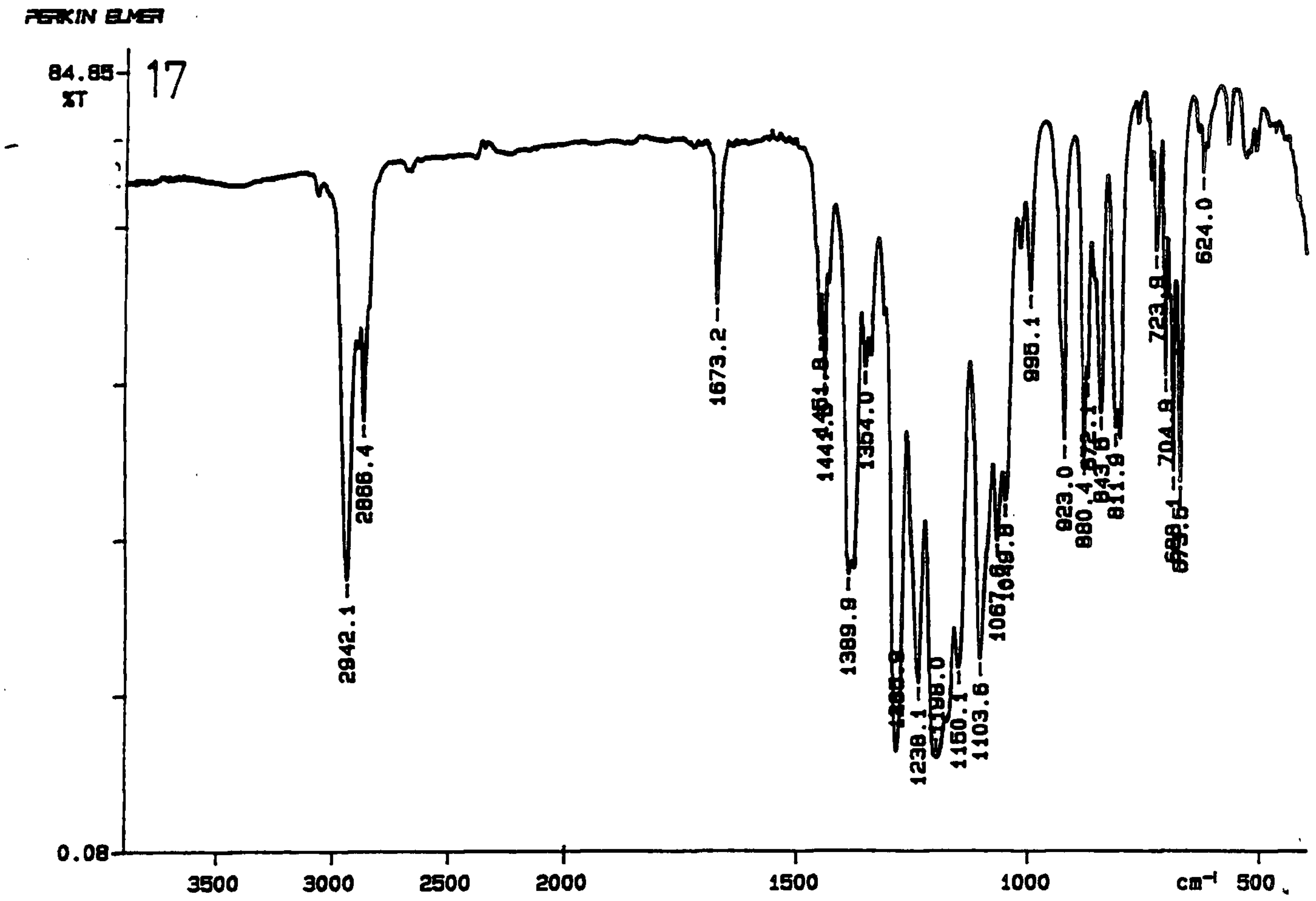


Arbitrary Y / Wavenumber (cm-1)

Number of Scans= 4 Apodization= Strong

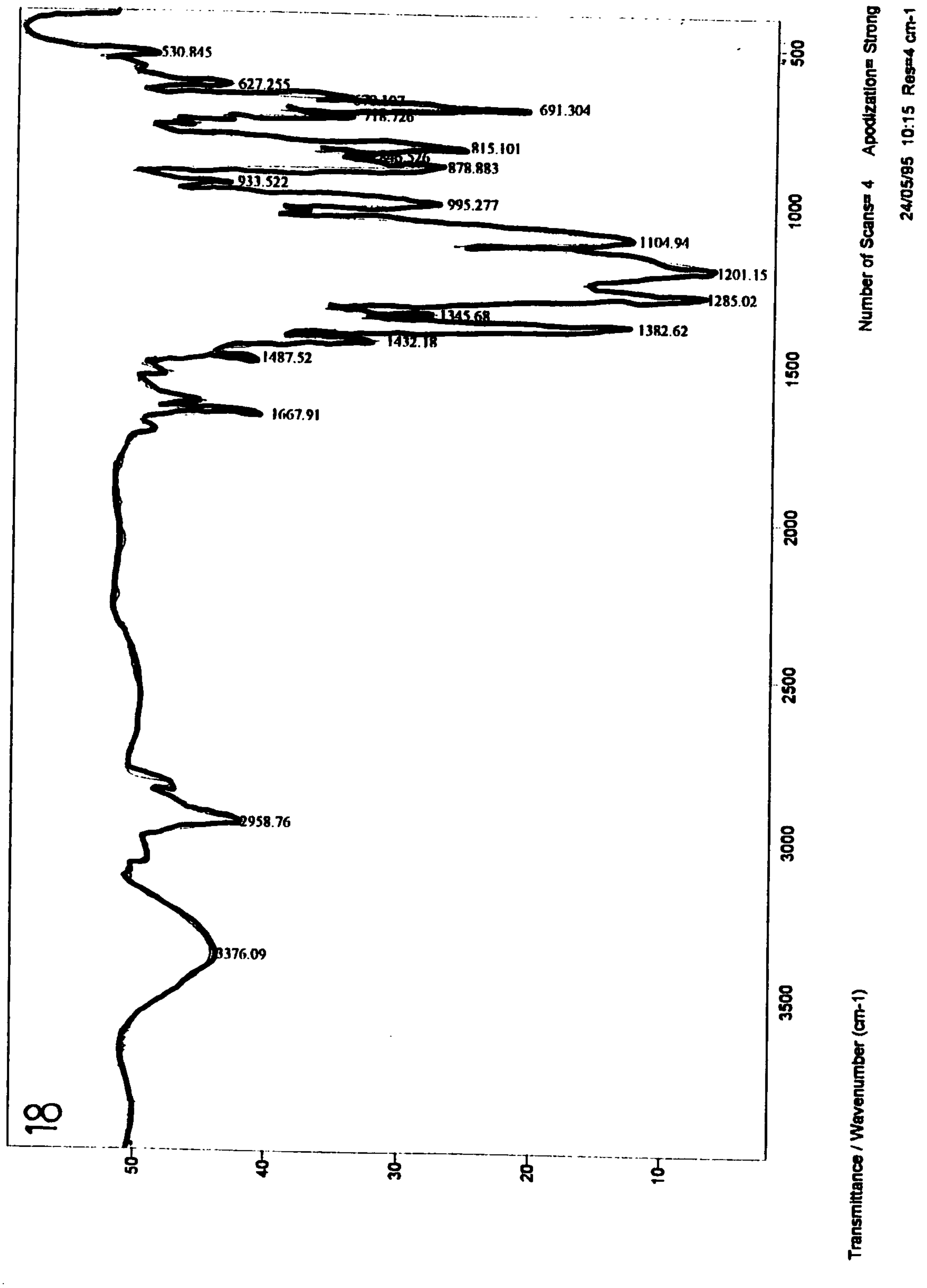
17/03/95 16:55 Res=4 cm-1

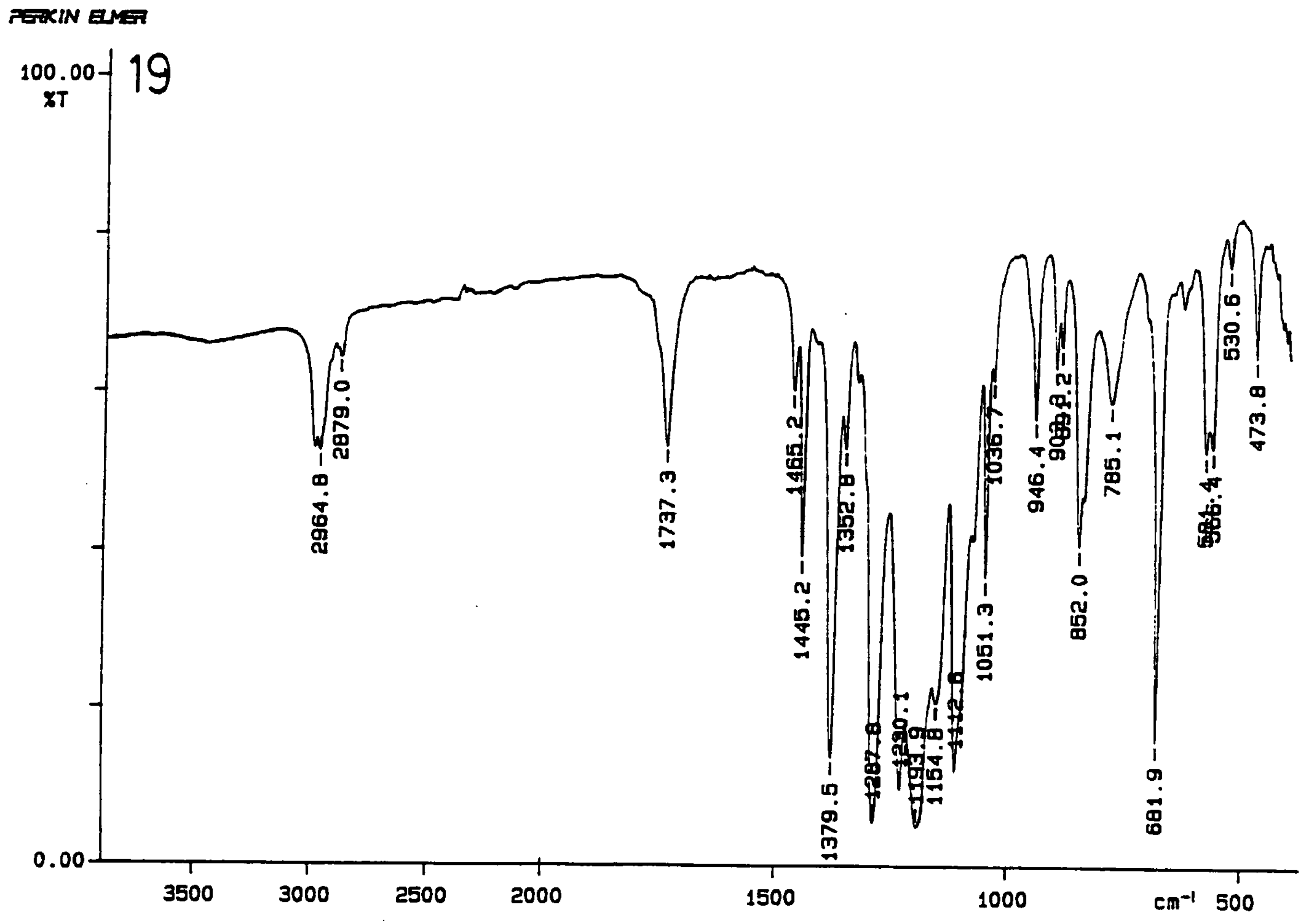

16
PERKIN ELMER
100.00
%T
0.00
4000
3500
3000
2500
2000
1500
1000
500
cm⁻¹
2965.2
2858.3
2358.0
1658.1
1442.4
1391.3
1283.9
1203.0
1161.4
1103.5
1074.8
951.0
883.8
841.2
785.1
726.3
687.8
94/05/24 09:16
X: 1 scan, 4.0cm-1



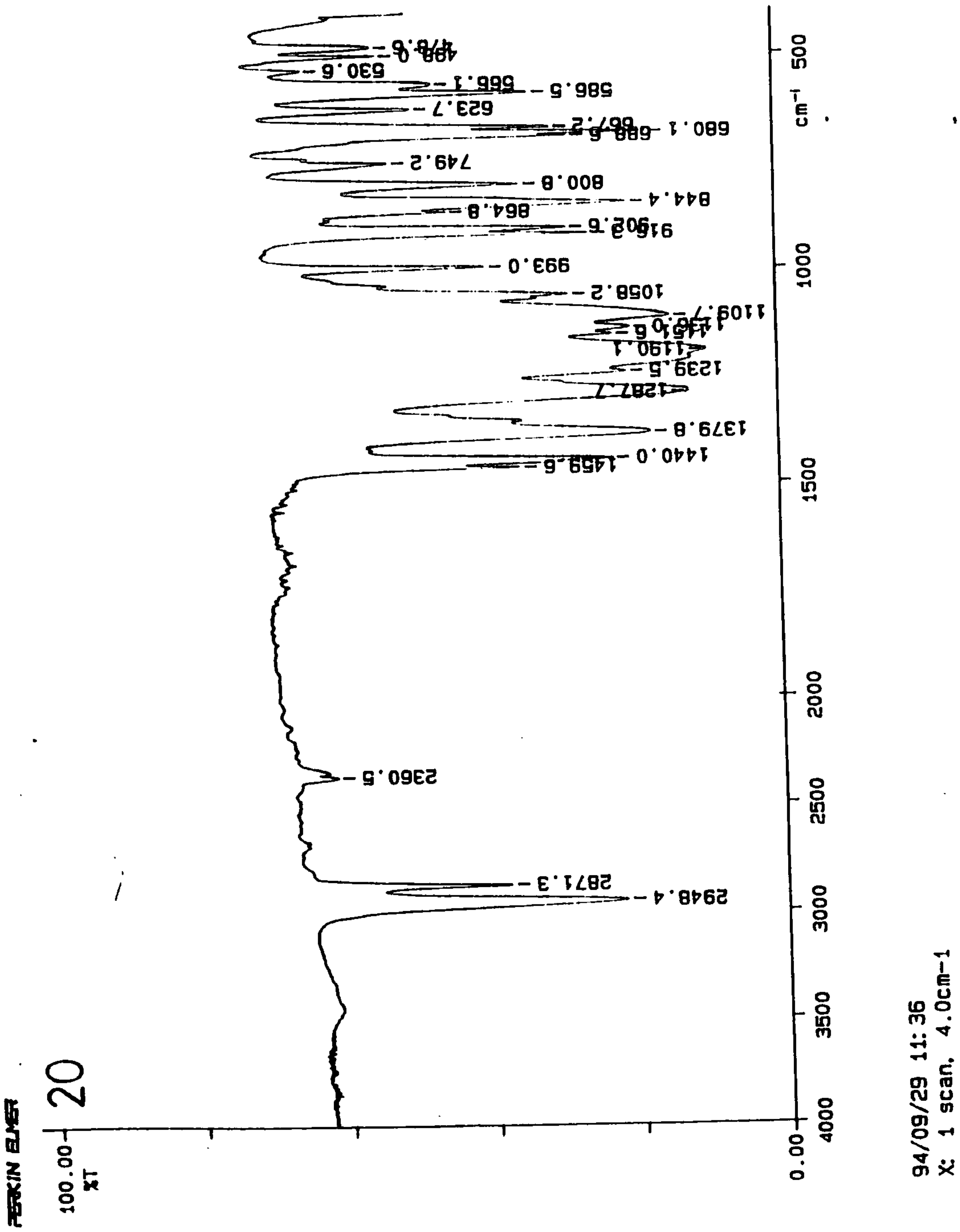
17

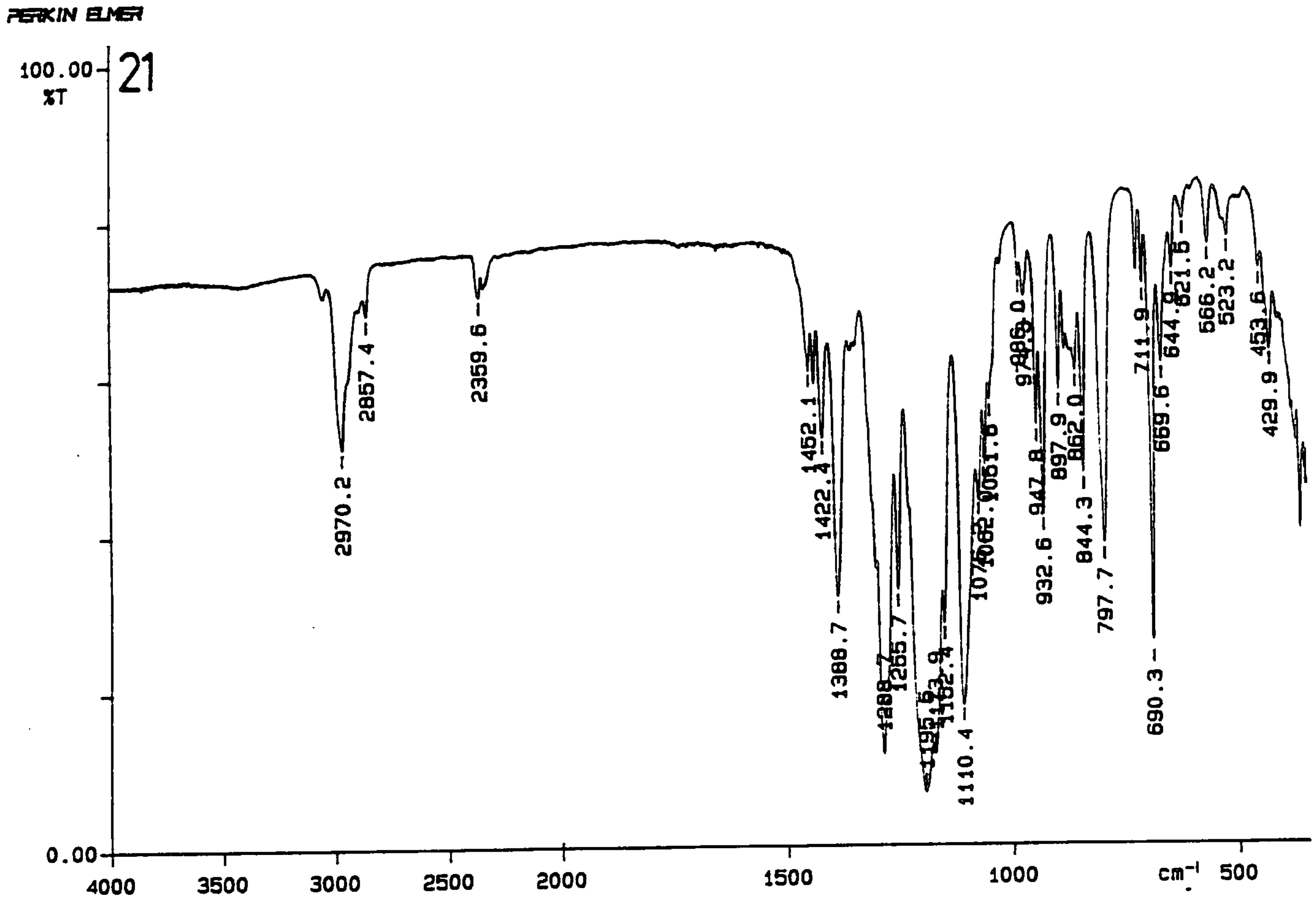
94/05/23 16:21
X: 1 scan, 4.0cm-1


18
530.845
627.255
670.107
718.726
691.304
815.101
846.526
878.883
933.522
995.277
1104.94
1201.15
1285.02
1345.68
1382.62
1432.18
1487.52
1667.91
2958.76
3376.09
50
40
30
20
10
500
1000
1500
2000
2500
3000
3500
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong
24/05/95 10:15 Res=4 cm-1



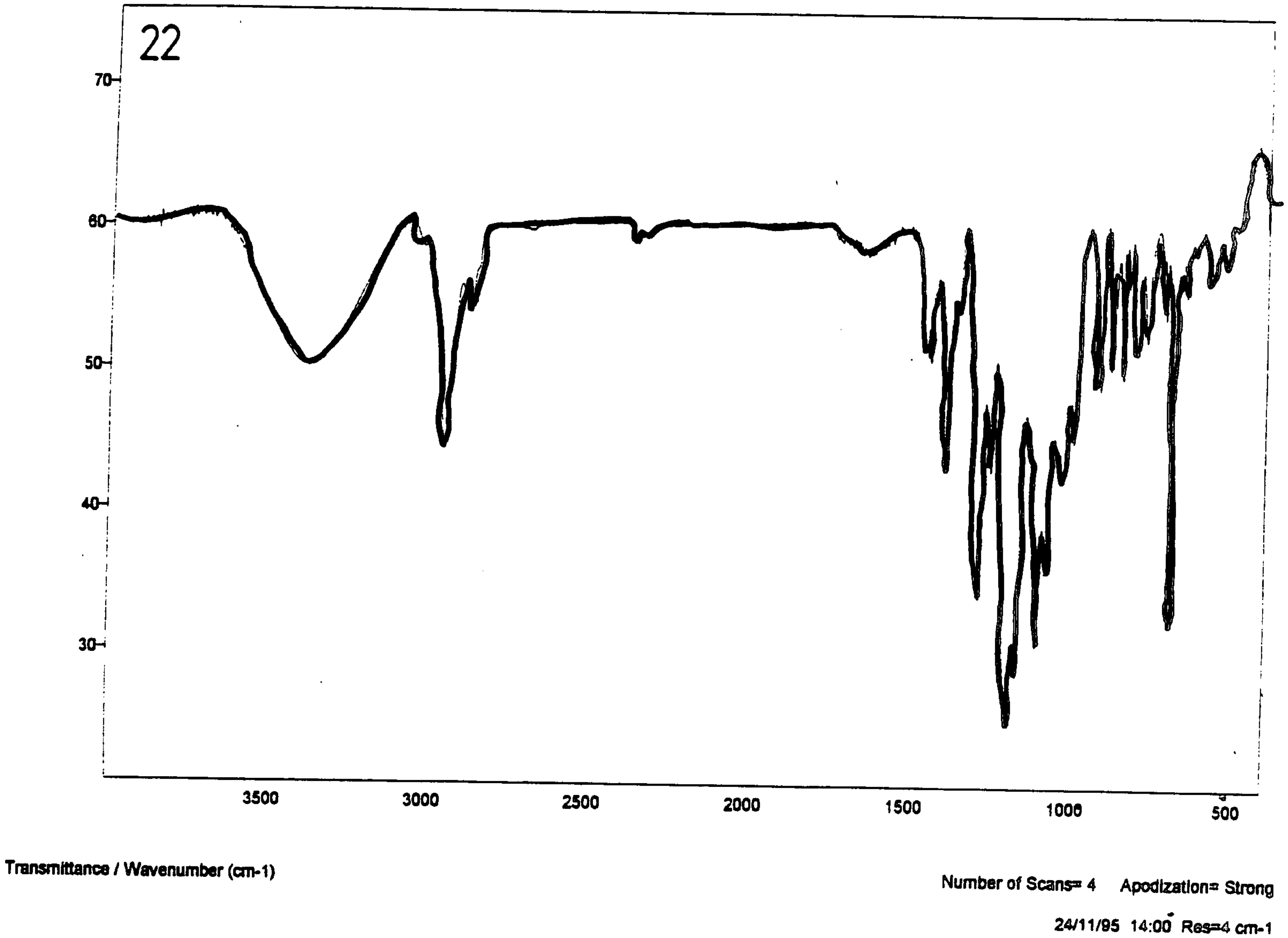
94/08/08 12:14
X: 1 scan, 4.0cm-1


PERKIN ELMER
20
100.00
%T
0.00
4000
3500
3000
2500
2000
1500
1000
500
cm-1
2948.4
2871.3
2360.5
1459.6
1440.0
1379.8
1287.7
1239.5
1190.1
1151.6
1140.0
1109.7
1058.2
993.0
916.3
902.6
864.8
844.4
800.8
749.2
688.6
680.1
667.2
623.7
586.5
566.1
530.6
498.0
478.6
94/09/29 11:36
X: 1 scan, 4.0cm-1

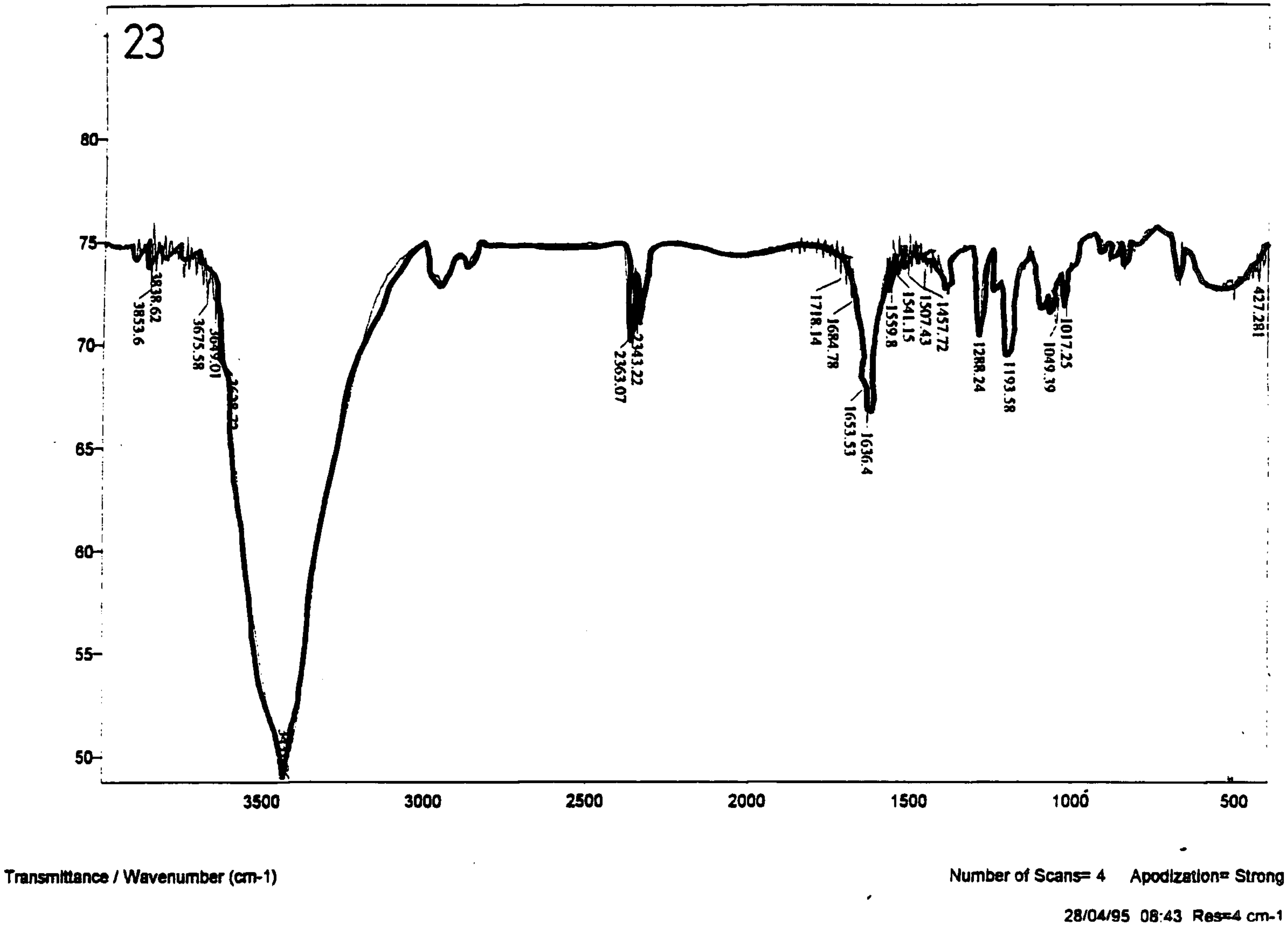


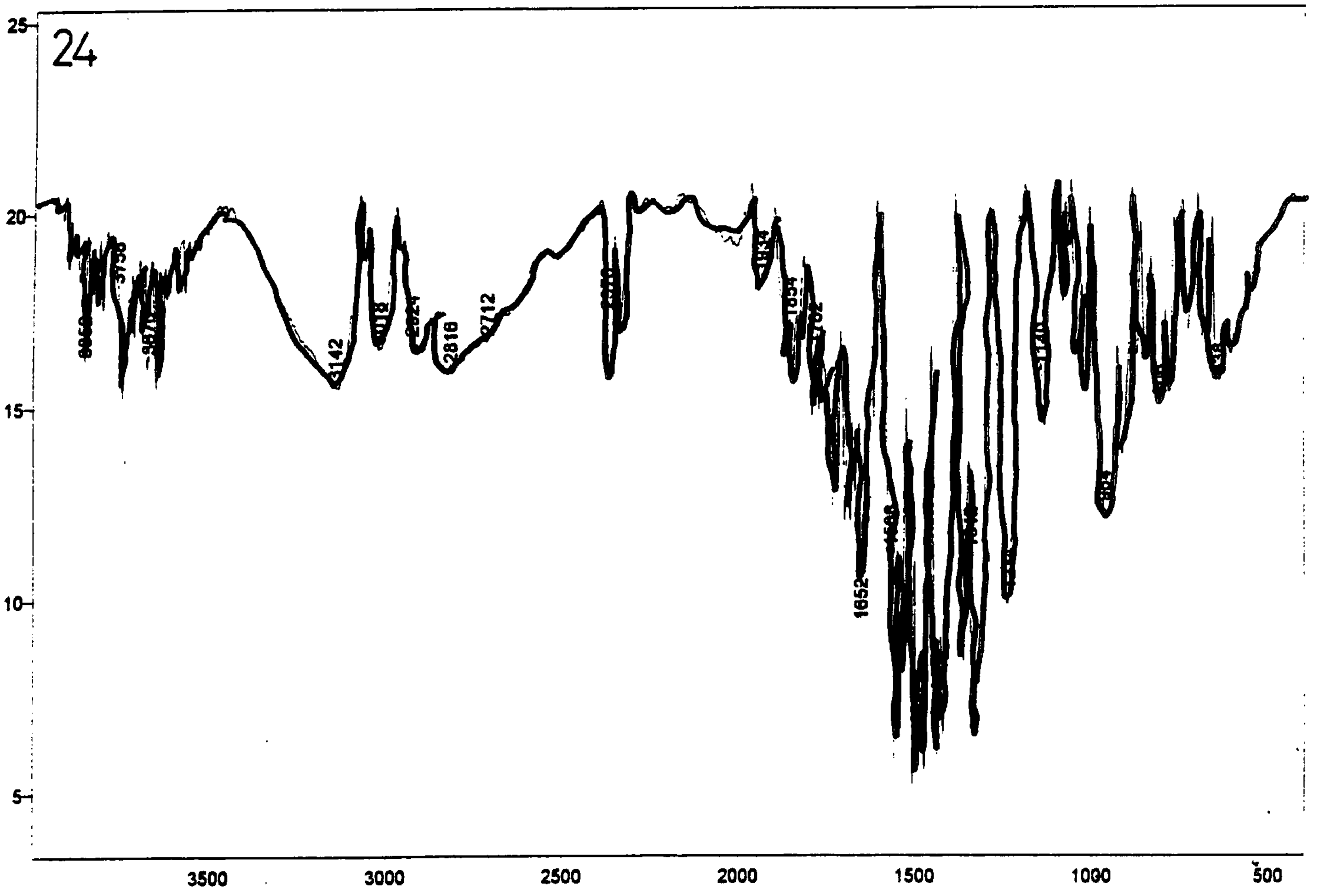
21

94/07/22 16: 16
Y: 4 scans, 4.0cm-1

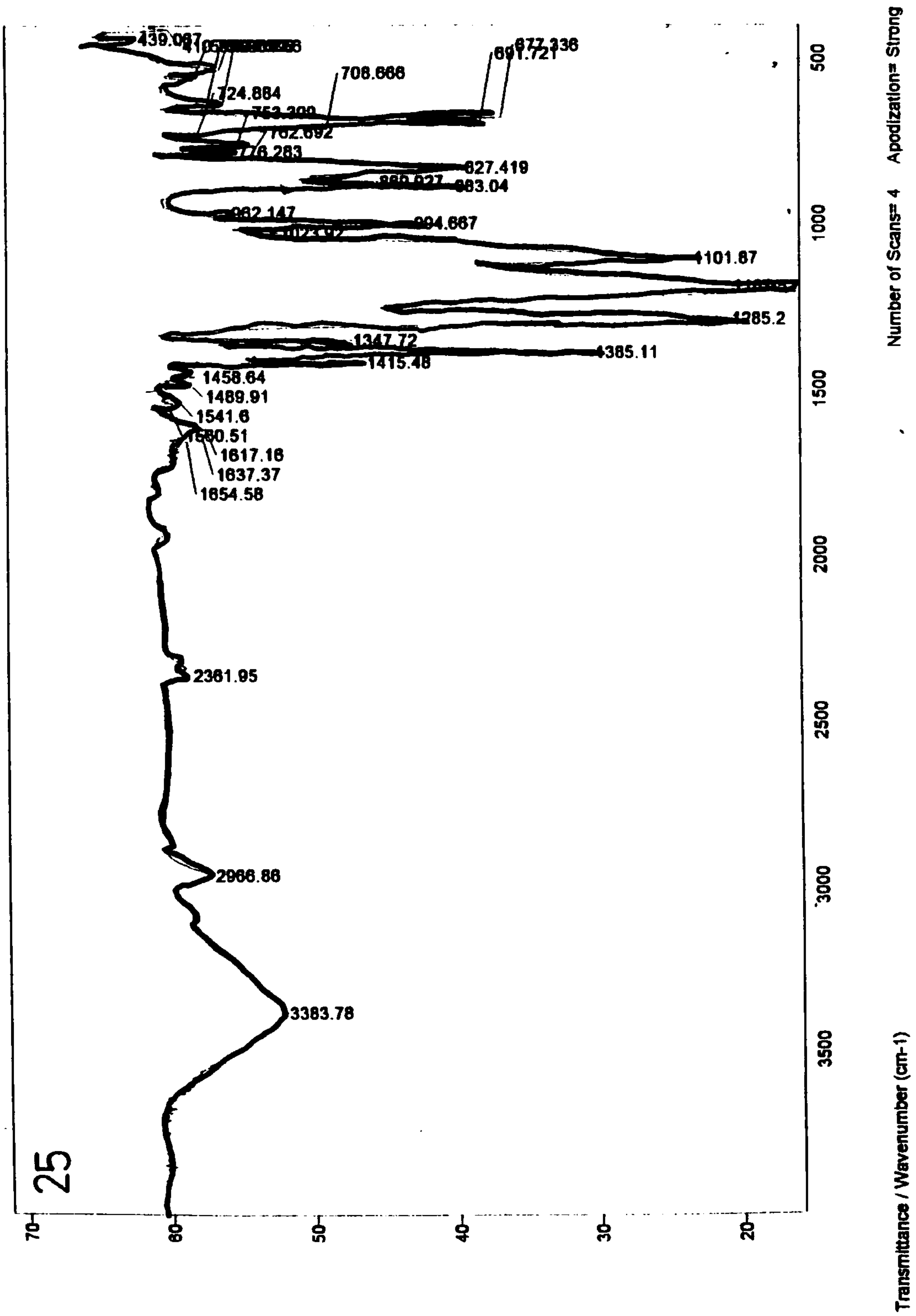

22
70
60
50
40
30
3500
3000
2500
2000
1500
1000
500
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong
24/11/95 14:00 Res=4 cm-1

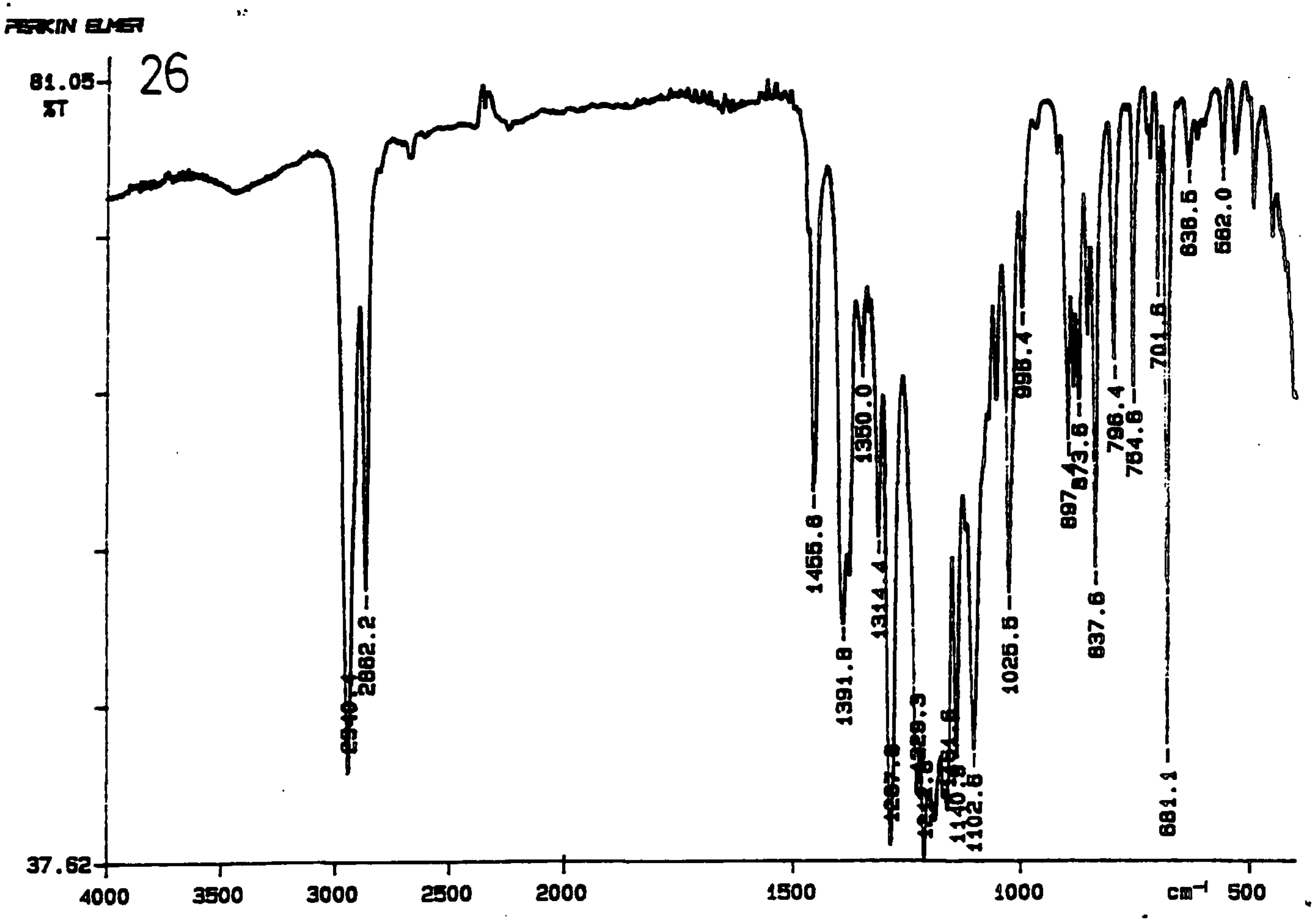
23


80
75
70
65
60
55
50
3500
3000
2500
2000
1500
1000
500
3853.6
3838.62
3675.58
3649.01
3628.72
2363.07
2343.22
1718.14
1684.78
1653.53
1636.4
1559.8
1541.15
1507.43
1457.72
1288.24
1193.58
1049.39
1017.25
427.281
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong
28/04/95 08:43 Res=4 cm-1

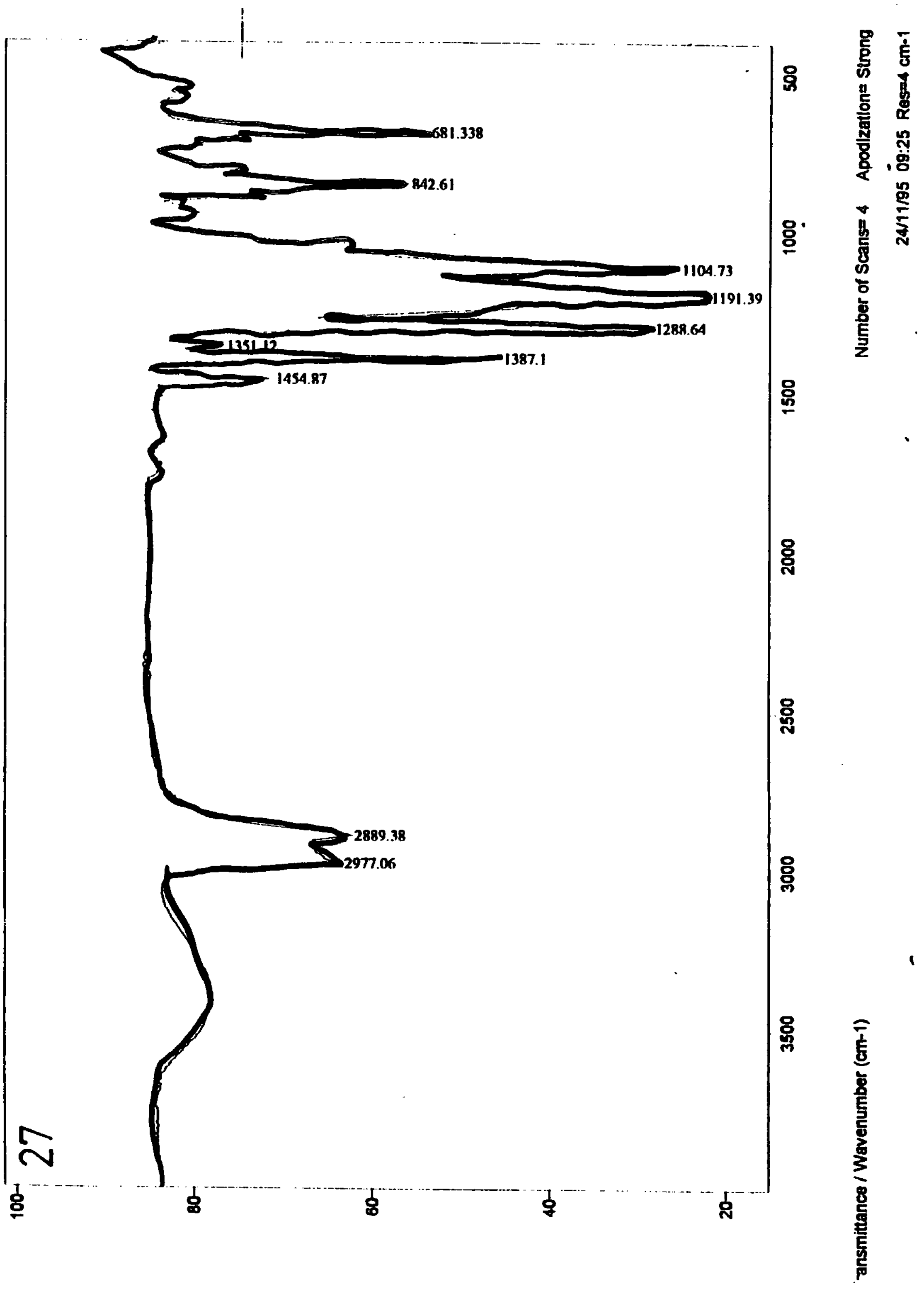

24
25
20
15
10
5
3500
3000
2500
2000
1500
1000
500
3736
3142
3018
2924
2816
2712
1652
1140

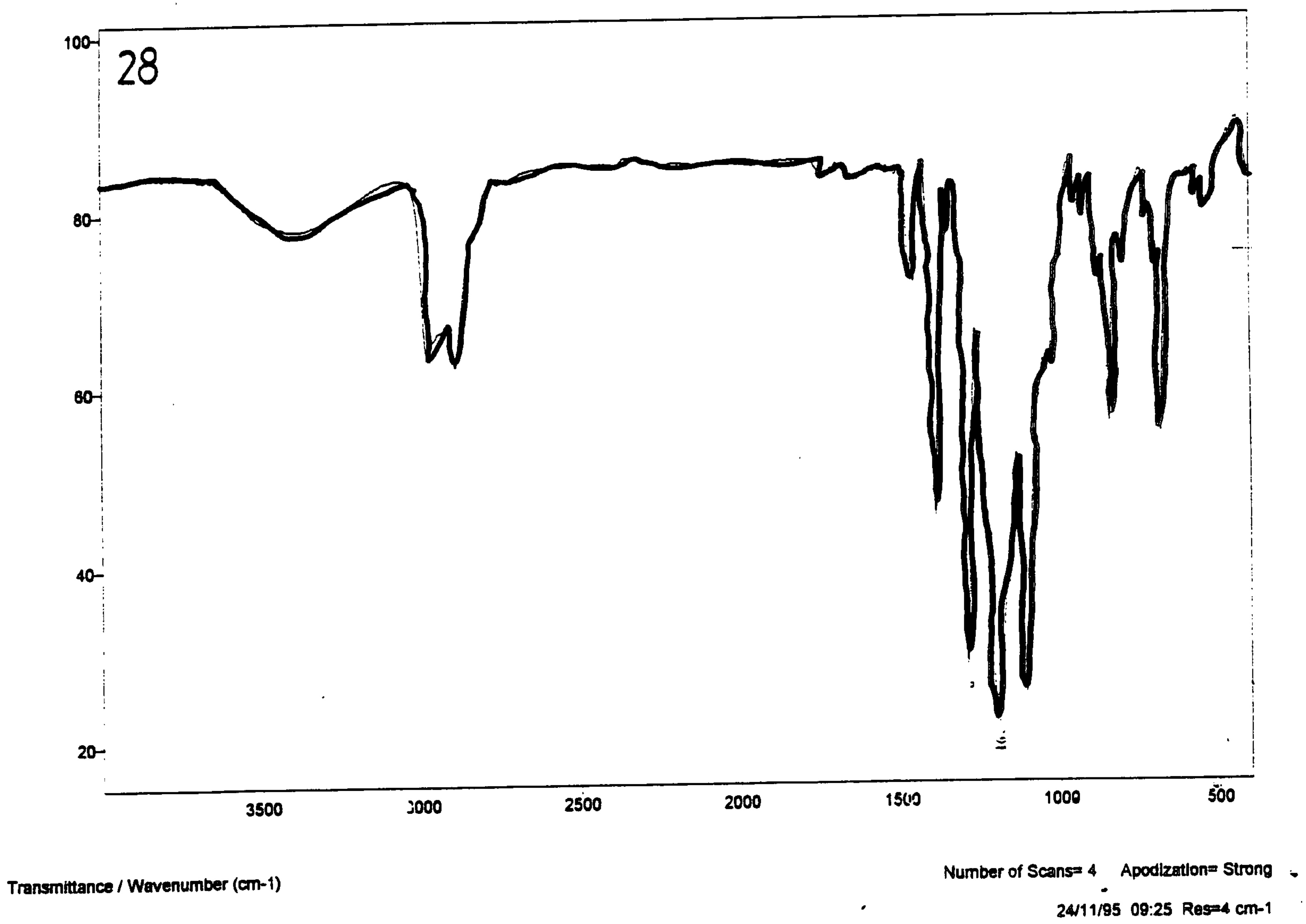
Arbitrary Y / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong
17/05/95- 15:43 Res=4 cm-1

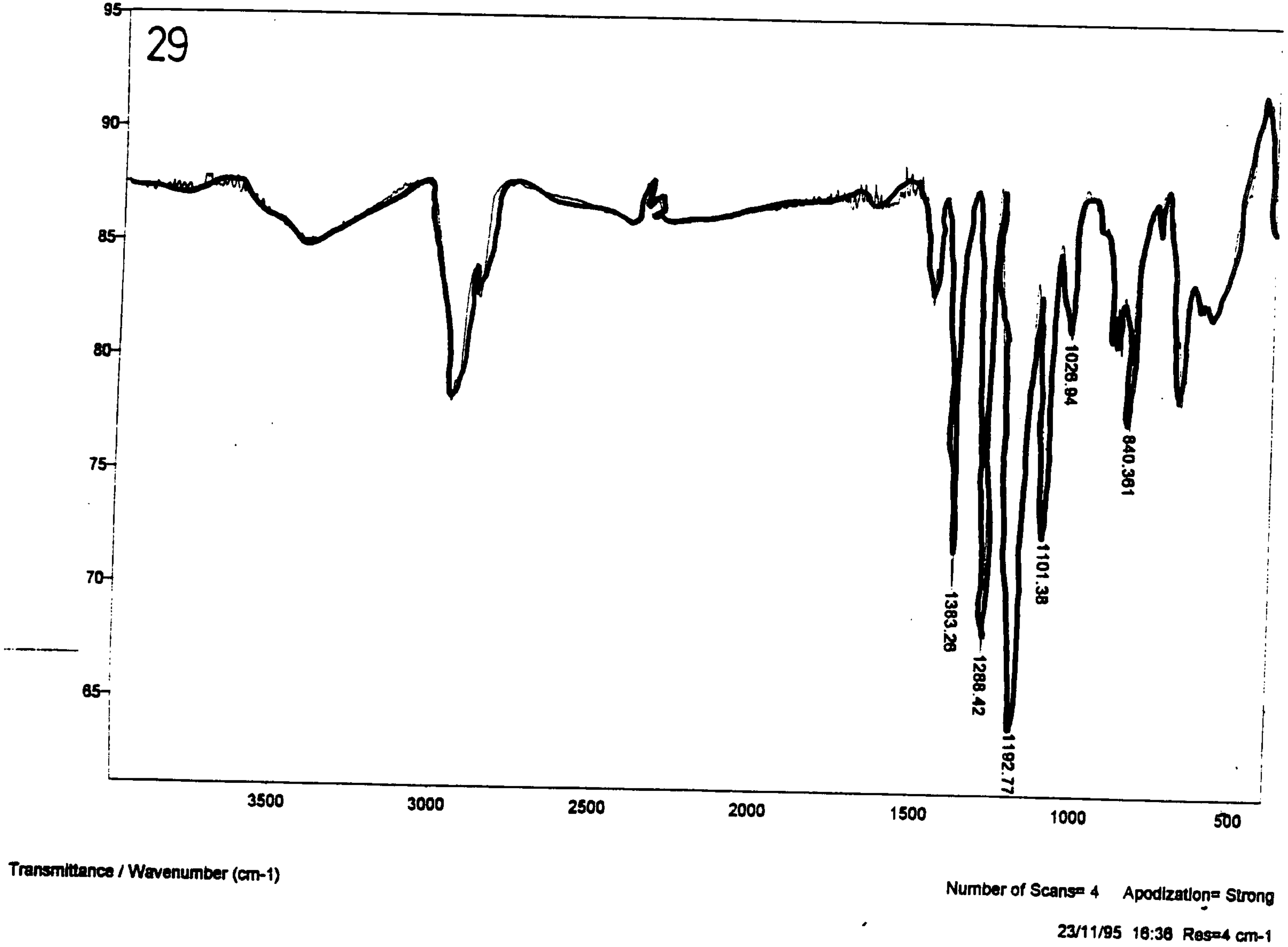

25
3383.78
2966.86
2361.95
1654.58
1637.37
1617.16
1560.51
1541.6
1489.91
1458.64
1415.48
1385.11
1347.72
1285.2
1101.67
1023.92
994.667
962.147
883.04
869.927
827.419
776.263
762.692
753.309
724.884
708.666
691.721
677.336
439.087
500
1000
1500
2000
2500
3000
3500
70
60
50
40
30
20
Transmittance / Wavenumber (cm-1)
Number of Scans= 4
Apodization= Strong



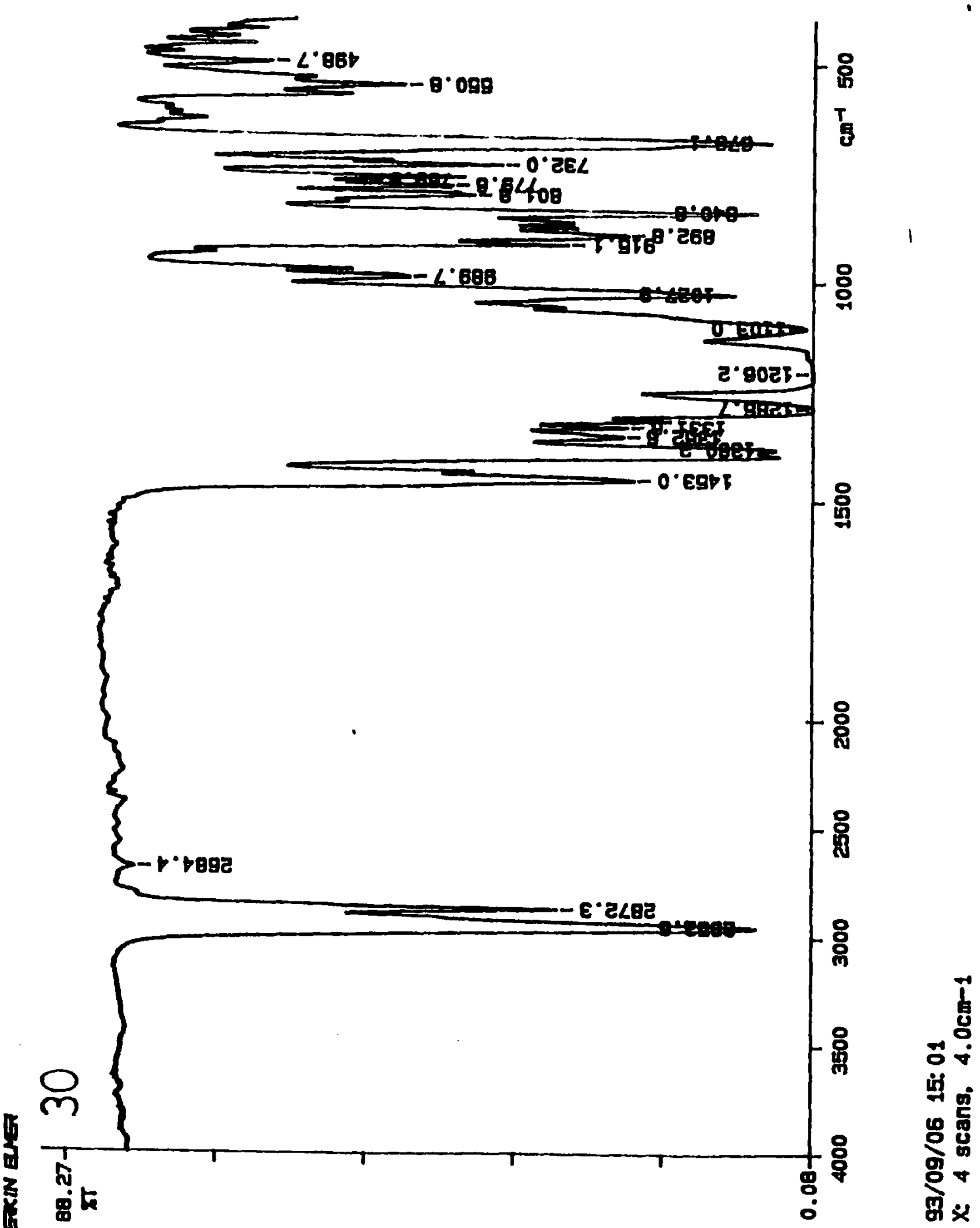
93/09/06 16:56
X: 4 scans, 4.0cm-1


27
100
80
60
40
20
500
1000
1500
2000
2500
3000
3500
681.338
842.61
1104.73
1191.39
1288.64
1351.12
1387.1
1454.87
2889.38
2977.06
ansmittance / Wavenumber (cm-1)
Number of Scans= 4   Apodization= Strong
24/11/95 09:25   Res=4 cm-1

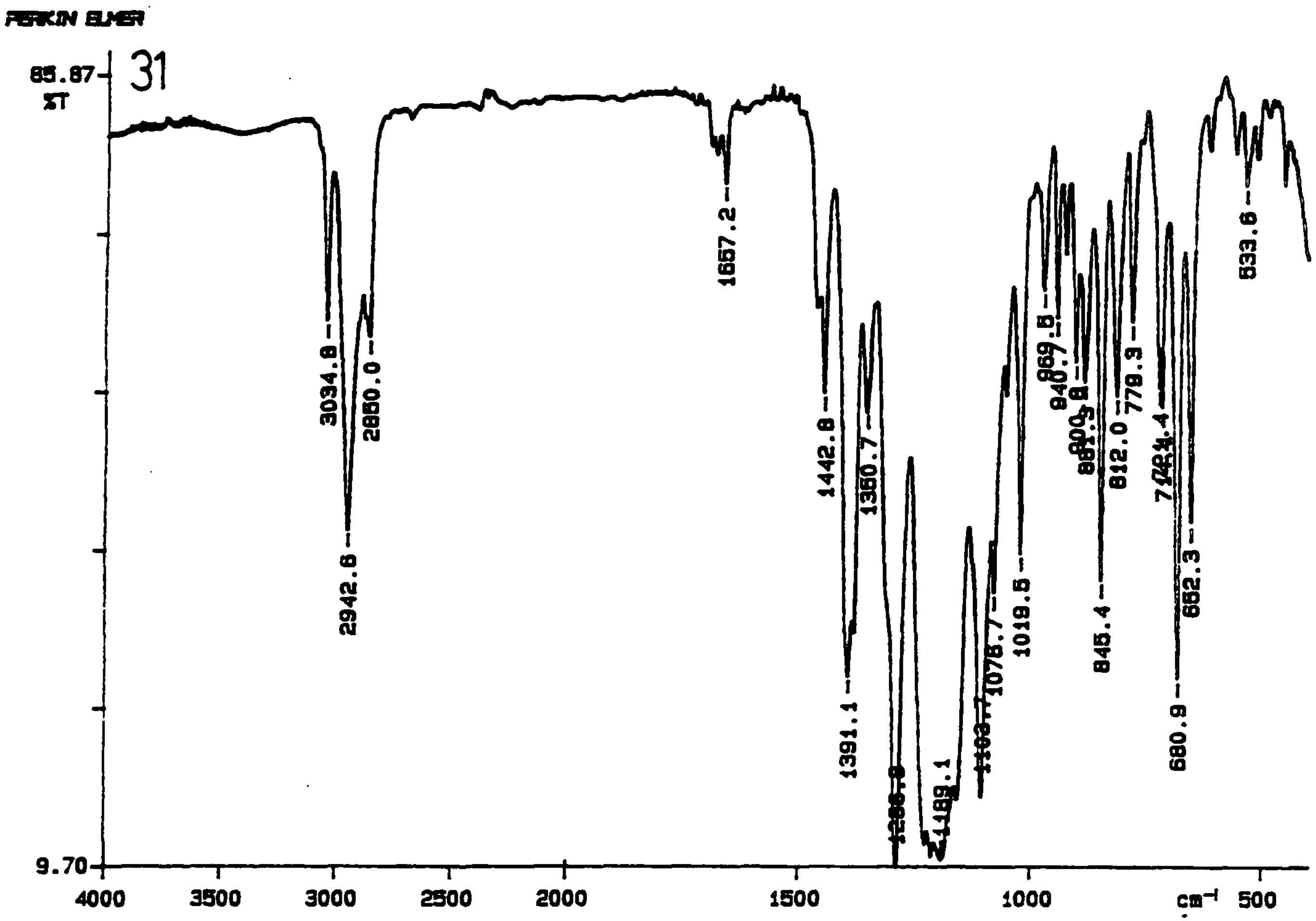

28
100
80
60
40
20
3500
3000
2500
2000
1500
1000
500
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong
24/11/95 09:25 Res=4 cm-1


29
95
90
85
80
75
70
65
3500
3000
2500
2000
1500
1000
500
1383.26
1288.42
1192.77
1101.38
1026.94
840.361
Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong
23/11/95 16:36 Res=4 cm-1

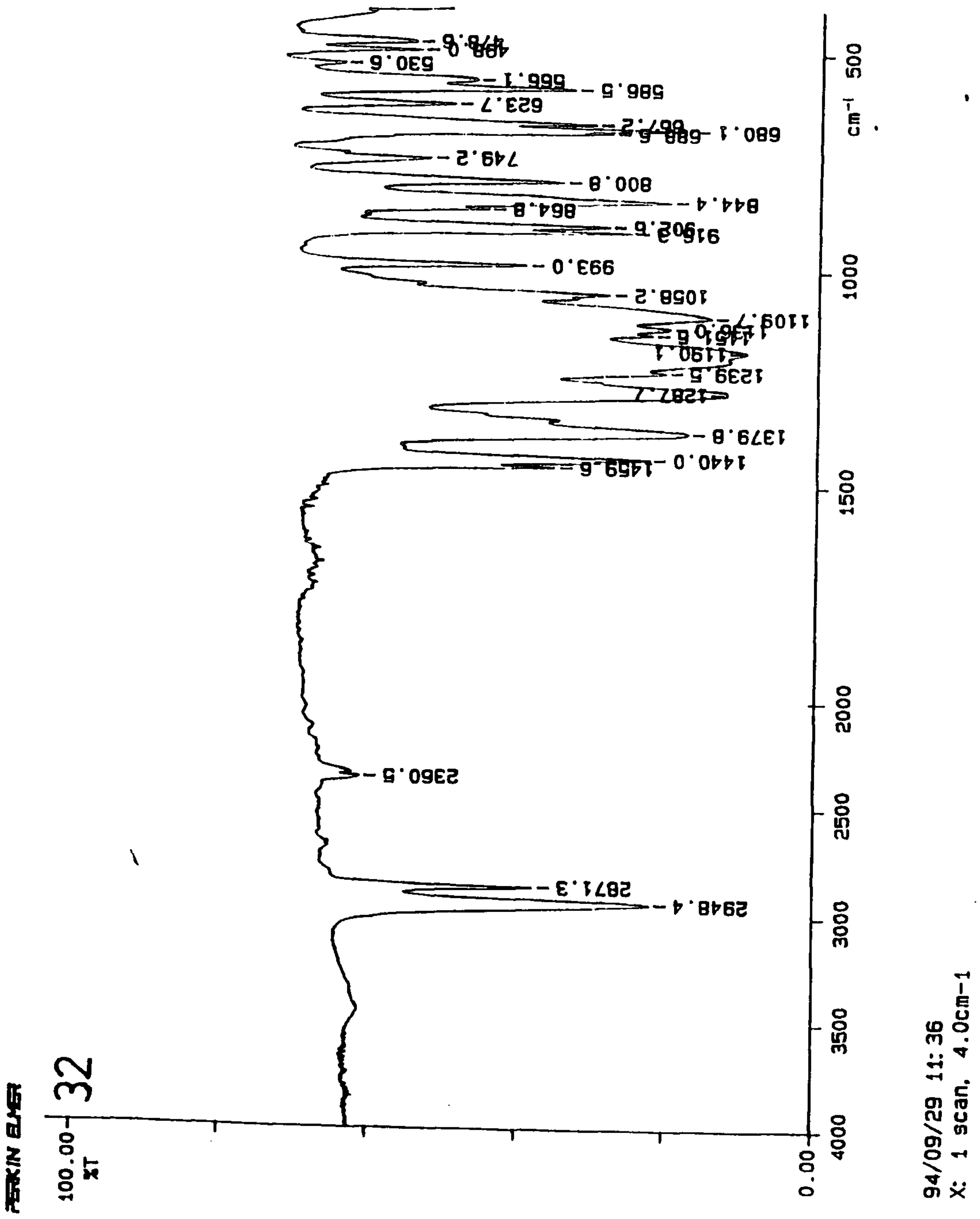
30


PERKIN ELMER
88.27
%T
0.08
4000
3500
3000
2500
2000
1500
1000
500
cm-1
2872.3
2684.4
1453.0
1384.3
1362.8
1331.8
1286.7
1208.2
1103.0
1027.8
988.7
916.1
892.8
840.8
804.8
778.8
732.0
678.1
550.8
498.7
93/09/06 15:01
X: 4 scans, 4.0cm-1

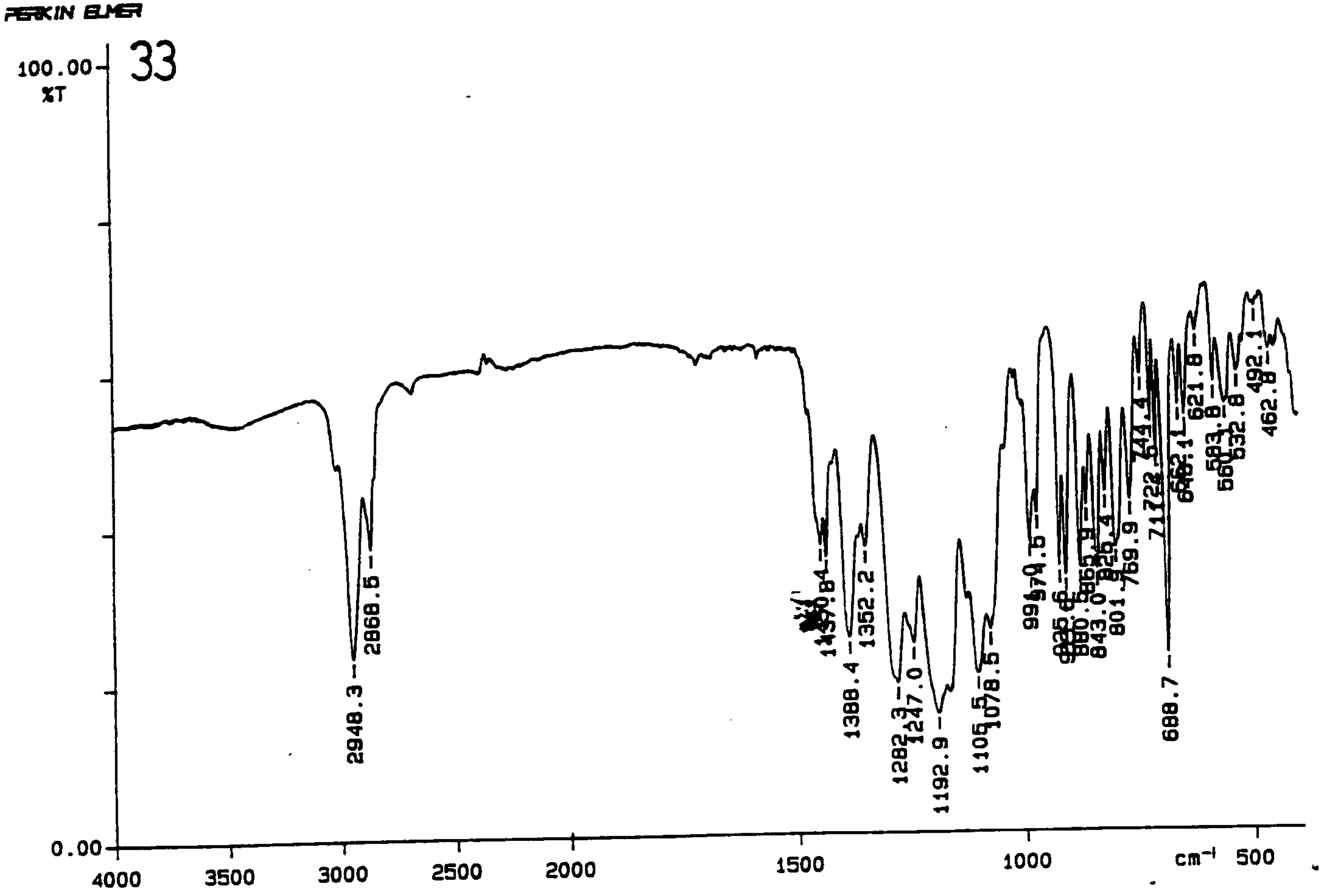
31



93/09/06 16:36
X: 4 scans, 4.0cm-1


PERKIN ELMER
32
100.00
%T
0.00
4000
3500
3000
2500
2000
1500
1000
500
cm⁻¹
2948.4
2871.3
2360.5
1459.6
1440.0
1379.8
1287.7
1239.5
1190.1
1150.6
1109.7
1058.2
993.0
916.3
902.5
864.8
844.4
800.8
749.2
688.5
680.1
667.2
623.7
586.5
566.1
530.6
498.0
478.6
94/09/29 11:36
X: 1 scan, 4.0cm-1

33



94/11/02 14:58
X: 1 scan, 4.0cm-1

APPENDIX 3
MASS SPECTRA

Appendix Three
Mass Spectra

1. Gamma ray initiated formation of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentanol **(20)**
2. Gamma ray initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentanols **(21)**
3. D.T.B.P. initiated formation of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentanol **(20)**
4. D.T.B.P. initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentanols **(21)**
5. Gamma ray initiated formation of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexanol **(22)**
6. Gamma ray initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexanols **(23)**
7. Gamma ray initiated formation of 1-(1,1,2,3,3,3-hexafluoropropyl)-cycloheptanol **(24)**
8. Gamma ray initiated formation of mainly 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclooctanol **(25)**
9. Gamma ray initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-cyclooctanols **(26)**
10. Gamma ray initiated formation of 1-(1,1,2,3,3,3-hexafluoropropyl)-4-methylcyclohexanol **(29)**
11. Gamma ray initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-4-methylcyclohexanols **(30)**
12. Gamma ray initiated formation of 1-(1,1,2,3,3,3-hexafluoropropyl)-3-methylcyclohexanol **(27)**
13. Gamma ray initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-3-methylcyclohexanols **(28)**
14. Gamma ray initated formation of 1,3-di-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentan-1,3-diol **(31)**
15. Gamma ray initiated formation of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexan-1,3-diol **(32)**
16. Gamma ray initiated formation of 1,3-di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexan-1,3-diol **(33)**
17. Gamma ray initiated formation of 1,4-di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexan-1,4-diol **(34)**
18. Gamma ray initiated formation of (1,1,2,3,3,3-hexafluoropropyl)-cyclooctane-1,5-diols **(35)**

19. Gamma ray initiated formation of 2,4-di-(1,1,2,3,3,3-hexafluoropropyl)-pentan-2,4-diol **(36)**

20. Gamma ray initiated formation of 2,5-di-(1,1,2,3,3,3-hexafluoropropyl)-hexan-2,5-diol **(37)**

21. Gamma ray initiated competition reaction between the addition of 2,4-pentanediol and 2,5-hexanediol to hexafluoropropene

22. Gamma ray initiated reaction between 2,4-pentanediol and a deficiency of hexafluoropropene, forming only 2,4-di-(1,1,2,3,3,3-hexafluoropropyl)-pentane-2,4-diol **(36)**

23. D.T.B.P. initiated formation of 2,4-di-(1,1,2,3,3,3-hexafluoropropyl)-pentane-2,4-diol **(36)**

24. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclopentene **(41)**

25. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene **(42)**

26. A mixture of 1,4-di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexa-1,3-diene **(44)** and 1,4-di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexa-1,4-diene **(43)**

27. 1-(1,1,2,3,3,3-Hexafluoropropyl)-1,2-dibromocyclopentane **(45)**

28. 1-(1,1,2,3,3,3-Hexafluoropropyl)-1,2-dibromocyclohexane **(46)**

29. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclopentene oxide **(47)**

30. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene oxide **(48)**

31. Epoxidation of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentene **(41)** using M.C.P.B.A. in an aqueous system

32. Attempted epoxidation of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentene **(41)** using sodium hypochlorite in dioxane

33. Attempted epoxidation of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentene **(41)** using sodium hypochlorite in anhydous pyridine

34. Attempted bromohydrin addition to 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentene **(41)**

35. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexan-1,2-diol **(49)**

36. 1-(1,1,2,3,3,3-Hexafluoropropyl)-benzene **(50)**

37. 1,4-Di-(1,1,2,3,3,3-hexafluoropropyl)-benzene **(51)**

38. Gamma ray initiated formation of (1,1,2,3,3,3-hexafluoropropyl)-methylcyclopentanes **(52)** / **(53)**

39. Gamma ray initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-methylcyclopentanes **(54)**

40. Gamma ray initiated formation of (1,1,2,3,3,3-hexafluoropropyl)-methylcyclohexanes **(55)** / **(56)**

41. Gamma ray initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-methylcyclohexanes **(57)**

42. D.T.B.P. initiated formation of (1,1,2,3,3,3-hexafluoropropyl)-methylcyclohexanes **(55)** / **(56)**

43. D.T.B.P. initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-methylcyclohexanes **(57)**

44. D.T.B.P. initiated formation of (1,1,2,3,3,3-hexafluoropropyl)-1,2-dimethylcyclohexanes **(58)** / **(59)**

45. D.T.B.P. initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-1,2-dimethylcyclohexanes **(60)**

46. Gamma ray initiated formation of (1,1,2,3,3,3-hexafluoropropyl)-1,3-dimethylcyclohexanes **(61)** / **(62)**

47. D.T.B.P. initiated formation of (1,1,2,3,3,3-hexafluoropropyl)-1,3-dimethylcyclohexanes **(61)** / **(62)**

48. Gamma ray initiated formation of 1-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dimethylcyclohexane **(63)**

49. Gamma ray initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dimethylcyclohexanes **(64)**

50. D.T.B.P. initiated formation of 1-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dimethylcyclohexane **(63)**

51. D.T.B.P. initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dimethylcyclohexanes **(64)**

52. Gamma ray initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-2-methylpentanes **(65)**

53. D.T.B.P. initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-2-methylpentanes **(65)**

54. Gamma ray initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-3-methylpentanes **(66)**

55. D.T.B.P. initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-3-methylpentanes **(66)**

56. Gamma ray initiated formation of (1,1,2,3,3,3-hexafluoropropyl)-cyclohexane **(13)**

57. G.C. to show direct chlorination of (1,1,2,3,3,3-hexafluoropropyl)-cyclohexane **(13)** using chlorine gas

58. Formation of 1-(1,1,2,3,3,3-hexafluoropropyl)-chlorocyclohexanes **(67)** / **(68)** / **(69)** using chlorine gas and carbon disulphide as a solvating solvent

59. Formation of a mixture of 1-(1,1,2,3,3,3-hexafluoropropyl)-3-chlorocyclohexane **(68)** and 1-(1,1,2,3,3,3-hexafluoropropyl)-4-chlorocyclohexane **(67)**

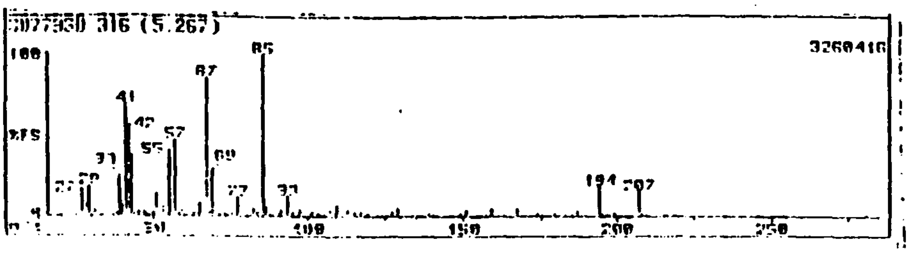
60. Attempted nucleophilic substitution of 1-(1,1,2,3,3,3-hexafluoropropyl)-chlorocyclohexanes **(67)** / **(68)** using thiophenol

61. A gamma ray initiated attempted addition of 1-methyl-4-chloro-cyclohexane to hexafluoropropene

62. A D.T.B.P. initiated attempted addition of 1-methyl-4-chloro-cyclohexane to hexafluoropropene

63. 4-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene **(71)**
64. 4-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene **(71)**
65. 1-(1,1,2,3,3,3-Hexafluoropropyl)-3,4-dibromocyclohexane **(73)**
66. 4-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene oxide **(75)**

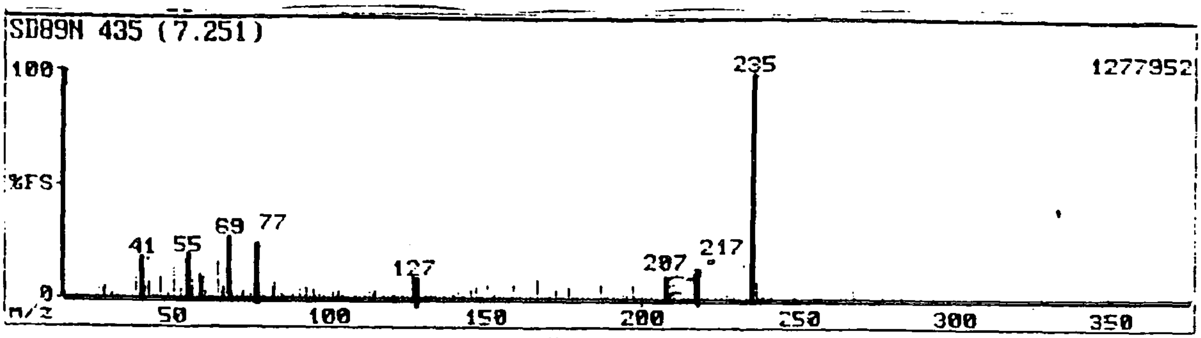
1 Gamma ray initiated formation of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentanol (20)



5077930 316 (5.267) 3260416

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
19	0.03	69	26.63	115	3.30	160	0.73
24	0.01	70	0.07	116	0.46	161	0.09
25	0.06	71	1.40	117	3.33	163	0.05
26	1.00	72	0.44	118	0.26	164	0.02
27	12.19	73	2.39	119	1.59	165	0.03
28	7.30	74	0.23	120	0.17	167	3.21
29	10.22	75	1.74	121	1.12	168	0.27
30	0.55	76	0.33	122	0.03	169	0.30
31	4.37	77	11.56	123	0.59	170	0.02
32	0.38	78	0.82	124	0.10	171	0.11
33	0.67	79	0.60	125	0.15	172	0.59
34	0.02	80	0.31	126	0.67	173	0.15
36	0.03	81	0.62	127	2.92	174	2.04
37	0.41	82	4.59	128	0.30	175	0.59
38	1.72	83	3.05	129	4.81	176	0.03
39	23.62	85	100.00	130	0.31	177	0.53
40	6.41	86	6.85	131	0.90	178	0.03
41	66.84	87	1.58	132	0.57	179	1.48
42	53.77	88	0.60	133	0.67	180	0.10
43	37.89	89	1.26	134	0.08	181	0.03
44	1.90	90	0.49	135	0.03	183	0.01
45	2.58	91	3.42	136	0.07	185	0.01
46	0.39	92	0.15	137	0.02	187	3.39
47	3.39	93	12.44	138	0.06	188	0.23
48	0.14	94	0.68	139	2.42	189	0.04
49	1.41	95	2.48	140	0.23	194	10.22
50	1.06	96	0.65	141	1.17	195	2.42
51	13.44	97	3.49	142	0.05	196	0.13
52	1.29	98	0.68	143	0.05	197	0.21
53	6.26	99	0.55	144	0.01	199	2.39
54	1.71	100	0.45	145	0.37	200	0.16
55	38.19	101	2.73	146	0.11	201	0.03
56	4.90	102	0.25	147	0.41	207	15.33
57	47.74	103	1.58	148	0.05	208	2.01
58	2.73	104	0.26	149	2.17	209	0.12
59	6.97	105	0.60	150	0.14	215	0.01
60	0.60	106	0.97	151	4.30	216	0.01
61	0.74	107	3.96	152	0.10	217	0.10
62	0.55	108	0.57	153	0.45	218	0.17
63	2.10	109	6.41	154	0.50	219	0.08
64	1.26	110	0.60	155	1.22	221	0.19
65	7.32	111	0.38	156	0.06	235	0.02
66	1.99	112	0.20	157	2.14	236	0.06
67	85.43	113	4.11	158	0.19	281	0.02
68	4.87	114	0.49	159	4.96		

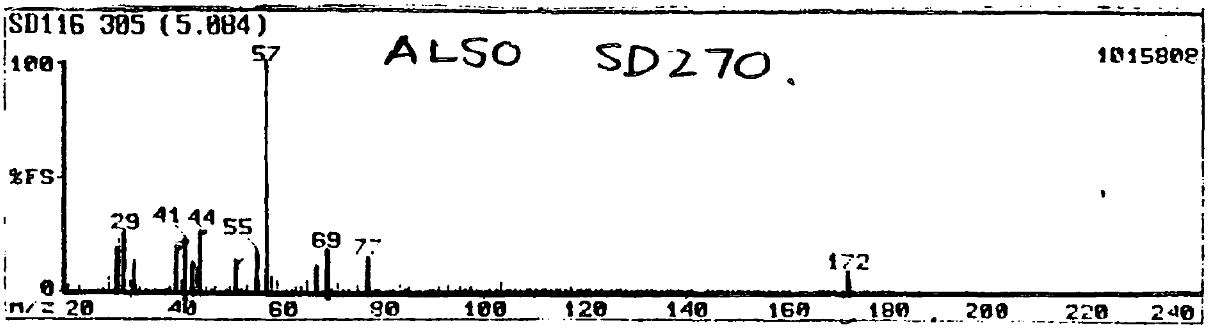
2. Gamma ray initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentanols (21)



SD89N 435 (7.251) 1277952

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.07	93	4.95	148	0.43	221	0.16
26	1.30	94	1.04	149	0.21	223	0.04
27	4.03	95	3.53	151	5.61	225	0.29
28	3.93	96	1.03	152	0.34	227	2.02
29	5.21	97	1.68	153	2.34	228	0.16
30	0.85	98	0.41	154	0.37	229	0.08
31	2.26	99	0.46	155	0.42	231	0.04
32	0.42	100	0.51	156	0.12	233	0.29
33	0.58	101	2.50	157	0.39	235	100.00
39	8.65	102	0.64	158	0.62	236	7.77
41	18.67	103	3.10	159	6.09	237	0.63
42	4.39	104	0.54	160	1.21	238	0.03
43	6.81	105	0.72	161	0.26	239	0.38
44	0.65	106	0.55	163	0.40	240	0.05
45	0.42	107	0.86	164	0.10	241	0.05
47	8.41	108	0.65	165	0.70	245	0.65
49	1.74	109	2.64	167	8.81	247	1.76
51	14.98	110	0.20	168	0.50	248	0.17
52	0.94	111	0.19	169	0.24	249	0.15
53	3.51	112	0.48	170	0.06	253	0.15
55	19.55	113	2.96	171	0.54	255	0.52
56	2.12	114	2.08	173	3.49	256	0.04
57	7.53	115	2.70	174	0.68	257	0.08
59	11.14	116	0.93	175	0.77	259	1.60
60	0.69	117	0.66	177	4.45	260	0.18
61	2.56	118	0.17	178	0.51	261	0.04
62	0.41	119	0.82	179	0.40	263	0.04
63	1.26	120	0.36	181	0.16	265	0.72
65	15.87	121	2.16	183	0.45	267	4.33
66	2.60	122	0.25	185	0.40	268	0.35
67	4.49	123	0.72	187	6.09	269	0.16
69	27.24	124	0.13	188	0.43	277	0.13
70	0.96	125	0.37	189	0.34	279	1.46
71	1.76	126	1.19	191	0.28	280	0.14
72	0.90	127	10.10	192	0.02	283	0.03
73	3.13	128	1.10	194	1.76	285	0.16
74	0.38	129	1.22	195	1.48	287	0.42
75	1.70	130	0.19	197	5.37	288	0.02
77	21.79	131	0.85	198	0.33	289	0.17
78	1.05	132	0.76	199	0.26	297	0.06
79	0.53	133	1.58	200	0.09	299	0.75
80	0.23	134	0.21	201	0.17	300	0.07
81	1.13	135	0.62	203	0.33	303	0.02
82	4.75	136	0.08	205	0.78	307	1.84
83	6.57	137	0.20	207	12.82	308	0.22
84	1.28	138	0.17	208	0.97	309	0.72
85	2.12	139	1.54	209	0.29	310	0.08
86	0.38	140	0.56	210	0.09	317	0.04
87	0.32	141	2.80	213	0.12	319	0.03
88	0.75	142	0.16	215	3.23	327	0.13
89	1.80	143	0.13	217	11.70	329	1.02
90	1.70	145	3.41	218	0.85	330	0.10
91	4.25	146	0.64	219	0.15	337	0.03
92	0.70	147	4.87	220	0.06	338	0.02
347	0.08	350	0.22	367	0.04		
349	2.30	357	0.10				

3. D.T.B.P. initiated formation of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentanol (20)

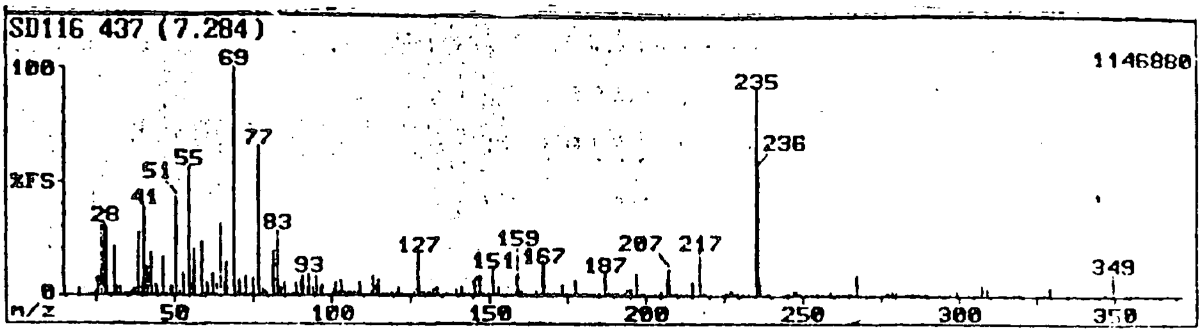


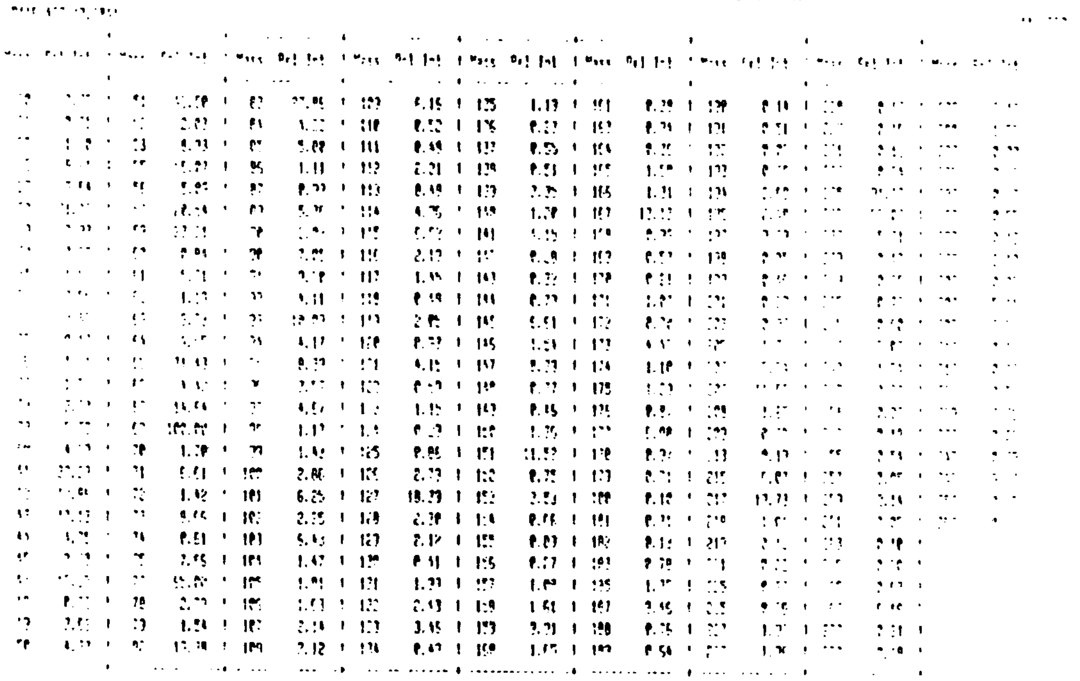
ALSO SD270.

SD116 305 (5.084) 1015808

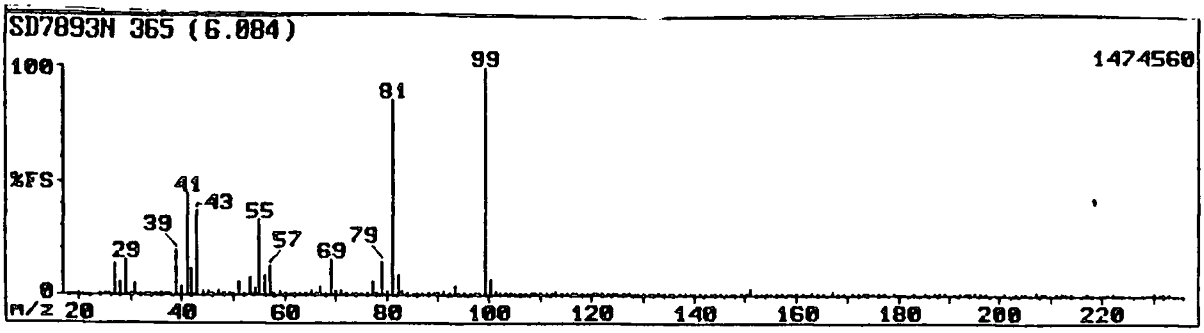
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.79	41	21.37	61	0.79	83	3.07	101	1.38	118	0.12	136	0.04	155	0.10	179	0.27
24	0.32	42	12.10	62	0.41	84	1.03	102	0.77	119	0.45	137	0.14	156	0.05	180	0.02
25	0.08	43	10.28	63	2.32	85	1.76	103	2.91	120	0.12	138	0.10	157	0.21	186	0.04
26	5.70	44	27.02	64	1.66	86	0.52	104	0.43	121	0.73	139	0.72	158	0.20	187	0.10
27	10.35	45	2.42	65	5.22	87	1.09	105	0.42	122	0.08	140	0.37	159	1.14	196	0.43
28	21.08	46	0.59	67	12.00	88	0.60	106	0.37	123	0.11	141	0.21	160	0.11	199	0.49
29	25.01	47	2.19	69	10.04	89	1.38	107	0.38	125	0.11	144	0.04	166	0.10	207	0.12
30	5.07	49	1.43	70	0.80	90	1.39	108	0.40	126	0.17	145	0.33	167	0.61	218	0.10
31	11.41	50	1.01	71	3.53	91	1.74	109	1.08	127	1.12	146	0.09	168	0.65	234	0.36
32	2.12	51	12.50	72	0.35	93	3.20	110	0.15	128	0.23	147	0.08	169	0.07	235	0.33
33	1.15	52	0.71	73	0.74	94	0.45	111	0.07	129	0.57	148	0.32	171	0.96	236	0.21
35	0.37	53	3.10	75	2.57	95	1.01	112	0.19	130	0.06	149	0.27	172	9.58		
36	0.96	55	16.63	77	15.63	96	0.76	113	0.96	131	0.17	150	0.09	173	0.80		
37	0.62	57	100.00	78	0.71	97	2.42	114	0.37	132	0.19	151	0.41	175	0.09		
38	2.27	58	6.05	79	0.77	98	0.40	115	0.79	133	0.51	152	0.06	176	0.50		
39	10.95	59	4.74	81	1.92	99	0.58	116	0.88	134	0.67	153	0.31	177	0.12		
40	4.91	60	0.32	82	1.57	100	0.35	117	1.51	135	0.23	154	0.24	178	0.14		

4. D.T.B.P. initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentanols (21)





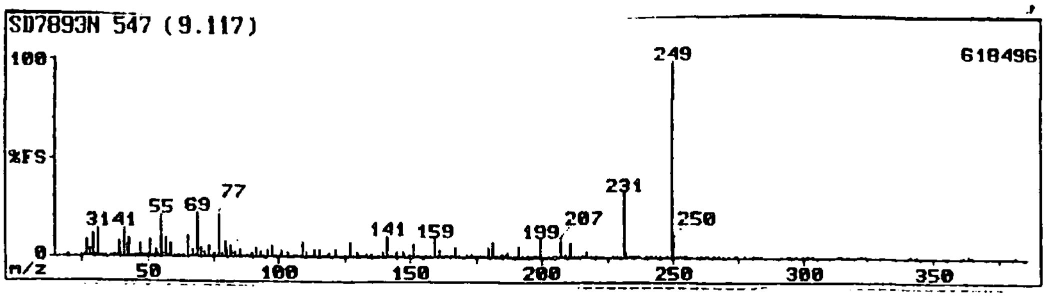
5. Gamma ray initiated formation of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexanol (22)



SD7893N 365 (6.084) 1474560

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.03	69	15.35	115	0.83	161	0.13
24	0.02	70	1.53	116	0.10	163	0.85
25	0.04	71	1.65	117	0.28	164	0.08
26	1.07	72	0.23	118	0.05	165	0.18
27	13.68	73	1.18	119	0.72	167	1.56
28	5.63	74	0.15	120	0.21	168	0.12
29	15.69	75	0.78	121	0.59	169	0.15
30	0.44	76	0.18	122	0.10	171	0.70
31	4.93	77	5.49	123	1.13	172	0.09
32	0.35	78	0.69	124	0.16	173	0.93
33	0.59	79	14.17	125	0.12	174	0.28
34	0.21	80	1.70	126	0.17	175	0.07
35	0.08	81	85.56	127	1.02	176	0.01
36	0.03	82	8.26	128	0.12	177	0.05
37	0.21	83	1.51	129	0.75	179	0.02
38	0.94	84	0.30	130	0.19	181	0.09
39	19.72	85	0.72	131	0.92	183	0.08
40	3.72	86	0.12	132	0.66	185	0.09
41	44.72	87	0.36	133	0.53	187	0.61
42	11.32	88	0.27	134	0.07	188	0.11
43	37.22	89	0.58	135	0.40	189	0.05
44	1.65	90	0.28	136	0.06	191	0.36
45	1.96	91	2.22	137	0.19	192	0.04
46	0.22	92	0.17	138	0.03	193	0.78
47	1.91	93	3.51	139	0.86	194	1.00
48	0.69	94	0.35	140	0.13	195	0.23
49	0.56	95	1.28	141	1.39	196	0.02
50	0.81	96	0.28	142	0.14	197	0.04
51	5.56	97	1.11	143	0.90	201	0.02
52	0.87	98	0.31	144	0.09	203	0.02
53	7.36	99	100.00	145	0.46	204	0.03
54	3.11	100	6.46	146	0.06	205	0.01
55	32.78	101	1.53	147	0.40	207	1.72
56	9.03	102	0.21	148	0.04	208	0.18
57	12.78	103	0.92	149	0.30	209	0.03
58	0.82	104	0.16	150	0.05	211	0.11
59	1.84	105	0.18	151	2.74	212	0.02
60	0.18	106	0.35	152	0.12	213	0.60
61	0.76	107	0.48	153	0.46	214	0.07
62	0.17	108	0.18	154	0.13	217	0.07
63	0.70	109	1.44	155	0.98	221	0.06
64	0.41	110	0.40	156	0.07	222	0.02
65	2.14	111	0.88	157	0.14	230	0.02
66	0.69	112	0.28	158	0.03	231	0.73
67	4.18	113	1.94	159	0.39	232	0.22
68	0.42	114	0.24	160	0.09	233	0.08

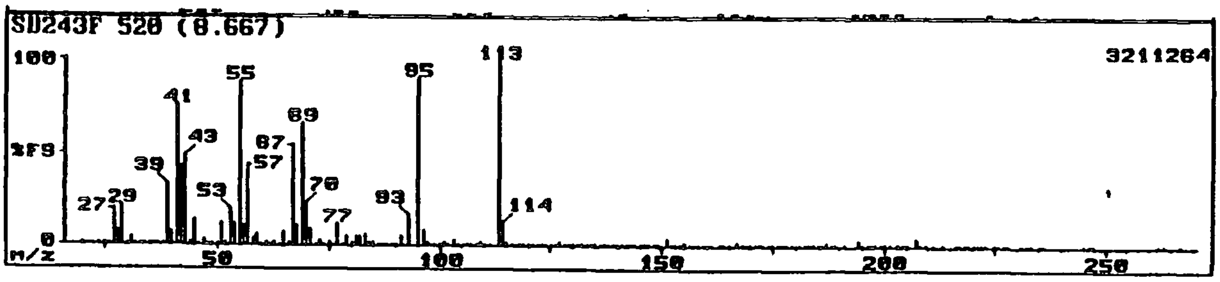
6. Gamma ray initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexanols (23)



SD7893N 547 (9.117) 618496

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.11	79	7.70	133	1.95	187	2.65
25	0.05	80	3.81	134	0.25	188	0.32
26	0.59	81	5.46	135	1.68	189	0.50
27	8.94	82	2.73	136	0.17	190	0.13
28	4.14	83	2.73	137	0.32	191	6.21
29	12.09	84	0.85	138	0.09	192	0.66
30	0.33	85	3.97	139	2.50	193	0.21
31	14.40	86	0.42	140	0.57	194	0.62
32	0.55	87	0.31	141	10.76	195	0.48
33	0.84	88	0.49	142	1.07	196	0.08
34	0.08	89	1.80	143	0.40	197	0.98
36	0.04	90	1.52	144	0.06	198	0.10
37	0.08	91	5.17	145	3.27	199	9.44
38	0.33	92	0.36	146	0.33	200	0.84
39	7.95	93	2.81	147	3.31	201	0.06
40	1.47	94	0.38	148	0.29	202	0.15
41	14.24	95	4.14	149	0.55	203	0.40
42	5.46	96	1.42	150	0.11	204	0.10
43	10.18	97	5.38	151	6.50	205	0.49
44	0.78	98	1.38	152	0.41	207	9.06
45	1.14	99	1.41	153	1.16	208	0.65
46	0.29	100	0.41	154	0.49	209	1.50
47	6.37	101	3.64	155	0.92	210	0.27
48	0.36	102	0.62	156	0.11	211	7.74
49	0.81	103	3.23	157	0.28	212	0.80
50	0.47	104	0.58	158	0.23	213	0.31
51	9.15	105	0.70	159	9.48	214	0.08
52	0.73	106	0.67	160	0.84	215	0.26
53	3.77	107	0.92	161	4.06	216	0.05
54	1.52	108	0.66	162	0.39	217	2.81
55	21.69	109	8.03	163	0.46	218	0.27
56	1.68	110	2.56	164	0.11	219	0.30
57	9.69	111	1.14	165	1.29	220	0.10
58	0.84	112	0.34	166	0.13	221	0.33
59	7.20	113	3.93	167	4.80	222	0.11
60	0.40	114	0.75	168	0.34	223	0.15
61	0.71	115	4.01	169	0.36	227	0.21
62	0.18	116	0.49	170	0.09	228	0.06
63	0.84	117	1.27	171	1.84	229	0.93
64	1.38	118	0.18	172	0.35	230	0.12
65	10.35	119	2.00	173	2.11	231	33.28
66	1.09	120	0.31	174	0.47	232	3.06
67	3.64	121	3.68	175	0.17	233	0.32
68	0.44	122	0.56	176	0.07	234	0.07
69	22.68	123	0.72	177	1.12	235	0.50
70	5.13	124	0.14	178	0.10	236	0.06
71	2.54	125	0.33	179	4.84	237	0.09
72	0.49	126	0.30	180	0.48	239	0.39
73	5.55	127	7.86	181	8.24	240	0.11
74	0.51	128	0.90	182	0.77	241	0.91
75	1.82	129	2.45	183	0.37	242	0.23
76	0.38	130	1.40	184	0.06	243	0.07
77	21.69	131	1.31	185	1.90	245	0.07
78	1.55	132	1.08	186	0.25	247	0.34
248	0.15	263	0.10	283	0.08	321	0.78
249	100.00	265	0.05	291	0.08	322	0.10
250	9.19	267	0.07	293	0.40	323	0.41
251	0.69	269	0.06	294	0.06	324	0.06
252	0.07	271	0.07	297	0.15	341	0.26
253	0.32	273	0.59	299	0.07	343	1.06
254	0.06	274	0.08	301	0.35	344	0.13
255	0.04	277	0.11	302	0.05	361	0.06
259	0.81	279	0.32	303	0.17	363	2.17
260	0.14	280	0.04	313	0.34	364	0.26
261	0.86	281	1.22	314	0.04	381	0.08
262	0.13	282	0.14	317	0.05		

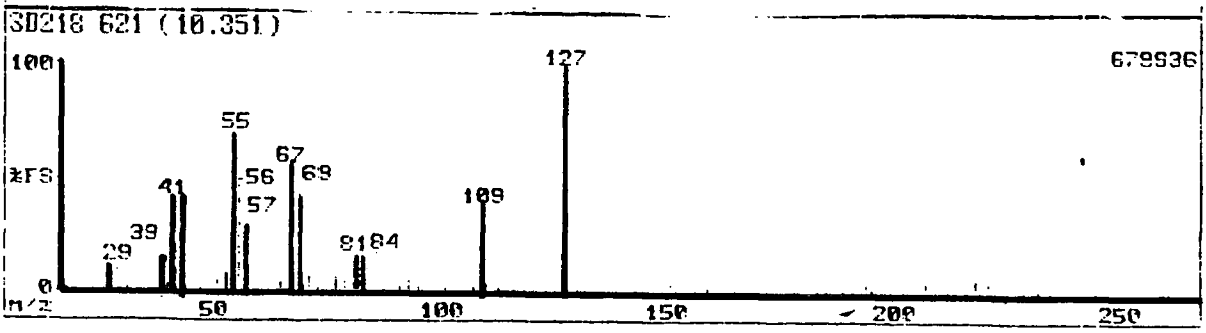
7. Gamma ray initiated formation of 1-(1,1,2,3,3,3-hexafluoropropyl)-cycloheptanol (24)



SD243F 520 (8.667) 3211264

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.05	74	0.30	128	0.20	182	0.04
24	0.02	75	1.74	129	0.75	183	0.27
25	0.05	76	0.33	130	0.07	184	0.02
26	1.36	77	11.48	131	0.56	185	0.72
27	16.71	78	1.28	132	1.26	186	0.06
28	7.37	79	5.07	133	0.59	187	1.72
29	21.05	80	2.02	134	0.08	188	0.22
30	0.59	81	5.33	135	1.21	189	0.13
31	4.27	82	4.50	136	0.12	191	0.09
32	0.30	83	6.22	137	0.77	194	2.58
33	0.57	84	1.72	138	0.09	195	0.69
34	0.10	85	2.30	139	1.20	196	0.04
35	0.01	86	0.30	140	0.17	197	0.28
36	0.03	87	0.59	141	1.10	198	0.05
37	0.24	88	0.45	142	0.08	199	0.13
38	1.20	89	1.08	143	0.46	200	0.01
39	31.12	90	0.46	144	0.06	201	0.03
40	6.76	91	5.33	145	1.01	203	0.06
41	76.02	93	14.16	146	0.10	204	0.67
42	42.86	95	90.31	147	0.51	205	0.52
43	46.43	96	7.56	148	0.05	207	4.24
44	2.14	97	2.02	149	0.26	208	0.48
45	13.39	98	0.31	151	4.05	209	0.05
46	0.63	99	0.77	152	0.13	211	0.07
47	3.28	100	0.30	153	0.31	213	0.03
48	0.52	101	2.02	154	0.16	216	0.06
49	0.97	102	0.22	155	2.26	217	0.94
50	1.42	103	2.49	156	0.14	218	0.29
51	11.99	104	0.34	157	0.57	219	0.03
52	2.04	105	0.63	158	0.04	220	0.03
53	17.73	106	0.69	159	1.42	221	0.29
54	11.35	107	0.99	160	0.18	222	0.03
55	88.78	108	0.32	161	0.37	223	0.07
56	10.84	109	1.75	163	0.63	225	0.13
57	40.31	110	0.24	164	0.03	226	0.04
58	3.99	111	0.57	165	0.50	227	0.54
59	6.15	113	100.00	167	2.20	228	0.02
60	0.58	114	10.71	168	0.14	231	0.67
61	1.96	115	2.23	169	0.23	232	0.05
62	0.48	116	0.34	170	0.02	233	0.02
63	2.10	117	1.22	171	0.15	235	0.01
64	1.30	118	0.12	172	0.05	236	0.03
65	7.11	119	1.04	173	0.19	245	0.96
66	1.98	120	0.12	174	0.51	246	0.60
67	51.53	121	0.74	175	0.17	247	0.22
68	11.10	122	0.12	176	0.01	262	0.02
69	65.82	123	0.80	177	0.46	263	0.02
70	21.56	124	0.41	178	0.03	267	0.01
71	8.42	125	0.80	179	0.35		
72	0.84	126	0.37	180	0.04		
73	3.32	127	1.86	181	0.48		

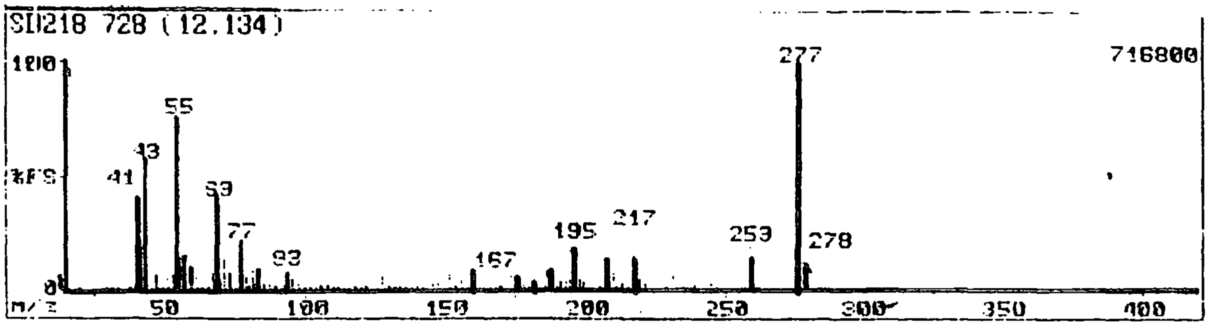
8. Gamma ray initiated formation of mainly 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclooctanol (25)



SD218 621 (10.351) 679936

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
25	0.06	48	0.64	70	4.14	92	0.25	114	0.28	137	0.39	163	0.34	191	0.39	218	5.72
26	0.63	49	0.44	71	7.00	93	5.53	115	1.30	138	0.13	165	0.25	193	0.40	219	0.84
27	9.56	50	0.60	72	0.62	94	0.92	116	0.20	139	1.31	167	2.86	194	3.04	220	0.34
28	4.63	51	4.93	73	2.14	95	3.20	117	1.95	140	0.21	168	0.30	195	1.70	221	4.53
29	12.50	52	0.94	74	0.19	96	0.58	118	0.20	141	1.12	169	0.70	196	0.11	222	0.23
30	0.33	53	8.13	75	0.93	97	4.03	119	1.16	142	0.12	170	0.07	197	1.01	223	0.49
31	1.98	54	8.66	76	0.21	98	1.04	120	0.20	143	0.24	171	0.39	198	0.21	229	0.06
32	0.21	55	71.08	77	7.27	99	1.01	121	0.66	145	0.59	172	0.10	199	1.22	231	2.22
33	0.24	56	46.39	78	0.78	100	0.24	122	0.13	146	0.11	173	0.93	200	0.12	232	2.30
34	0.86	57	25.75	79	4.82	101	1.60	123	0.42	147	0.29	174	0.71	201	0.30	233	0.21
35	0.04	58	2.06	80	1.10	102	0.23	124	0.13	149	0.02	175	0.44	202	0.08	235	0.46
37	0.09	59	6.17	81	17.92	103	1.59	125	0.23	151	4.18	177	1.09	203	0.12	236	0.15
38	0.37	60	0.40	82	10.54	104	0.26	127	100.00	152	0.17	178	0.09	204	0.56	237	0.04
39	13.25	61	0.08	83	14.16	105	0.50	128	8.40	153	0.45	179	1.45	205	0.26	239	0.06
40	3.01	62	0.19	84	10.54	106	0.59	129	1.22	154	0.22	180	0.12	207	6.02	241	0.16
41	41.57	63	0.78	85	4.33	107	2.29	130	0.17	155	1.01	181	0.50	208	0.09	245	0.74
42	20.18	64	0.53	86	0.37	108	0.48	131	0.70	156	0.08	183	0.34	209	0.03	246	0.03
43	40.36	65	3.93	87	0.54	109	39.16	132	0.63	157	0.77	185	0.35	211	0.24	249	0.14
44	1.64	66	1.07	88	0.28	110	3.54	133	0.65	158	0.08	186	0.09	212	0.12	250	0.03
45	4.25	67	56.63	89	0.80	111	0.83	134	0.03	159	2.00	187	1.06	213	0.09	259	0.28
46	0.23	68	6.36	90	0.34	112	0.10	135	0.64	160	0.26	188	0.39	216	0.61	260	0.52
47	1.76	69	40.96	91	3.35	113	2.00	136	0.08	161	0.67	189	0.21	217	2.52	261	0.15

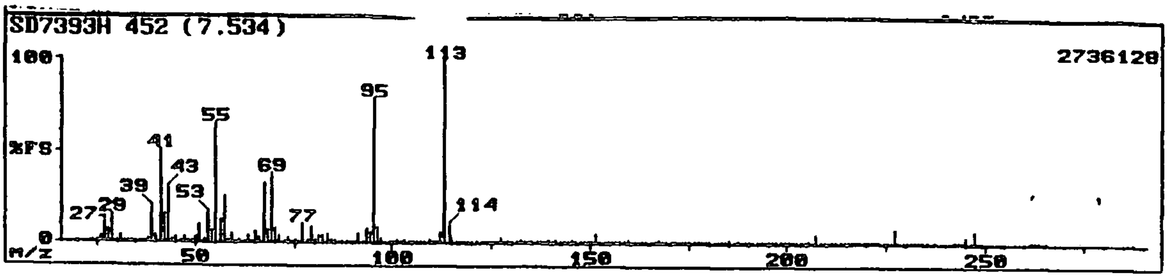
9. Gamma ray initaiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-cyclooctanols (26)



SU218 728 (12.134) 716800

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
25	0.04	62	0.46	97	3.32	132	1.23	169	2.03	204	1.65	240	0.43	283	0.07	339	0.29
26	0.20	63	1.01	98	1.05	133	1.65	170	0.26	205	2.50	241	0.95	285	0.13	341	0.45
27	2.87	64	1.11	99	1.29	134	0.25	171	0.79	206	0.29	242	0.12	287	0.40	342	0.07
28	1.62	65	10.27	100	0.34	135	2.00	172	1.70	207	13.71	243	0.73	288	0.04	343	0.13
29	6.29	66	1.50	101	3.50	136	0.35	173	6.86	208	1.23	244	0.11	289	1.43	345	0.10
30	0.17	67	13.43	102	0.54	137	0.64	174	2.20	209	7.50	245	2.50	290	0.21	346	0.32
31	1.10	68	5.25	103	5.04	138	0.40	175	6.10	210	0.32	246	0.34	291	0.35	347	0.33
32	0.17	69	40.57	104	1.06	139	1.78	176	0.69	211	1.73	247	1.63	293	0.12	348	0.16
33	0.37	70	4.00	105	1.51	140	0.42	177	2.02	212	0.40	248	0.92	297	0.13	349	1.43
34	0.04	71	13.71	106	0.28	141	3.43	178	0.32	213	2.46	249	1.32	299	0.29	350	0.13
37	2.06	72	1.27	107	2.22	142	0.34	179	2.61	214	0.36	250	0.22	301	0.57	351	1.04
38	0.21	73	7.50	108	1.75	143	0.43	180	0.23	215	1.60	251	0.15	302	0.10	352	0.10
39	9.54	74	0.53	109	4.83	145	2.71	181	4.39	216	0.20	253	0.13	303	0.17	353	0.06
40	1.35	75	2.33	110	0.70	146	0.35	182	0.51	217	20.29	255	0.47	305	0.15	357	0.05
41	37.71	76	0.45	111	1.21	147	2.54	183	0.84	218	2.75	257	0.64	307	0.71	359	0.16
42	10.43	77	22.57	112	0.35	148	0.24	184	0.11	219	4.51	258	0.08	308	0.09	361	0.12
43	57.71	78	1.66	113	3.33	149	1.40	185	1.06	220	0.87	259	21.71	309	0.67	366	0.15
44	2.42	79	5.64	114	0.65	151	6.36	186	0.53	221	3.00	260	2.43	310	0.08	367	0.21
45	6.07	80	1.59	115	3.00	152	0.33	187	0.32	222	0.28	261	0.63	311	0.40	368	0.22
46	0.43	81	0.61	116	0.60	153	1.47	188	0.31	223	0.75	262	0.07	313	0.11	369	0.34
47	7.21	82	3.29	117	1.57	154	0.64	189	2.04	224	0.09	263	0.24	315	0.06	371	1.46
48	0.62	83	3.05	118	0.34	155	3.71	190	0.26	225	0.53	265	0.41	317	0.14	372	0.21
49	0.82	84	2.09	119	1.13	156	0.35	191	3.64	227	5.14	266	0.05	319	0.15	381	0.10
50	0.50	85	2.64	120	0.28	157	1.04	192	0.63	228	0.62	267	0.92	321	0.25	382	0.07
51	3.43	86	0.57	121	2.04	158	0.25	193	1.35	229	1.65	268	0.10	323	0.36	385	0.21
52	0.30	87	2.68	122	0.31	159	0.64	194	17.57	230	0.97	269	1.68	325	0.17	388	0.62
53	6.33	88	0.61	123	1.37	160	0.78	195	21.06	231	7.07	270	0.25	326	0.06	389	0.21
54	4.33	89	2.19	124	0.27	161	1.68	196	2.00	232	3.57	271	0.16	327	0.26	390	0.05
55	76.57	90	1.71	125	0.65	162	0.18	197	4.75	233	0.78	273	0.20	329	1.03	391	0.49
56	15.09	91	7.50	126	0.45	163	0.73	198	0.71	234	1.13	275	0.27	330	0.13	392	0.09
57	14.29	92	0.57	127	5.02	164	0.31	199	3.71	235	2.21	277	100.00	331	0.38	400	0.37
58	3.23	93	10.57	128	0.65	165	1.03	200	0.52	236	0.29	278	11.00	332	0.07	403	0.09
59	11.14	94	1.34	129	1.62	166	0.16	201	1.05	237	1.23	279	1.05	333	0.13	410	0.33
60	0.01	95	5.04	130	0.31	167	10.14	202	0.21	238	0.20	280	0.09	337	0.05	411	0.03
61	5.79	96	1.02	131	1.39	168	0.04	203	0.60	239	3.07	281	0.37	338	0.07		

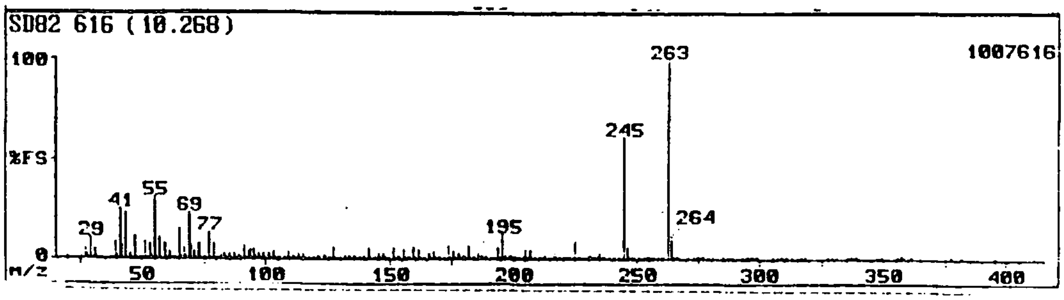
10. Gamma ray initiated formation of 1-(1,1,2,3,3,3-hexafluoropropyl)-4-methylcyclohexanol (29)



SD7393H 452 (7.534)

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel In
20	0.58	77	10.33	131	0.83	185	1.87
24	0.23	78	2.00	132	1.53	186	0.26
25	0.51	79	9.13	133	1.19	187	1.93
26	2.69	80	2.24	134	0.24	188	0.50
27	10.48	81	3.59	135	0.87	189	0.26
28	6.47	82	3.89	136	0.27	190	0.08
29	15.57	83	4.60	137	0.80	191	0.49
30	0.45	84	1.53	138	0.20	192	0.11
31	3.89	85	1.67	139	1.56	193	0.11
32	0.58	86	0.25	140	0.42	194	0.45
33	0.46	87	0.51	141	1.98	195	0.26
34	0.05	88	0.44	142	0.33	196	0.08
35	0.07	89	1.13	143	0.86	197	0.71
36	0.15	90	0.59	144	0.30	198	0.10
37	0.94	91	5.09	145	1.89	199	0.28
38	1.78	92	0.95	146	0.47	200	0.05
39	18.41	93	7.86	147	0.95	201	0.07
40	4.23	94	5.84	148	0.21	202	0.03
41	50.90	95	78.44	149	0.37	203	0.15
42	15.72	96	8.79	150	0.27	204	0.28
43	28.89	97	2.73	151	4.98	205	1.59
44	2.40	98	0.48	152	0.27	206	0.36
45	3.07	99	0.82	153	0.62	207	5.05
46	0.45	100	0.37	154	0.24	208	0.94
47	2.84	101	1.82	155	1.35	209	0.21
48	0.35	102	0.37	156	0.20	210	0.05
49	0.83	103	1.59	157	0.80	211	0.40
50	2.69	104	0.36	158	0.23	212	0.06
51	9.51	105	0.61	159	1.99	213	0.07
52	2.28	106	0.81	160	0.33	214	0.02
53	15.12	107	1.01	161	0.52	215	0.05
54	6.51	108	0.43	162	0.11	216	0.05
55	65.27	109	2.38	163	0.69	217	0.59
56	12.28	110	0.54	164	0.24	218	0.08
57	24.85	111	0.97	165	0.94	219	0.06
58	1.82	112	5.50	166	0.18	220	0.03
59	4.72	113	100.00	167	2.40	221	0.05
60	0.45	114	9.73	168	0.27	222	0.01
61	1.86	115	2.84	169	0.38	223	0.06
62	0.76	116	0.63	170	0.09	224	0.05
63	3.63	117	0.73	171	0.38	225	1.09
64	1.22	118	0.20	172	0.14	226	0.25
65	5.39	119	1.40	173	0.35	227	7.52
66	2.73	120	0.24	174	0.30	228	0.82
67	32.04	121	0.98	175	0.21	229	0.08
68	6.36	123	0.45	176	0.07	230	0.05
69	38.02	123	0.80	177	1.08	231	1.34
70	7.45	124	0.41	178	0.17	232	0.13
71	4.23	125	0.86	179	0.91	233	0.04
72	0.65	126	0.39	180	0.13	234	0.03
73	2.43	127	2.88	181	0.58	235	0.03
74	0.66	128	0.55	182	0.10	237	0.01
75	2.06	129	1.30	183	0.44	242	0.01
76	0.56	130	0.29	184	0.10	243	0.05

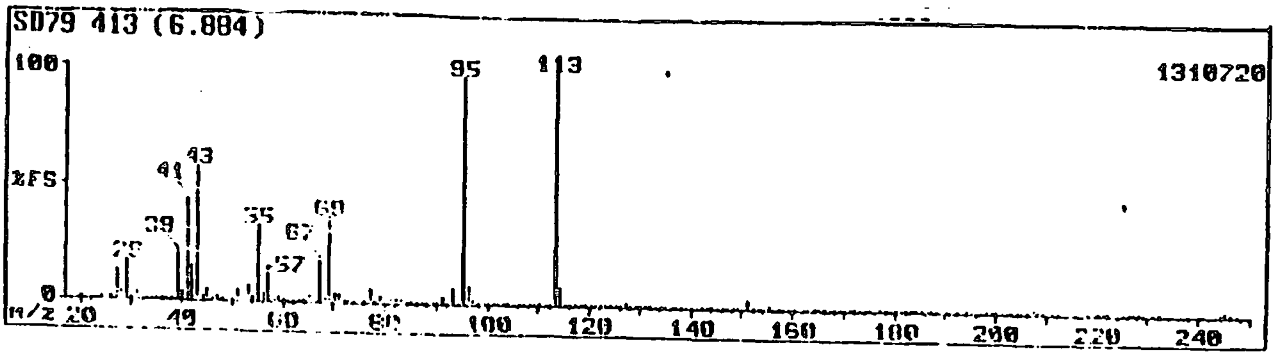
11. Gamma ray initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-4-methylcyclohexanols (30)



SD82 616 (10.268) 1007616

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.07	80	1.27	134	0.27	189	0.41
26	0.30	81	1.31	135	1.93	191	0.93
27	5.18	82	2.11	136	0.33	192	0.11
28	2.08	83	3.02	137	0.40	193	5.54
29	10.26	84	0.78	138	0.08	194	0.83
30	0.28	85	2.54	139	1.62	195	12.60
31	4.88	86	0.29	140	0.34	196	1.22
32	0.33	87	2.79	141	5.36	197	2.01
33	0.57	88	0.51	142	0.82	198	0.19
34	0.05	89	1.53	143	0.92	199	1.52
36	0.04	90	0.60	144	0.78	200	0.16
37	0.07	91	6.71	145	2.95	201	0.69
38	0.27	92	0.76	146	0.33	202	0.08
39	8.43	93	4.17	147	2.46	203	1.18
40	2.29	94	5.23	148	0.21	204	0.38
41	24.80	95	4.93	149	0.56	205	5.16
42	6.81	96	1.98	151	5.44	206	0.51
43	23.17	97	3.07	152	0.26	207	5.03
44	1.27	98	0.64	153	1.65	208	0.46
45	2.64	99	3.28	154	0.33	209	0.81
46	0.34	100	0.40	155	4.88	210	0.15
47	11.48	101	2.82	156	0.53	211	0.68
48	0.48	102	0.44	157	0.45	212	0.07
49	0.76	103	3.84	158	0.13	213	2.26
50	0.51	104	0.79	159	6.28	214	0.26
51	8.33	105	1.23	160	0.54	215	0.43
52	1.09	106	0.51	161	5.11	216	0.09
53	7.72	107	0.84	162	0.46	217	3.23
54	2.03	108	0.30	163	0.84	218	0.30
55	30.89	109	4.34	164	0.20	219	0.57
56	2.34	110	0.64	165	2.69	220	0.07
57	10.67	111	1.53	166	0.26	221	0.26
58	0.96	112	0.58	167	4.07	222	0.06
59	7.42	113	3.13	168	0.34	223	0.97
60	0.50	114	0.55	169	0.55	224	0.16
61	3.61	115	2.72	170	0.08	225	8.33
62	0.28	116	0.46	171	0.94	226	0.90
63	0.81	117	1.06	172	0.15	227	0.44
64	0.85	118	0.17	173	7.11	228	0.06
65	15.75	119	1.18	174	0.78	229	0.64
66	1.47	120	0.16	175	4.04	230	0.09
67	6.07	121	2.03	176	0.41	231	1.91
68	1.51	122	0.46	177	2.54	232	0.20
69	22.97	123	2.11	178	0.21	233	0.55
70	6.48	124	2.01	179	2.39	234	0.09
71	3.40	125	0.71	180	0.22	235	2.57
72	0.67	126	0.28	181	6.40	236	0.29
73	7.62	127	5.74	182	0.56	237	0.16
74	0.42	128	0.63	183	0.72	239	0.08
75	1.37	129	1.68	184	0.10	241	0.25
76	0.30	130	0.19	185	3.20	243	1.33
77	13.11	131	0.78	186	0.36	245	60.98
78	1.28	132	1.75	187	2.18	246	6.15
79	8.13	133	1.68	188	1.24	247	0.58
248	0.05	274	0.10	305	0.06	339	0.03
249	0.25	275	0.74	307	0.42	347	0.06
251	0.04	276	0.14	308	0.04	349	0.04
253	0.28	277	0.21	309	0.48	355	0.57
254	0.07	279	0.10	310	0.05	356	0.07
255	0.41	281	0.05	311	0.28	357	2.08
256	0.13	285	0.06	313	0.10	358	0.27
257	0.07	287	0.50	315	0.48	361	0.29
259	0.36	288	0.06	316	0.06	375	0.11
260	0.08	289	0.07	317	0.38	377	1.57
261	0.21	291	0.18	318	0.16	378	0.23
263	100.00	293	0.50	327	0.23	381	0.56
264	9.96	294	0.06	329	0.14	382	0.08
265	0.78	295	0.78	331	0.10	395	0.19
266	0.07	296	0.10	335	1.02	411	0.33
267	0.28	297	0.21	336	0.13		
271	0.05	298	0.10	337	0.81		
273	0.31	299	0.05	338	0.27		

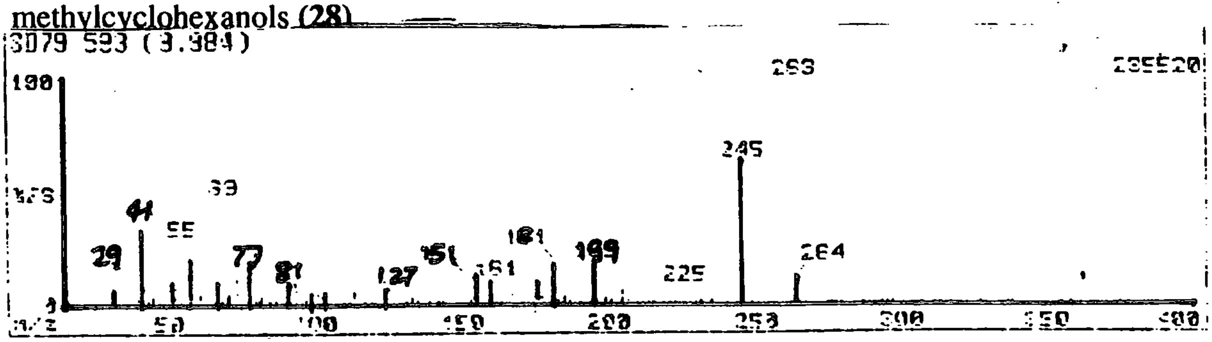
12. Gamma ray initiated formation of 1-(1,1,2,3,3,3-hexafluoropropyl)-3-methylcyclohexanol (27)



SD79-413 (6.884) 1310720

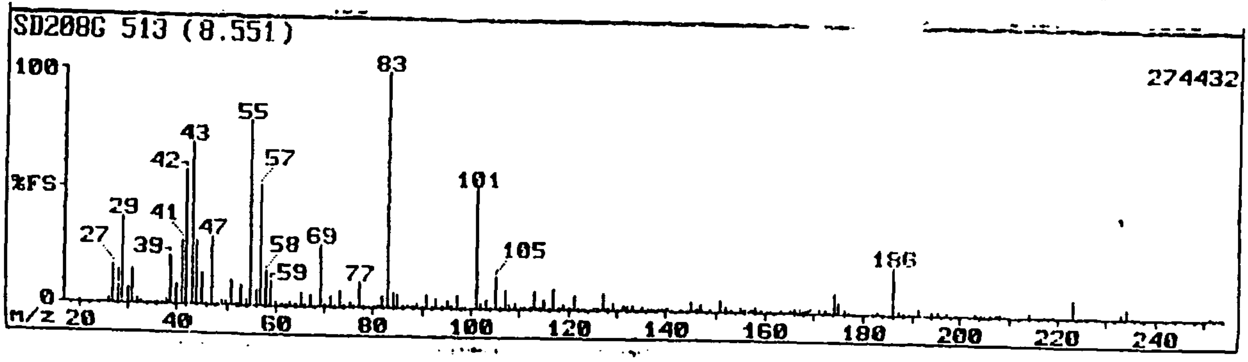
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.04	74	0.14	125	0.54	179	0.35
24	0.01	75	0.77	126	0.22	180	0.02
25	0.04	76	0.16	127	1.60	181	0.43
26	0.66	77	5.39	128	0.19	182	0.04
27	12.73	78	0.73	129	0.55	183	0.35
28	3.40	79	3.14	130	0.15	184	0.04
29	13.35	80	1.33	131	0.39	185	0.56
30	0.44	81	1.95	132	0.89	186	0.08
31	2.95	82	2.15	133	0.73	187	0.05
32	0.28	83	2.27	134	0.09	188	0.13
33	0.45	84	0.72	135	0.57	189	0.14
34	0.14	85	1.01	136	0.09	190	0.02
35	0.03	86	0.14	137	0.55	191	0.22
36	0.03	87	0.30	138	0.09	192	0.03
37	0.16	88	0.24	139	0.65	194	0.29
38	0.74	89	0.60	140	0.12	195	0.09
39	19.05	90	0.22	141	1.09	197	0.21
40	3.98	91	3.32	142	0.12	198	0.03
41	43.13	92	0.31	143	0.41	199	0.12
42	15.00	93	7.27	144	0.10	200	0.02
43	56.88	94	1.29	145	0.92	201	0.11
44	1.82	95	97.50	146	0.10	202	0.04
45	5.15	96	7.65	147	0.50	203	0.07
46	0.29	97	1.88	148	0.05	204	0.08
47	2.07	98	0.27	149	0.15	205	0.52
48	0.67	99	0.48	151	3.91	206	0.05
49	0.45	100	0.21	152	0.14	207	1.64
50	0.55	101	1.21	153	0.23	208	0.17
51	4.49	102	0.20	154	0.08	209	0.04
52	0.74	103	0.99	155	1.46	211	0.17
53	6.64	104	0.18	156	0.11	212	0.02
54	1.56	105	0.35	157	0.43	217	0.26
55	32.50	106	0.33	158	0.06	218	0.05
56	3.55	107	0.32	159	1.15	220	0.02
57	11.89	108	0.15	160	0.11	221	1.27
58	1.20	109	1.25	161	0.22	222	0.10
59	2.05	110	0.29	162	0.03	223	0.03
60	0.18	111	0.52	163	0.51	225	0.18
61	0.81	112	0.22	164	0.05	226	0.04
62	0.15	113	100.00	165	0.47	227	0.57
63	0.57	114	7.58	166	0.05	228	0.09
64	0.29	115	1.27	167	1.13	229	0.02
65	2.73	116	0.13	168	0.10	231	0.57
66	0.59	117	0.55	169	0.15	232	0.09
67	17.27	118	0.08	171	0.15	244	0.07
68	1.95	119	0.43	172	0.23	245	1.52
69	35.63	120	0.10	173	0.37	246	0.31
70	3.48	121	0.40	174	0.12	247	0.09
71	4.06	122	0.10	175	0.05		
72	0.32	123	0.51	177	0.35		
73	1.45	124	0.30	178	0.03		

13. Gamma ray initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-3-methylcyclohexanols (28)



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
19	0.25	79	11.29	133	3.10	187	2.17
20	0.80	80	1.02	134	0.47	188	0.21
26	0.50	81	1.23	135	4.46	189	0.56
27	2.70	82	3.67	136	0.63	190	[illegible]
28	2.50	83	5.03	137	0.77	191	[illegible]
29	12.70	84	1.77	138	0.17	192	[illegible]
30	0.47	85	4.05	139	1.96	193	3.37
31	0.23	86	0.40	140	0.52	194	[illegible]
32	0.67	87	1.60	141	3.46	195	28.97
33	0.32	88	0.63	142	1.02	196	2.17
34	0.20	89	2.74	143	1.43	197	2.77
36	0.97	90	1.16	144	1.03	198	0.30
37	0.13	91	12.17	145	4.46	199	3.97
38	0.46	92	1.43	146	0.56	200	0.47
39	10.72	93	6.79	147	3.27	201	0.63
40	2.10	94	8.70	148	0.34	202	0.26
41	29.57	95	3.24	149	1.09	203	3.76
42	3.13	96	2.12	150	0.21	204	[illegible]
43	32.61	97	6.17	151	11.52	205	6.17
44	1.64	98	1.16	152	0.56	206	[illegible]
45	4.10	99	5.60	153	2.55	207	3.51
46	0.14	100	0.09	154	0.51	208	0.31
47	11.63	101	4.73	155	12.07	209	1.43
48	0.46	102	0.04	156	1.02	210	0.37
49	0.09	103	6.11	157	0.92	211	0.35
50	0.59	104	1.20	158	0.31	212	0.17
51	3.70	105	1.51	159	10.11	213	1.33
52	0.97	106	0.69	160	0.09	214	0.29
53	0.37	107	1.16	161	12.93	215	0.75
54	1.73	108	0.55	162	1.17	216	0.16
55	30.09	109	0.40	163	1.19	217	3.70
56	2.26	110	1.16	164	0.31	218	0.42
57	11.05	111	6.03	165	3.45	219	1.25
58	4.21	112	1.27	166	0.42	220	[illegible]
59	10.33	113	6.03	167	4.43	221	1.41
60	0.75	114	1.09	168	0.41	222	0.19
61	5.24	115	5.20	169	1.10	223	1.73
62	0.42	116	0.08	170	0.17	224	0.24
63	1.41	117	2.20	171	1.02	225	2.35
64	1.24	118	0.50	172	0.30	226	1.07
65	23.91	119	1.50	173	3.67	227	0.19
66	2.09	120	0.35	174	1.00	228	0.04
67	9.35	121	3.07	175	10.33	229	0.70
68	1.67	122	0.75	176	1.03	230	0.13
69	48.26	123	3.42	177	3.59	231	2.48
70	3.29	124	3.29	178	0.33	232	0.27
71	4.62	125	1.15	179	3.29	233	0.36
72	0.24	126	0.30	180	0.34	234	0.11
73	12.04	127	7.46	181	10.77	235	1.09
74	0.71	128	1.09	182	1.74	236	0.14
75	2.12	129	2.77	183	2.17	239	0.62
76	0.43	130	0.34	184	0.31	240	2.07
77	13.92	131	1.55	185	4.62	241	0.78
78	1.90	132	3.02	186	0.57	243	[illegible]
244	0.17	264	10.65	295	0.50	337	0.62
245	64.35	265	0.80	297	0.13	338	0.10
246	6.58	267	0.35	305	0.10	347	0.07
247	0.84	273	0.52	307	0.33	355	0.36
248	0.10	274	0.11	309	0.46	357	1.60
249	0.40	275	1.27	311	0.24	358	0.24
251	0.09	276	0.23	313	0.12	361	0.21
253	0.20	277	0.22	315	0.39	375	0.08
[illegible]	0.52	279	0.12	317	0.34	377	0.73
[illegible]	0.15	285	0.12	327	0.20	378	0.13
[illegible]	0.26	287	0.41	329	0.15	381	0.34
261	0.38	289	0.07	331	0.18	395	0.13
262	0.16	291	0.17	335	0.01		
263	100.00	293	0.46	336	0.13		

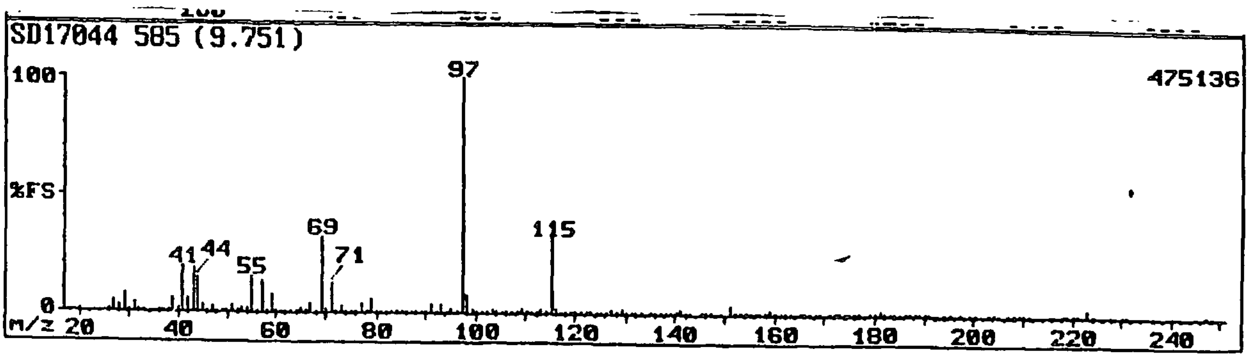
14. Gamma ray initiated formation of 1,3-di-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentane-1,3-diol (31)



SD208G 563 (9.3 | 1458176

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.04	54	2.84	85	0.69	115	4.34	151	10.82	188	0.46	219	0.12	254	0.07	307	0.07
26	0.52	55	16.92	86	0.18	116	0.73	152	0.67	189	0.60	221	0.48	255	0.30	313	0.03
27	5.34	56	4.46	87	0.50	117	0.70	153	0.57	191	4.71	223	0.83	257	0.40	315	0.13
28	3.77	57	17.63	88	0.65	119	1.44	155	1.03	192	0.35	224	0.12	258	0.04	317	1.39
29	9.53	58	1.91	89	1.42	121	4.85	157	1.18	193	1.19	225	0.89	259	0.12	318	0.13
30	0.14	59	10.91	91	5.12	122	0.55	159	17.39	194	1.08	227	0.95	261	0.17	323	0.22
31	3.33	60	0.30	93	4.22	123	1.21	160	1.37	195	2.46	228	0.12	263	0.71	325	10.22
32	0.15	61	0.41	94	0.55	124	0.17	161	0.74	196	0.51	229	0.03	265	1.95	326	1.04
33	0.72	62	2.19	95	2.50	125	0.52	163	1.63	197	2.35	230	0.11	266	0.19	327	0.63
35	0.85	63	1.67	96	0.81	127	4.71	165	7.79	198	0.20	231	0.43	267	0.22	329	0.03
37	2.25	64	1.25	97	1.16	128	0.33	166	0.58	199	0.15	233	100.00	271	0.93	333	0.33
38	0.34	65	4.25	99	2.81	129	3.07	167	1.53	201	0.37	234	0.79	273	0.08	335	0.04
39	7.44	66	1.12	100	1.30	131	6.60	168	0.29	202	0.23	235	1.21	275	0.36	337	0.06
40	1.83	67	4.71	101	4.13	132	5.12	169	0.54	203	1.09	236	0.12	277	1.40	343	0.10
41	5.11	69	37.92	102	0.94	133	1.76	171	1.25	205	15.10	237	0.17	278	0.15	345	1.03
42	7.58	70	0.96	103	3.53	134	0.30	173	1.95	206	1.80	239	8.89	279	0.38	347	1.79
43	53.89	71	4.34	104	0.30	135	1.58	174	0.21	207	2.23	241	0.26	281	0.18	348	0.39
44	2.14	72	0.52	105	0.72	136	0.21	175	2.74	208	0.50	243	0.38	283	0.24	353	0.05
45	2.91	73	2.21	106	0.63	137	0.41	176	0.52	209	0.73	244	0.06	285	0.29	363	0.05
46	0.39	75	1.95	107	2.52	139	2.09	177	2.49	210	0.06	245	0.67	287	0.02	364	0.07
47	6.25	77	9.30	108	0.57	141	2.72	178	0.22	211	0.33	246	0.19	293	0.34	365	0.29
48	0.19	78	0.47	109	2.46	142	0.17	179	0.21	213	6.60	247	0.61	295	0.34	367	0.28
49	2.02	79	0.24	110	0.24	143	0.50	181	0.40	214	0.62	248	0.07	297	3.02	373	1.63
50	1.46	80	0.40	111	0.47	145	15.00	183	3.72	215	1.20	249	0.11	298	0.29		
51	16.01	82	12.27	112	1.46	146	1.22	185	10.39	216	0.13	251	78.65	303	0.17		
52	1.72	83	3.40	113	5.13	147	0.61	186	0.83	217	1.26	252	6.95	305	1.35		
53	11.73	84	1.44	114	0.99	149	0.53	187	0.82	218	0.13	253	0.84	306	0.14		

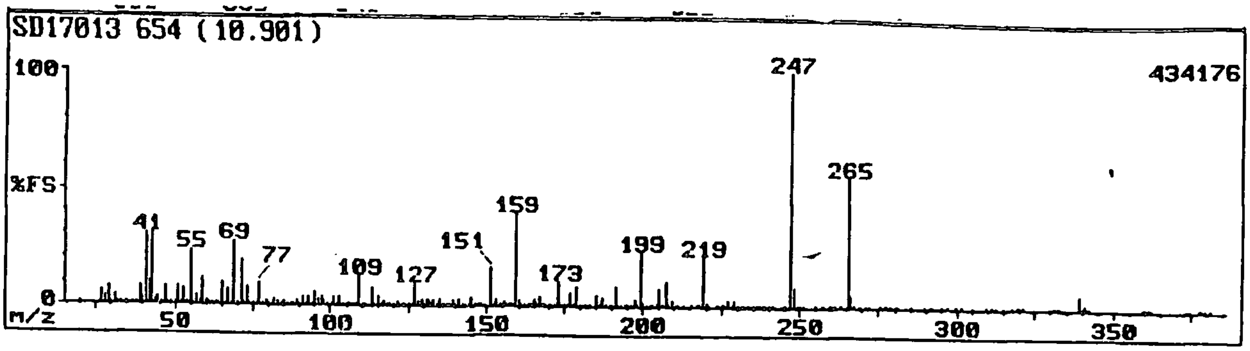
15. Gamma ray initiated formation of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexane-1,3-diol (32)



SD17044 585 (9.751) 475136

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.05	48	0.13	69	31.68	90	0.39	111	0.63	132	0.33	157	0.29	181	1.53	209	0.43
26	0.39	49	0.38	70	2.20	91	3.41	112	0.17	133	0.53	158	0.19	182	0.20	210	0.09
27	5.20	50	0.37	71	12.55	92	0.21	113	1.66	135	1.01	159	1.00	183	0.62	211	0.21
28	3.39	51	2.49	72	0.70	93	3.61	114	0.21	136	0.14	160	0.22	184	0.03	218	0.08
29	7.30	52	0.29	73	2.00	94	0.34	115	31.68	137	0.22	161	0.69	185	0.30	219	0.22
30	0.32	53	2.41	74	0.32	95	1.58	116	2.30	138	0.11	162	0.09	186	1.00	220	0.21
31	4.20	54	1.71	75	0.59	96	0.58	117	1.19	139	0.89	163	0.20	187	0.38	221	0.07
32	0.45	55	15.52	76	0.21	97	100.00	118	0.15	140	0.22	165	0.48	188	0.06	223	2.92
33	0.25	56	0.98	77	3.99	98	7.54	119	0.68	141	1.71	166	0.19	189	0.04	224	0.20
36	0.22	57	13.69	78	0.45	99	1.74	120	0.10	142	0.18	167	0.92	190	0.11	230	0.14
37	0.10	58	1.39	79	6.14	100	0.25	121	0.77	143	0.22	168	0.07	191	0.53	231	0.47
38	0.35	59	7.60	80	0.76	101	1.16	122	0.17	145	0.66	169	0.20	194	0.70	247	0.49
39	6.03	60	0.79	81	0.62	102	0.19	123	0.21	146	0.18	171	0.29	195	0.63	248	0.23
40	1.66	61	0.29	82	1.20	103	1.64	124	0.06	147	0.57	172	0.18	197	0.24		
41	19.61	62	0.28	83	0.78	104	0.27	125	0.20	149	0.26	173	0.51	199	0.59		
42	5.71	63	0.39	84	0.23	105	0.22	126	0.27	151	3.45	174	0.34	200	0.15		
43	18.75	64	0.32	85	0.60	106	0.23	127	1.90	152	0.17	175	1.12	203	0.09		
44	14.66	65	1.91	86	0.28	107	0.66	128	0.27	153	0.43	176	0.12	204	0.22		
45	3.03	66	0.39	87	0.19	108	0.44	129	2.28	154	0.19	177	0.24	205	0.21		
46	0.23	67	3.77	88	0.21	109	1.91	130	0.22	155	1.01	179	0.41	207	0.62		
47	2.64	68	0.73	89	0.66	110	0.29	131	0.63	156	0.13	180	0.08	208	0.09		

16. Gamma ray initiated formation of 1,3-di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexane-1,3-diol(33)

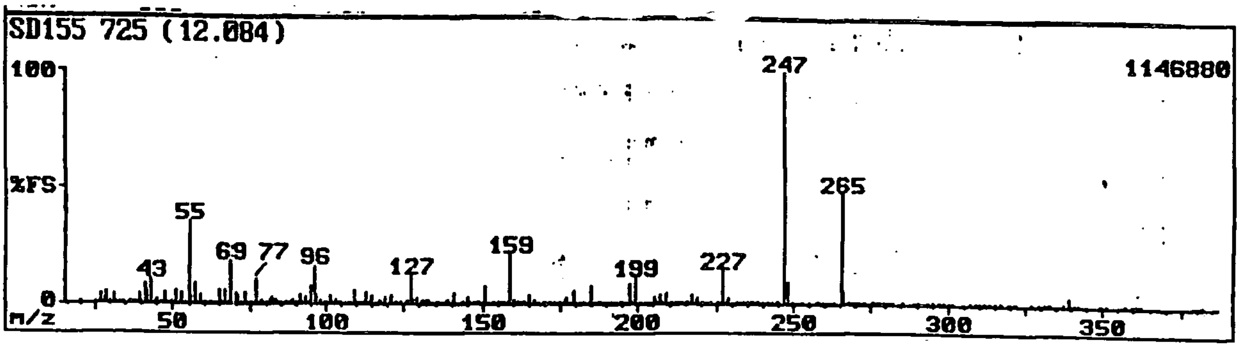


SD17013 654 (10.901)

434176

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.16	57	3.03	87	0.31	118	0.43	148	0.11	179	0.25	210	0.53	249	0.96	309	0.06
26	0.35	58	2.20	88	0.40	119	1.22	149	0.66	180	0.74	211	0.54	250	0.09	311	1.37
27	5.60	59	11.97	89	1.46	120	0.29	151	16.51	181	0.55	213	0.20	251	0.25	312	0.17
28	3.89	60	1.96	90	0.53	121	1.80	152	0.61	182	0.21	215	0.21	253	0.12	315	0.10
29	7.31	61	0.91	91	4.36	122	0.20	153	2.73	183	0.73	217	1.12	257	0.27	317	0.14
30	0.24	62	0.22	92	0.25	123	0.69	154	0.32	185	4.54	218	0.25	259	1.12	319	1.30
31	4.01	63	0.87	93	3.60	124	0.12	155	2.26	186	0.39	219	21.23	260	0.25	320	0.16
32	0.73	64	0.73	94	0.81	125	0.55	156	0.24	187	3.66	220	1.83	261	0.23	321	0.43
33	0.63	65	10.02	95	5.78	126	0.02	157	1.27	188	0.41	221	0.94	263	0.11	331	1.37
35	0.20	66	1.19	96	3.33	127	10.02	158	0.37	189	0.72	223	1.36	265	54.95	332	0.16
37	0.42	67	7.02	97	3.42	128	1.67	159	39.86	190	0.26	224	0.11	266	4.83	333	0.25
38	0.37	68	1.42	98	2.03	129	2.86	160	2.62	191	0.49	225	0.21	267	0.58	339	5.42
39	0.14	69	27.12	99	0.75	130	0.30	161	0.02	192	0.57	226	0.15	269	0.09	340	0.62
40	2.71	70	1.33	100	0.33	131	2.76	162	0.16	193	0.20	227	3.35	271	0.45	341	1.46
41	38.42	71	19.58	101	3.42	132	1.98	163	0.66	194	1.14	228	0.35	272	0.08	342	0.19
42	9.73	72	1.15	102	0.49	133	2.48	164	0.10	195	1.00	229	2.89	275	0.21	359	0.73
43	38.42	73	7.78	103	3.51	134	0.23	165	3.14	196	0.15	230	0.29	277	1.15	360	0.12
44	1.77	74	0.42	104	0.67	135	3.11	166	0.27	197	2.64	231	0.70	278	0.15	361	0.98
45	2.98	75	1.08	105	0.54	136	0.32	167	3.77	198	0.26	232	0.09	279	1.39	362	0.12
46	0.39	76	0.32	106	0.63	137	0.56	168	0.32	199	22.08	233	0.15	280	0.17	373	0.94
47	7.49	77	10.02	107	0.70	138	0.19	169	0.44	200	1.95	235	0.39	281	0.14	374	0.08
48	0.60	78	1.05	108	0.43	139	2.04	170	0.15	201	0.43	236	0.08	285	0.19	377	0.07
49	1.43	79	1.95	109	12.50	140	0.68	171	1.25	202	0.20	237	0.15	289	0.11	378	0.09
50	0.49	80	0.41	110	1.24	141	2.87	172	0.22	203	0.49	238	0.13	291	1.34	379	0.10
51	7.96	81	0.80	111	0.79	142	0.23	173	10.26	204	1.11	239	0.27	292	0.17	381	0.26
52	0.59	82	2.62	113	7.72	143	0.63	174	0.91	205	7.55	240	0.14	295	0.08		
53	6.72	83	1.53	114	0.78	144	0.14	175	1.15	206	0.52	241	0.38	297	0.48		
54	0.96	84	0.53	115	3.95	145	4.07	176	0.24	207	10.55	245	0.41	299	0.25		
55	22.08	85	2.17	116	0.49	146	0.04	177	5.72	208	0.86	247	100.00	301	0.08		
56	1.28	86	0.53	117	2.30	147	0.57	178	0.47	209	3.07	248	0.73	305	0.11		

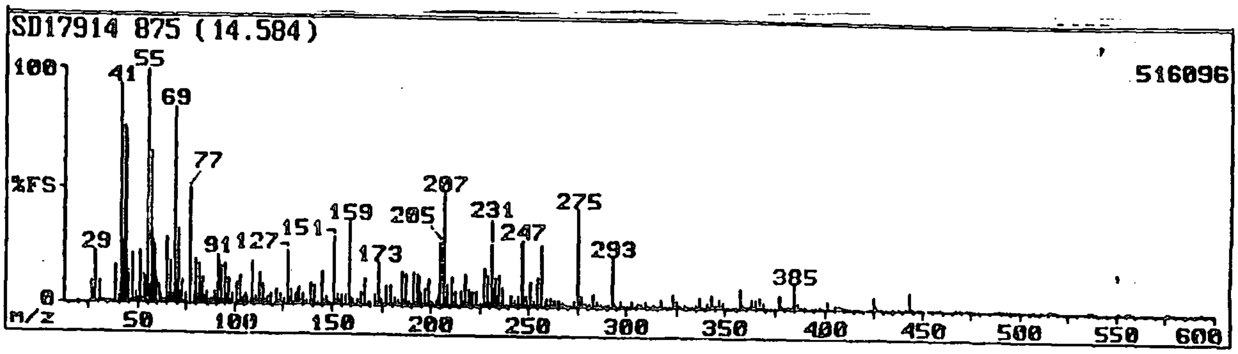
17. Gamma ray initiated formation of 1,4-di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexane-1,4-diol (34)



SD155 725 (12.084) 1146880

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
24	0.06	58	1.04	91	3.08	124	0.10	157	0.90	190	0.68	223	0.08	260	0.22	307	0.02
25	0.02	59	4.20	92	0.21	125	0.57	158	0.33	191	1.24	225	0.27	261	0.22	309	0.33
26	0.27	60	0.60	93	3.35	126	1.50	159	21.25	192	0.12	226	0.07	262	0.04	310	0.04
27	3.64	61	0.20	94	0.94	127	12.60	160	1.72	193	0.17	227	14.11	263	0.05	311	1.40
28	2.30	62	0.19	95	7.59	128	1.92	161	1.29	194	0.57	228	1.36	265	47.14	312	0.17
29	5.00	63	0.73	96	16.43	129	2.57	162	0.08	195	0.47	229	3.33	266	4.62	313	0.03
30	0.17	64	0.72	97	3.42	130	0.45	163	0.61	196	0.10	230	0.30	267	0.51	315	0.04
31	3.79	65	5.71	98	1.79	131	1.72	164	0.13	197	0.66	231	0.73	268	0.05	317	0.17
32	0.40	66	1.27	99	0.77	132	1.61	165	3.53	198	0.76	232	0.12	269	0.18	319	0.05
33	0.46	67	5.98	100	0.25	133	1.99	166	0.25	199	12.85	233	0.13	270	0.03	320	0.09
34	0.03	68	0.80	101	2.75	134	0.21	167	1.67	200	1.05	234	0.02	271	0.34	321	0.22
35	0.03	69	18.21	102	0.49	135	1.43	168	0.28	201	0.26	235	0.63	272	0.06	322	0.04
37	0.09	70	4.04	103	2.19	136	0.18	169	0.49	202	0.08	236	0.08	273	0.05	327	0.02
38	0.20	71	3.97	104	0.37	137	0.42	170	0.12	203	0.33	237	0.13	275	0.12	329	0.07
39	4.06	72	0.50	105	0.45	138	0.20	171	0.93	204	0.15	238	0.11	276	0.02	331	1.29
40	1.08	73	4.73	106	0.69	139	2.12	172	0.14	205	3.08	239	0.24	277	0.67	332	0.15
41	0.64	74	0.40	107	1.38	140	0.63	173	1.27	206	0.23	240	0.12	278	0.09	333	0.03
42	5.09	75	1.00	108	0.51	141	4.58	174	0.30	207	4.11	241	0.36	279	0.55	337	0.10
43	11.16	76	0.23	109	5.56	142	0.29	175	0.24	208	1.11	242	0.06	280	0.11	339	4.08
44	0.99	77	10.98	110	0.98	143	0.68	176	0.13	209	4.04	243	0.03	281	0.09	340	0.50
45	1.65	78	1.24	111	0.66	144	0.12	177	3.10	210	0.60	244	0.04	282	0.01	341	0.05
46	0.16	79	2.41	112	0.45	145	3.30	178	0.30	211	0.71	245	0.30	285	0.05	342	0.11
47	4.44	80	0.46	113	4.44	146	1.12	179	5.51	212	0.09	247	100.00	289	0.21	349	0.03
48	0.45	81	1.50	114	0.59	147	0.69	180	0.50	213	0.13	248	9.02	290	0.03	351	0.02
49	1.24	82	2.59	115	3.42	148	0.15	181	0.36	214	0.04	249	1.17	291	1.12	357	0.04
50	0.30	83	1.92	116	0.46	149	0.48	182	0.14	215	0.20	250	0.11	292	0.14	359	0.69
51	5.09	84	0.60	117	1.58	150	0.10	183	0.76	216	0.04	251	0.15	293	0.03	360	0.09
52	0.59	85	1.10	118	0.25	151	0.13	184	0.07	217	3.95	252	0.04	295	0.05	361	0.40
53	4.55	86	0.21	119	2.43	152	0.37	185	0.21	218	0.40	253	0.09	297	0.30	362	0.07
54	0.65	87	0.46	120	0.31	153	1.24	186	0.63	219	2.52	255	0.05	298	0.04	379	0.13
55	34.64	88	0.39	121	3.48	154	0.40	187	1.16	220	0.28	257	0.23	299	0.25	380	0.02
56	2.79	89	1.67	122	0.33	155	1.07	188	1.32	221	0.26	258	0.06	300	0.03	381	0.23
57	0.04	90	0.50	123	0.69	156	0.15	189	0.85	222	0.05	259	1.03	301	0.05	382	0.02

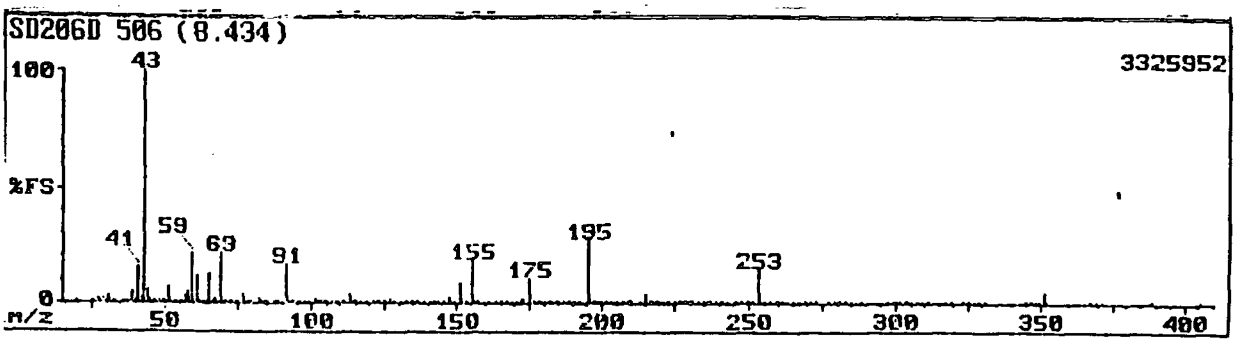
18. Gamma ray initiated formation of (1,1,2,3,3,3-hexafluoropropyl)-cyclooctanols (25)



SD17914 875 (14.584)

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
25	0.21	70	9.22	116	1.30	167	11.31	212	2.22	257	25.39	310	0.45	363	3.42	426	2.11
26	0.50	71	31.75	117	4.27	168	1.19	213	5.30	258	1.17	311	1.37	364	0.73	427	0.52
27	3.28	72	4.51	118	0.34	169	2.30	214	1.23	259	1.57	312	0.17	365	4.32	429	0.11
28	4.21	73	10.51	119	2.21	170	3.24	215	1.45	260	0.52	313	1.32	366	1.13	435	0.17
29	22.92	74	1.12	120	1.51	171	4.41	216	1.55	261	2.37	314	0.32	367	4.31	437	0.34
30	1.32	75	6.41	121	5.70	172	1.72	217	12.39	262	0.54	315	1.12	368	0.23	441	0.16
31	2.37	77	43.50	122	1.35	173	18.29	218	2.41	263	2.58	316	0.39	369	2.39	443	0.12
32	0.23	78	4.37	123	1.35	174	2.31	219	7.49	264	0.51	317	4.12	370	0.32	444	1.12
33	1.30	79	13.35	124	1.12	175	1.75	220	5.25	265	2.34	318	0.31	371	1.50	445	0.13
34	1.35	80	2.57	125	1.31	176	3.73	221	5.34	266	0.20	319	1.43	372	1.54	447	2.13
35	0.20	81	17.56	127	22.41	177	1.73	222	0.73	267	1.72	321	0.74	375	0.41	449	0.29
36	1.15	82	1.22	128	2.32	178	1.12	223	7.35	268	0.57	322	2.21	377	2.16	453	0.12
37	0.41	83	11.50	129	5.50	179	0.22	224	0.23	269	1.29	324	1.07	378	5.25	455	0.15
38	0.52	84	4.22	130	1.19	180	1.15	225	2.10	271	0.23	325	2.58	379	1.22	457	0.30
39	15.37	85	2.75	131	4.46	181	3.37	226	0.53	272	2.56	326	0.34	380	0.41	459	0.11
40	4.75	86	1.25	132	5.30	182	1.25	227	16.47	275	41.57	327	1.19	381	0.72	461	0.12
41	92.35	87	2.31	133	7.59	183	2.74	228	2.15	276	4.31	329	2.33	382	1.54	463	0.24
42	25.79	88	1.50	134	1.51	184	0.48	229	12.29	277	4.95	330	0.39	383	1.07	473	0.17
43	75.40	89	5.25	135	4.55	185	14.39	230	1.79	278	0.59	331	0.74	384	1.75	475	0.17
44	73.11	90	1.72	136	1.44	186	2.22	231	26.53	279	1.85	333	0.33	385	10.22	477	0.38
45	14.39	91	21.23	137	2.18	187	13.49	232	8.23	280	0.50	335	2.36	386	1.50	479	0.14
46	1.41	92	2.07	139	9.47	188	2.92	233	12.70	281	1.49	336	0.31	387	2.32	487	0.20
47	21.53	93	16.87	140	2.82	189	3.81	234	4.86	283	5.36	337	4.91	388	0.74	489	0.12
48	0.39	94	2.34	141	9.38	190	8.47	235	13.89	284	0.95	338	0.31	389	0.97	491	0.48
49	4.46	95	17.86	142	0.79	191	14.48	236	2.88	285	2.44	339	0.35	390	0.13	493	0.39
50	1.20	96	2.72	143	1.30	192	1.63	237	0.83	286	0.53	341	2.44	391	0.30	495	0.26
51	22.42	97	11.41	145	14.39	193	12.29	238	1.13	287	2.05	342	0.56	393	0.41	497	0.61
52	1.80	98	2.34	146	1.35	194	12.30	239	1.25	288	0.37	343	5.70	395	0.39	499	0.35
53	12.90	99	4.86	147	4.27	195	5.56	240	0.28	289	0.98	344	1.18	397	1.56	507	0.20
54	10.37	100	0.59	148	0.38	196	1.33	241	4.76	290	0.15	345	1.31	398	1.23	511	0.08
55	100.00	101	9.42	149	1.45	197	7.54	242	0.56	291	0.81	346	0.34	399	0.29	513	0.41
56	9.43	102	2.31	151	25.37	198	1.25	243	3.13	293	21.43	347	1.67	401	1.57	515	0.08
57	35.38	103	12.15	152	1.56	199	11.81	244	0.53	294	2.36	348	0.54	402	0.42	517	0.57
58	26.79	104	2.04	153	4.31	200	2.11	245	3.31	295	0.31	349	2.31	403	0.13	518	0.07
59	25.20	105	4.17	154	2.70	201	2.34	246	1.25	297	2.08	350	0.41	405	2.37	519	0.74
60	11.11	106	4.71	155	4.76	202	1.39	247	28.17	298	0.49	351	0.33	406	0.35	525	0.17
61	0.78	107	3.27	156	0.23	203	2.58	248	1.57	299	1.34	353	0.58	407	2.18	537	0.30
62	1.57	108	2.38	157	4.21	204	4.56	249	4.46	300	0.24	354	0.15	408	0.76	539	0.25
63	2.18	109	13.36	159	25.21	205	25.28	250	0.38	301	0.48	355	0.30	409	0.25	551	0.14
64	2.12	110	2.36	160	2.34	206	1.74	251	10.31	302	2.44	357	0.29	411	0.19	555	0.13
65	27.30	111	2.32	161	3.17	207	48.31	252	0.33	304	0.56	358	1.72	413	0.10	556	0.21
66	1.57	112	2.08	162	0.75	208	4.37	253	2.72	305	2.83	359	1.45	415	0.19	557	0.10
67	13.25	113	12.59	163	2.40	209	9.37	254	0.33	306	0.29	360	0.24	417	0.22	575	0.12
68	2.42	114	2.22	164	0.73	210	1.24	255	12.45	307	1.49	361	1.20	423	0.45	576	0.09
69	82.33	115	0.83	165	6.15	211	13.10	256	1.35	309	3.08	362	1.40	425	6.15	593	0.19

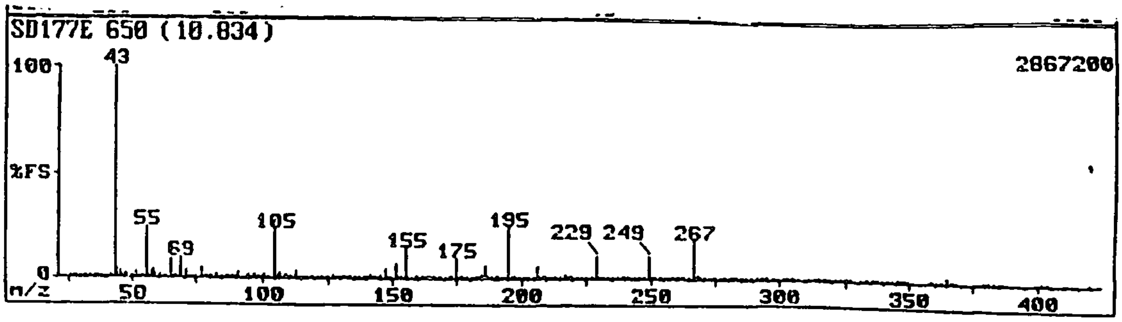
19. Gamma ray initiated formation of 2,4-di-(1,1,2,3,3,3-hexafluoropropyl)-pentane-2,4-diol (36)



SD206D 506 (8.434) 3325952

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.03	53	0.77	83	0.63	115	0.23	151	0.37	185	0.93	223	0.05	261	0.03	317	0.02
25	0.02	54	0.15	84	0.18	116	0.06	152	0.31	187	0.10	225	0.04	263	0.16	319	0.32
26	0.12	55	1.10	85	0.51	117	0.10	153	1.20	189	0.21	226	0.26	265	0.19	323	0.06
27	1.40	56	0.13	87	0.29	118	0.06	155	10.10	190	0.04	227	0.21	267	0.11	325	0.02
28	3.59	57	2.77	88	3.11	119	0.22	156	0.33	191	0.53	228	0.06	269	0.13	327	0.45
29	2.40	58	4.71	89	1.90	121	0.70	157	0.35	192	0.85	229	0.08	271	0.06	329	0.32
30	0.15	59	21.38	91	15.37	122	0.12	159	0.03	193	3.38	230	0.02	273	0.34	330	0.27
31	2.49	60	0.55	92	0.58	123	0.21	160	0.04	195	25.85	231	0.03	277	0.10	331	0.39
32	0.30	61	12.37	93	1.27	125	0.29	161	0.04	196	1.55	233	0.39	279	0.54	345	0.02
33	0.51	62	0.43	94	0.58	127	1.99	163	0.15	197	0.48	235	1.22	280	0.95	347	0.77
36	0.32	63	1.32	95	0.92	128	0.15	165	0.10	198	0.05	236	0.19	281	0.05	348	0.05
37	0.15	64	1.09	96	0.08	129	0.91	167	0.21	199	0.35	237	0.16	283	0.19	349	0.24
38	0.22	65	12.19	97	0.35	131	0.73	169	0.18	200	0.51	239	0.21	285	0.04	351	4.39
39	4.37	66	0.54	98	0.33	132	1.00	170	0.31	201	0.22	241	0.13	287	0.66	352	0.43
40	1.22	67	2.34	99	0.17	133	1.32	171	1.11	202	3.02	243	0.32	288	0.08	357	0.03
41	15.76	69	21.80	101	1.55	134	0.10	172	2.06	203	0.09	245	0.30	289	0.04	363	0.15
42	2.53	70	0.43	102	0.14	135	0.27	173	1.03	205	0.10	246	0.10	297	0.02	371	0.53
43	100.00	71	0.36	103	0.84	136	0.04	175	10.36	207	0.12	247	0.15	299	0.29	389	0.25
44	5.54	72	0.16	104	0.17	137	0.18	176	0.62	209	0.25	249	0.34	300	0.03	405	0.03
45	1.49	73	0.58	105	0.19	139	0.45	177	0.64	210	0.34	250	0.02	301	0.02		
46	0.53	74	0.26	107	1.25	141	0.40	178	0.08	213	0.34	251	0.03	303	0.47		
47	1.34	75	0.51	108	0.23	142	0.13	179	0.19	215	4.06	253	14.90	304	0.02		
48	0.84	77	4.06	109	1.28	143	0.07	180	0.02	216	0.33	254	1.19	305	0.10		
49	0.78	78	0.24	110	0.08	145	0.37	181	0.13	217	0.24	255	0.12	307	0.42		
50	0.32	79	0.09	111	0.29	147	3.20	182	0.03	219	0.34	257	0.04	308	0.03		
51	6.62	80	0.06	113	3.69	148	0.15	183	0.06	221	0.41	259	0.49	309	0.09		
52	0.30	82	2.34	114	0.28	149	0.15	184	0.01	222	0.03	260	0.06	311	0.04		

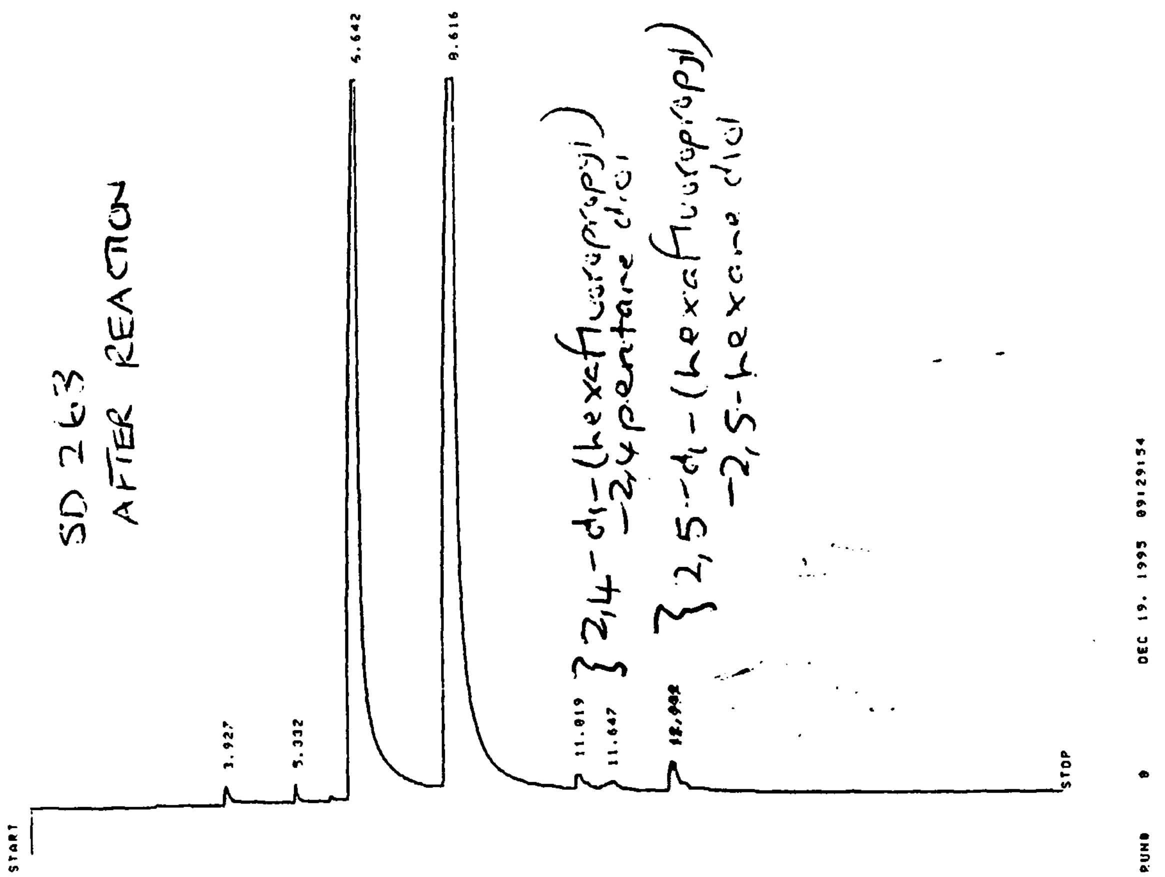
20. Gamma ray initiated formation of 2,5-di-(1,1,2,3,3,3-hexafluoropropyl)-hexane-2,5-diol (37).



SD177E 650 (10.834) 2867200

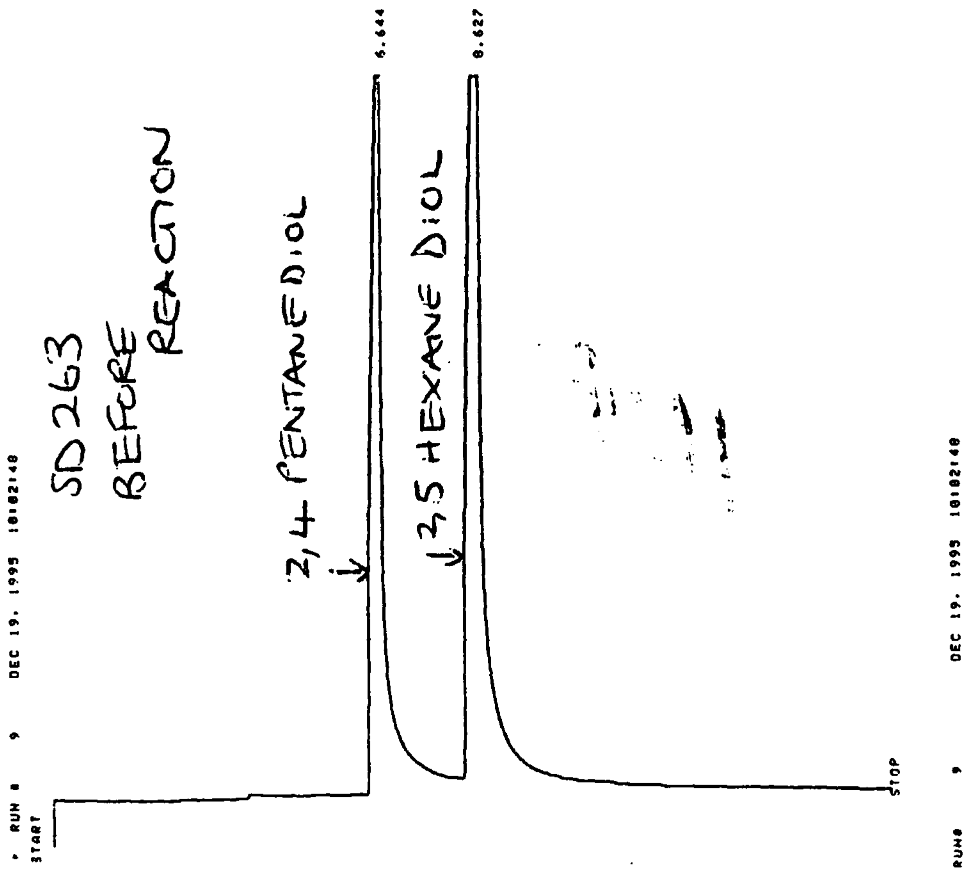
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.03	59	2.36	96	0.51	132	0.34	171	1.01	206	5.46	242	0.07	283	0.07	333	0.02
27	0.53	60	0.22	97	1.56	133	0.71	172	0.04	207	1.14	243	0.09	285	0.62	336	0.02
28	0.31	61	2.27	98	0.66	134	0.11	173	1.44	208	0.21	244	0.09	286	0.03	337	0.06
29	1.22	62	0.09	99	0.37	135	0.62	175	9.29	209	0.30	245	0.16	287	0.01	339	0.04
30	0.36	63	1.04	100	0.20	136	0.11	176	0.74	210	0.09	246	0.05	289	0.01	341	1.31
31	0.71	65	0.02	101	1.59	137	0.34	177	0.57	211	0.70	247	0.16	291	0.11	342	0.16
32	0.04	66	0.35	102	0.21	139	0.08	178	0.06	212	0.10	249	11.14	293	0.37	343	0.26
33	0.16	67	1.15	103	1.03	140	0.31	179	0.10	213	0.35	250	0.96	294	0.04	345	0.54
35	0.41	69	9.71	105	23.14	141	1.79	181	1.27	214	0.17	251	0.20	295	0.04	346	0.04
36	0.19	71	3.20	106	1.73	142	0.19	182	0.13	215	0.22	253	0.20	297	0.27	347	0.33
37	0.43	72	0.37	107	2.54	143	0.57	183	0.08	217	2.24	254	0.02	298	0.02	348	0.05
38	0.06	73	1.25	108	0.43	145	2.12	184	1.19	218	0.19	255	0.06	299	0.08	349	0.02
39	1.44	74	0.71	109	1.95	147	4.75	185	1.99	219	0.23	257	0.12	301	0.20	350	0.02
40	0.19	75	0.49	110	0.25	148	0.23	186	6.10	220	0.04	258	0.02	302	0.04	351	0.07
41	2.71	77	3.00	111	0.32	149	0.15	187	1.30	221	0.37	259	0.24	303	0.06	352	0.10
42	1.29	78	0.23	113	3.64	151	6.64	188	0.10	222	0.06	260	0.03	304	0.01	353	0.25
43	100.00	79	0.55	114	0.26	152	0.24	189	0.67	223	0.64	261	0.21	305	0.03	355	3.18
44	3.64	80	0.42	115	1.36	153	0.76	190	0.05	224	0.07	262	0.04	307	0.02	356	0.35
45	2.09	81	0.30	116	0.21	155	14.43	191	1.54	225	0.14	263	0.10	311	0.04	357	0.17
46	0.37	82	1.49	117	1.38	156	1.11	192	0.15	227	0.21	265	0.11	313	0.23	358	0.02
47	1.74	83	1.55	118	0.13	157	0.32	193	0.34	229	11.00	267	18.14	314	0.03	379	0.02
48	0.09	84	0.29	119	0.39	159	1.96	194	0.51	230	0.96	268	1.70	315	0.02	381	0.04
49	0.56	85	0.75	121	1.02	160	0.20	195	24.43	231	0.76	269	0.17	317	0.36	383	0.25
50	0.99	86	0.10	122	0.22	161	0.96	196	1.32	232	0.10	271	0.13	318	0.04	385	0.70
51	2.02	87	0.28	123	0.32	162	0.04	197	0.41	233	0.53	273	0.40	319	0.06	386	0.07
52	0.21	88	0.15	124	0.05	163	0.54	198	0.03	234	0.06	274	0.05	321	0.56	401	0.02
53	1.35	89	0.92	125	0.21	164	0.06	199	0.25	235	0.17	275	0.06	322	0.07	403	0.09
54	0.39	90	0.30	127	2.29	165	1.23	200	0.03	236	0.01	277	0.21	323	0.26	404	0.01
55	24.57	91	2.57	128	0.26	166	0.10	201	0.35	237	0.10	278	0.02	325	0.99	419	0.04
56	1.35	93	1.27	129	1.30	167	1.24	202	0.03	239	0.13	279	0.13	326	0.12		
57	2.93	94	1.03	130	0.17	168	0.10	203	0.02	240	0.27	281	0.05	327	0.09		
58	4.00	95	1.52	131	0.69	169	0.45	205	1.05	241	0.21	282	0.03	331	0.03		

21. Gamma ray initiated competition reaction between the addition of 2,4-pentanediol and 2,5-hexanediol to hexafluoropropene



```
RUN#     9           DEC 19, 1995  09:29:54

AREA%
      RT        AREA TYPE  WIDTH       AREA%
   3.927        9875   PB   .109      .50824
   5.332        4312   PB   .047      .22193
   6.642      782053   PB   .180    40.25005
   8.616     1103358   PB   .250    56.78669
  11.019        3278   PV   .043      .16871
  11.647        7265   BV   .214      .37391
  12.932       12597   BV   .078      .64833
```



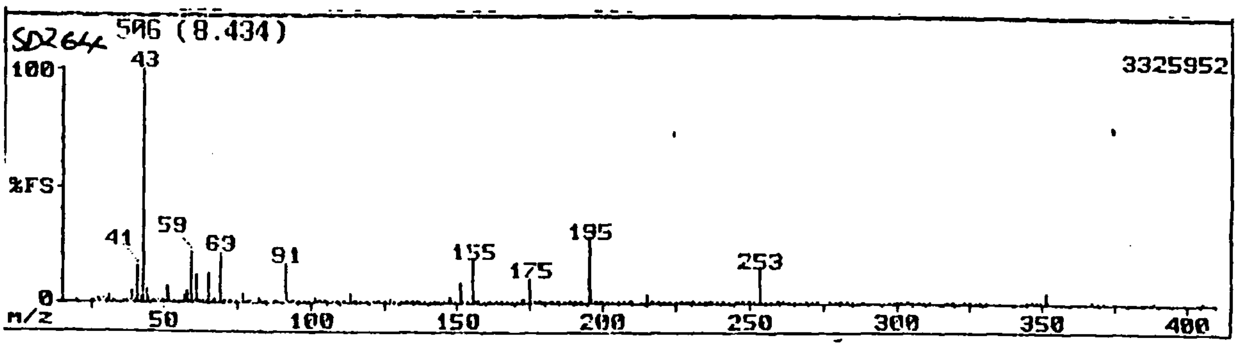
```
• RUN #     9      DEC 19, 1995  10:02:48
START

RUN#     9           DEC 19, 1995  10:02:48

AREA%
      RT        AREA TYPE  WIDTH       AREA%
   6.644      716011   PB   .150    36.30344
   8.627     1256284   PB   .271    63.69656

TOTAL AREA=1972295
MUL FACTOR=1.0000E+00
```

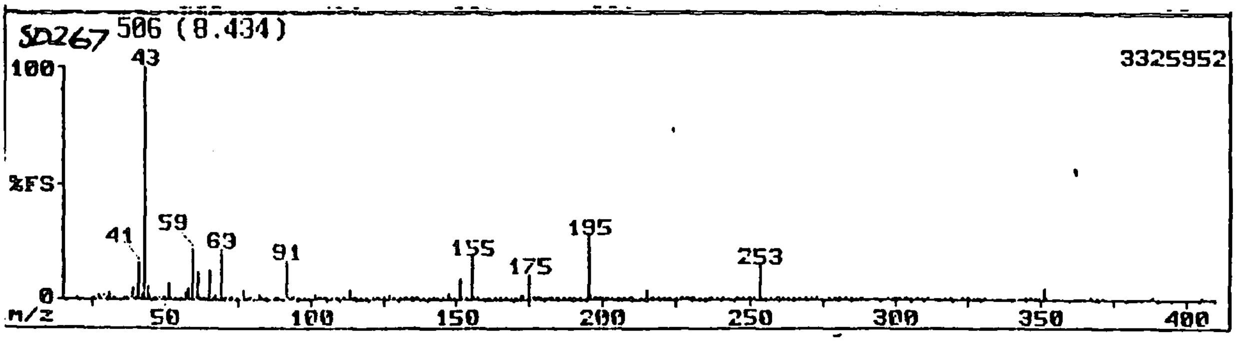
22. Gamma ray initiated reaction between 2,4-pentanediol and a deficiency of hexafluoropropene, forming only 2,4-di-(1,1,2,3,3,3-hexafluoropropyl)-pentane-2,4-diol (36)



596 (8.434) 3325952

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.22	53	0.77	83	0.63	115	0.23	151	0.37	185	0.39	223	0.05	251	0.03	317	0.02
25	0.02	54	0.15	84	0.19	116	0.36	152	0.31	187	0.10	225	0.04	253	0.16	319	0.32
26	0.12	55	1.10	85	0.51	117	0.10	153	1.28	189	0.21	226	0.26	255	0.19	323	0.26
27	1.48	56	0.13	87	0.29	118	0.06	155	10.10	190	0.04	227	0.21	257	0.11	325	0.03
28	3.58	57	2.77	88	0.11	119	0.22	156	0.23	191	0.53	228	0.26	259	0.13	327	0.45
29	2.40	58	4.71	89	1.98	121	0.70	157	0.35	192	0.95	229	0.08	271	0.06	328	0.32
30	3.15	59	21.36	91	16.37	122	0.12	159	0.93	193	3.38	230	0.82	273	0.34	329	0.27
31	2.43	60	0.55	92	0.28	123	0.21	160	0.84	195	25.95	231	0.03	277	0.10	331	0.20
32	0.20	61	12.37	93	1.27	125	0.29	161	0.34	196	1.55	232	0.29	279	0.54	345	0.82
33	0.51	62	0.43	94	0.58	127	1.99	162	0.15	197	0.48	233	1.22	280	0.35	347	0.77
36	0.32	63	1.22	95	0.92	128	0.15	163	0.10	198	0.25	235	0.19	281	0.05	348	0.05
37	0.15	64	1.09	96	0.08	129	0.91	167	0.21	199	0.35	237	0.16	283	0.19	349	0.24
38	0.22	65	12.19	97	0.25	131	0.73	169	0.18	200	0.51	239	0.21	285	0.04	351	4.73
39	4.37	66	0.54	98	0.33	132	1.80	170	0.31	201	0.22	241	0.13	287	0.66	352	0.43
40	1.22	67	2.24	99	0.17	133	1.22	171	1.11	202	3.13	243	0.32	288	0.38	357	0.83
41	15.76	69	21.90	101	1.95	134	0.10	172	2.86	203	0.09	245	0.20	289	0.04	363	0.15
42	2.93	70	0.43	102	0.14	135	0.27	173	1.83	205	0.10	246	0.10	291	0.32	371	0.55
43	100.00	71	0.36	103	0.94	136	0.04	175	10.35	207	0.12	247	0.15	293	0.29	389	0.25
44	5.54	72	0.16	104	0.17	137	0.13	176	0.52	209	0.25	249	0.24	300	0.03	405	0.03
45	1.49	73	0.58	105	0.19	139	0.45	177	0.64	210	0.34	250	0.02	301	0.02		
46	0.53	74	0.26	107	1.25	141	0.48	178	0.08	213	0.24	251	0.03	303	0.47		
47	1.34	75	0.51	108	0.23	142	0.13	179	0.19	215	4.06	253	14.90	304	0.02		
48	0.24	77	4.06	109	1.23	143	0.07	180	0.02	216	0.33	254	1.19	305	0.10		
49	0.78	78	0.24	110	0.08	145	0.37	181	0.13	217	0.24	255	0.12	307	0.42		
50	0.32	79	0.09	111	0.29	147	3.20	182	0.03	219	0.34	257	0.04	308	0.03		
51	6.62	80	0.06	113	3.69	148	0.15	183	0.06	221	0.41	259	0.49	309	0.09		
52	0.28	82	2.34	114	0.28	149	0.15	184	0.01	222	0.33	260	0.06	311	0.04		

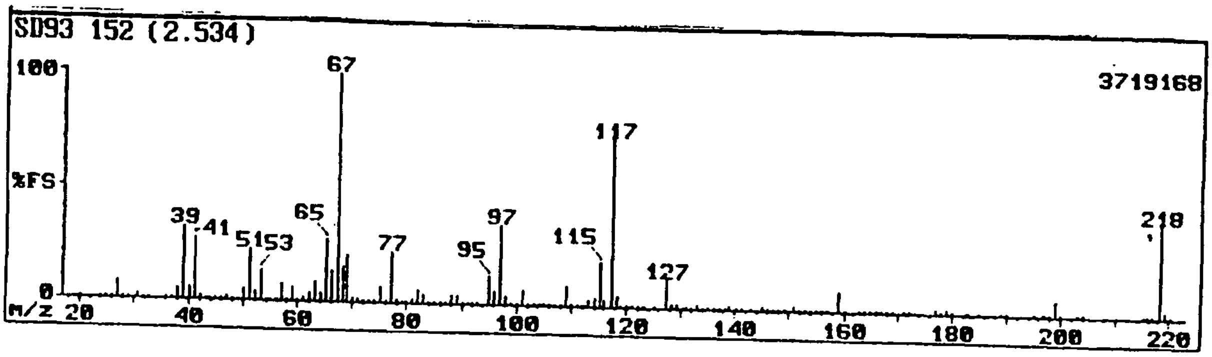
23. D.T.B.P. initiated formation of 2,4-di-(1,1,2,3,3,3-hexafluoropropyl)-pentane-2,4-diol (36)



SD267. (8.434) 3325952

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.82	53	0.77	83	0.69	115	0.23	151	0.37	185	0.39	223	0.05	261	0.03	317	0.02
25	0.02	54	0.15	84	0.19	116	0.96	152	0.31	187	0.10	225	0.04	263	0.16	319	0.32
26	0.12	55	1.10	85	0.51	117	0.10	153	1.28	189	0.21	226	0.26	265	0.19	323	0.36
27	1.48	56	0.13	87	0.29	118	0.06	155	18.10	190	0.84	227	0.21	267	0.11	325	0.03
28	9.59	57	2.77	89	9.11	119	0.22	156	0.33	191	0.53	228	0.36	269	0.13	327	0.45
29	2.40	58	4.71	90	1.98	121	2.72	157	0.35	192	0.85	229	0.08	271	0.06	328	0.32
30	0.15	59	21.36	91	15.37	122	0.12	159	0.93	193	3.38	230	0.82	273	0.04	329	0.27
31	2.43	60	0.55	92	0.58	123	0.21	160	0.84	195	25.92	231	0.03	277	0.10	331	0.29
32	0.50	61	12.37	93	1.27	125	0.35	161	0.34	196	1.55	232	0.39	279	0.54	345	0.02
33	0.51	62	0.43	94	0.58	127	1.99	163	0.15	197	0.48	233	1.22	280	0.95	347	0.77
36	0.32	63	1.32	95	0.82	128	0.15	165	0.10	198	0.25	235	0.19	281	0.05	348	0.05
37	0.15	64	1.89	96	3.08	129	0.91	167	0.21	199	0.35	237	0.16	283	0.19	349	0.24
38	0.22	65	12.19	97	0.25	131	0.73	169	0.18	200	0.51	239	0.21	285	0.04	351	4.73
39	4.37	66	0.54	98	0.33	132	1.80	170	0.31	201	0.22	241	0.13	287	0.65	352	0.43
40	1.22	67	2.34	99	0.17	133	1.22	171	1.11	202	3.46	243	0.32	288	0.36	357	1.83
41	15.76	69	21.30	101	1.85	134	0.10	172	2.86	203	0.89	245	0.30	289	0.04	369	0.15
42	2.93	70	0.43	102	0.14	135	0.27	173	1.83	205	0.10	246	0.10	291	0.02	371	0.53
43	100.00	71	0.36	103	0.94	136	0.84	175	10.35	207	0.12	247	0.15	293	0.29	389	0.25
44	5.54	72	0.16	104	0.17	137	0.18	176	0.52	209	0.25	249	0.24	300	0.03	405	0.03
45	1.49	73	0.58	105	0.19	139	0.45	177	0.64	210	0.94	250	0.02	301	0.02		
46	0.53	74	0.86	107	1.25	141	0.48	178	0.08	213	0.24	251	0.03	303	0.47		
47	1.34	75	0.51	108	0.23	142	0.13	179	0.19	215	4.86	253	14.90	304	0.02		
48	0.84	77	4.86	109	1.29	143	0.37	180	0.02	216	0.33	254	1.19	305	0.10		
49	0.70	78	0.24	110	0.08	145	0.37	181	0.13	217	0.24	255	0.12	307	0.42		
50	0.22	79	0.79	111	0.29	147	1.20	182	0.03	219	0.34	257	0.04	308	0.03		
51	6.62	80	0.06	113	3.69	148	0.15	183	0.06	221	0.41	259	0.49	309	0.09		
52	0.20	82	2.24	114	0.28	149	0.15	184	0.01	222	0.03	260	0.06	311	0.04		

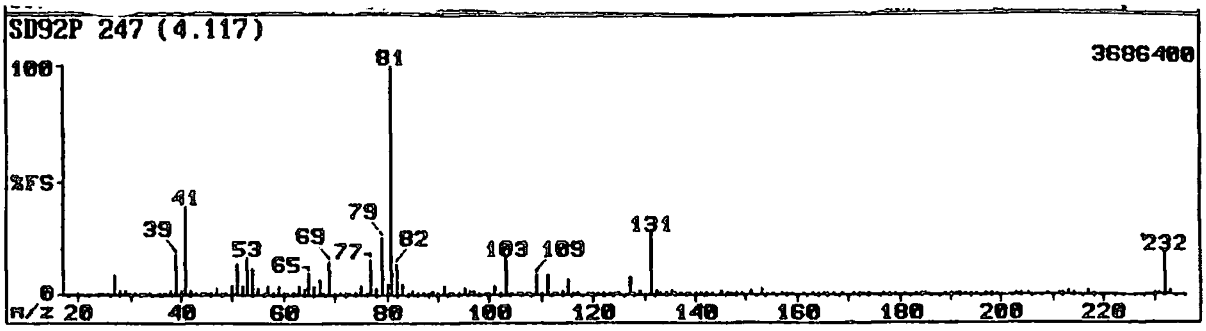
24. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclopentene (41)



SD93 152 (2.534) 3719168

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.03	66	13.88	107	1.05	152	0.09
24	0.02	67	100.00	108	0.47	153	0.85
25	0.06	68	15.97	109	8.81	154	0.08
26	1.27	69	20.59	110	1.09	155	0.03
27	7.82	70	1.98	111	0.25	156	0.04
28	1.40	71	2.34	112	0.18	157	0.42
29	0.67	72	0.37	113	2.97	159	8.92
31	1.90	73	0.22	114	4.13	160	0.64
32	0.40	74	0.65	115	19.05	163	0.36
33	0.87	75	7.27	116	3.36	164	0.07
36	0.03	76	1.01	117	73.57	165	0.09
37	1.31	77	22.47	118	4.74	166	0.02
38	5.04	78	1.82	119	1.44	167	0.24
39	31.72	79	1.45	120	0.21	168	0.01
40	5.62	80	0.50	121	0.98	169	0.11
41	26.98	81	1.87	122	0.10	171	0.33
42	1.56	82	5.34	123	0.06	172	0.04
43	0.10	83	3.69	125	0.50	177	2.26
44	0.31	84	1.34	127	12.44	178	0.16
45	0.52	85	1.23	128	1.82	179	2.06
46	0.33	86	0.22	129	1.67	180	0.16
47	1.82	87	0.65	130	0.45	183	0.09
48	0.08	88	4.13	131	0.44	185	0.05
49	0.36	89	3.77	132	0.49	189	0.06
50	4.98	90	1.16	133	2.26	190	0.02
51	22.47	91	1.04	134	0.20	195	0.07
52	3.91	92	0.18	135	0.92	197	1.06
53	13.22	93	0.67	136	0.07	198	0.14
54	0.75	95	12.22	137	0.50	199	6.47
55	0.15	96	5.40	138	0.11	200	0.44
56	0.85	97	35.24	139	1.46	203	0.31
57	7.71	98	3.96	140	0.14	204	0.01
58	1.01	99	1.21	141	0.04	215	0.01
59	5.45	100	0.47	143	0.10	216	0.05
60	1.13	101	7.16	145	1.72	217	1.19
61	1.54	102	1.02	146	0.23	218	40.97
62	3.47	103	1.34	147	0.55	219	2.67
63	8.48	104	0.12	148	0.11	220	0.10
64	3.41	105	0.14	149	0.20		
65	26.76	106	0.27	151	1.56		

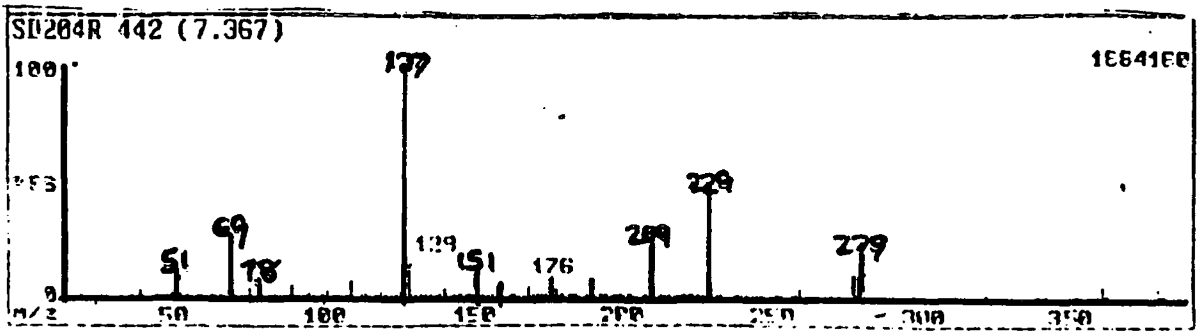
25. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene (42)



SD92P 247 (4.117) 3686400

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.02	67	6.94	110	1.41	161	0.04
24	0.01	68	0.47	111	8.56	163	0.29
25	0.02	69	14.44	112	1.01	164	0.03
26	0.90	70	1.11	113	1.31	165	0.34
27	8.56	71	1.22	114	1.78	166	0.02
28	1.89	72	0.41	115	7.11	167	0.46
29	2.19	73	0.63	116	1.20	169	0.19
30	0.04	74	0.72	117	0.18	171	0.56
31	0.77	75	4.00	119	0.67	172	0.27
32	0.19	76	0.85	120	0.27	173	1.24
33	0.53	77	15.89	121	1.36	174	0.11
34	0.01	78	3.19	122	0.43	177	0.92
36	0.01	79	25.00	123	1.14	178	0.08
37	0.31	80	4.64	124	0.19	179	0.02
38	1.53	81	100.00	125	0.33	181	0.04
39	17.11	82	14.00	127	8.11	183	0.09
40	2.17	83	5.19	128	0.95	184	0.08
41	39.11	84	0.93	129	2.03	185	0.20
42	1.81	85	2.19	131	27.11	189	0.20
43	0.17	86	0.31	132	2.06	190	0.05
44	0.15	87	0.21	133	1.41	191	0.43
45	0.27	88	1.23	134	0.15	192	0.04
46	0.25	89	1.59	135	1.92	193	1.20
47	2.56	90	0.97	136	0.12	194	0.11
48	0.07	91	3.67	137	0.19	195	0.03
49	0.16	92	0.41	138	0.08	197	0.88
50	3.50	93	0.40	139	0.77	198	0.06
51	13.78	94	0.22	140	0.94	199	0.02
52	4.28	95	3.31	141	1.34	203	0.06
53	16.33	96	1.72	142	0.22	204	0.94
54	11.78	97	1.69	143	0.46	205	0.05
55	3.11	98	0.34	145	1.92	209	0.03
56	0.43	99	0.62	146	0.11	211	0.16
57	3.67	100	0.28	147	0.92	212	0.13
58	0.46	101	3.83	148	0.08	213	1.78
59	4.19	102	0.67	149	0.13	214	0.15
60	0.32	103	16.22	151	1.51	217	1.67
61	0.43	104	0.95	153	2.44	218	0.11
62	0.81	105	0.06	154	0.15	230	0.02
63	3.44	106	0.13	155	0.01	231	0.53
64	2.94	107	0.53	157	0.21	232	18.78
65	10.11	108	0.60	158	0.37	233	1.48
66	3.94	109	9.22	159	0.24		

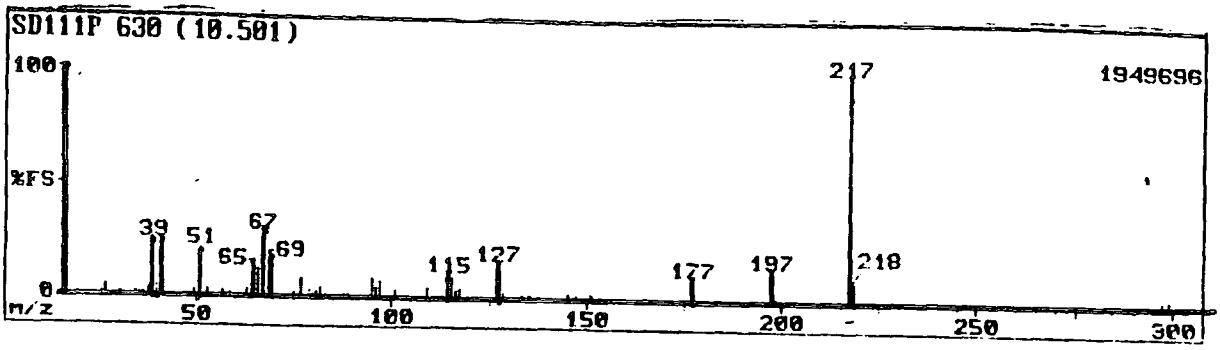
26. A mixture of 1,4-di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexa-1,3-diene (44) and 1,4-di-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexa-1,4-diene (43)



[illegible] 17.327 180111

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
28	0.02	57	2.00	87	0.44	115	0.46	143	0.28	174	0.05	207	0.50	241	0.25	292	0.05
29	0.23	58	0.12	88	1.03	116	0.05	144	0.20	176	9.67	208	0.20	242	0.03	295	0.06
30	0.85	59	0.26	89	5.27	117	0.11	145	2.60	177	4.18	209	23.91	244	0.02	297	0.12
31	0.22	60	0.11	90	0.18	118	0.12	146	0.38	178	2.76	210	2.83	245	0.11	301	3.12
32	0.22	61	0.14	91	1.14	119	1.52	147	0.25	179	0.09	211	0.20	246	0.03	303	[illegible]
33	0.52	62	2.64	92	0.16	120	1.03	148	0.04	180	0.06	213	0.17	247	0.10	311	4.26
34	0.33	63	2.31	93	0.33	121	0.73	149	0.19	181	0.15	214	0.04	250	0.04	315	0.02
35	0.26	64	1.15	94	0.35	122	0.22	150	0.15	182	0.36	215	0.39	251	0.10	321	0.21
36	2.82	65	0.84	95	1.52	123	0.15	151	13.10	183	0.21	216	0.04	252	0.05	322	0.03
37	0.39	66	0.10	96	0.63	124	0.11	152	0.63	184	0.03	218	0.07	253	0.02	327	0.04
38	0.57	69	27.23	97	0.14	125	1.60	153	0.13	187	0.08	219	0.50	257	0.40	340	0.02
39	2.76	70	0.83	98	0.88	126	2.96	155	0.05	188	0.19	220	0.22	258	0.09	341	0.22
40	0.33	71	0.17	99	1.06	127	100.00	156	0.27	189	7.93	221	0.14	259	4.08	342	0.06
41	0.17	72	0.84	100	0.52	128	11.47	157	0.40	190	1.32	222	0.01	260	0.02	359	0.11
43	2.84	73	0.07	101	3.19	129	0.71	158	4.46	191	1.06	223	0.02	261	0.12	361	4.48
44	0.14	74	0.60	102	0.41	130	0.29	159	4.13	192	0.10	225	0.03	265	0.04	362	0.40
45	0.17	75	1.53	103	0.21	131	0.61	160	0.48	193	0.06	226	0.10	269	0.03	363	0.02
46	0.26	76	0.07	104	0.05	132	0.47	161	0.12	194	0.26	227	0.44	270	0.03	378	0.37
47	2.26	77	0.37	105	0.19	133	0.68	162	0.07	195	1.26	228	0.20	271	0.16	380	2.46
48	2.01	78	9.16	106	0.22	134	0.09	163	1.09	196	0.10	229	47.61	272	0.05	381	2.26
49	0.27	79	5.27	107	1.36	135	0.03	164	0.21	197	0.35	230	3.37	277	0.42	382	0.32
50	2.38	80	0.45	108	0.69	136	0.04	165	0.22	198	0.05	231	0.26	278	0.72		
51	12.29	81	0.82	109	6.60	137	0.50	167	0.08	199	0.04	232	0.10	279	38.07		
52	1.24	82	2.01	110	0.62	138	0.96	169	4.18	200	0.30	233	0.14	280	1.94		
53	0.76	83	1.26	111	0.11	139	1.21	170	0.73	201	0.23	237	0.03	281	0.14		
54	0.80	84	0.16	112	0.38	140	3.70	171	1.47	202	0.19	238	0.24	287	0.04		
55	2.82	85	0.18	113	1.78	141	1.45	172	0.18	203	0.07	239	1.29	290	0.03		
56	0.26	86	0.18	114	2.04	142	0.14	173	0.02	205	0.08	240	0.33	291	0.30		

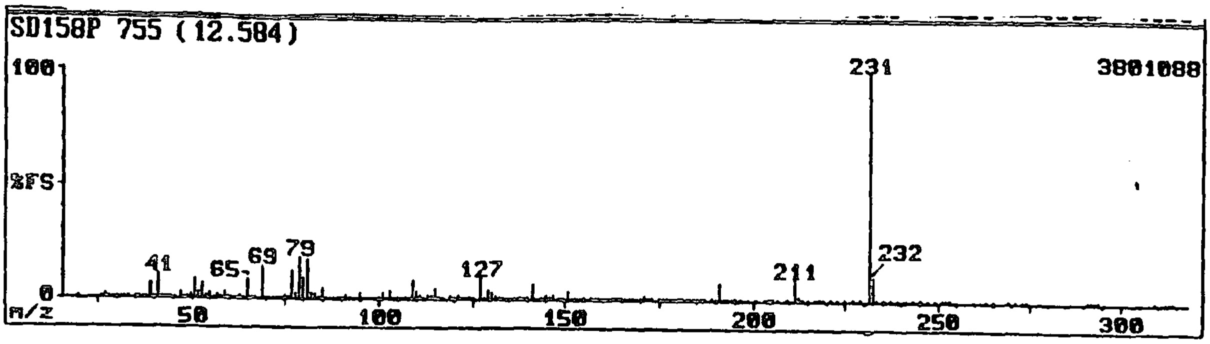
27. 1-(1,1,2,3,3,3-Hexafluoropropyl)-1,2-dibromocyclopentane (45)



SD111P 630 (10.501) 1949696

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.22	46	0.21	67	20.99	88	1.88	113	1.47	142	0.05	170	0.31	199	1.31	247	0.03
24	0.19	47	1.30	68	1.27	89	2.42	115	11.76	145	2.98	171	1.05	200	0.05	249	0.03
25	0.31	48	0.03	69	17.02	90	0.82	115	9.02	146	0.66	173	0.16	201	0.08	251	0.07
26	1.51	49	0.30	70	1.09	91	0.45	116	4.31	147	1.63	175	0.25	203	0.03	253	0.03
27	5.15	50	2.70	71	1.12	92	0.12	117	5.15	148	0.31	177	10.56	205	0.04	257	0.09
28	1.40	51	11.03	72	0.11	93	0.74	119	1.43	149	0.09	178	1.08	207	0.09	259	0.14
29	0.54	52	1.62	73	0.15	94	0.14	120	0.19	151	2.46	179	0.37	209	0.04	263	0.03
31	2.20	53	3.03	74	0.42	95	0.46	121	1.42	153	1.50	180	0.06	211	0.04	271	0.02
32	0.51	54	0.24	75	2.14	96	4.99	122	0.30	155	0.80	181	0.14	213	0.04	277	0.35
33	0.69	55	0.13	76	0.73	97	0.14	123	0.05	157	1.37	182	0.07	215	0.16	279	0.95
35	1.69	56	0.29	77	0.61	98	1.01	125	0.37	158	0.19	183	0.05	217	100.00	280	0.04
36	2.11	57	2.47	78	0.93	99	0.47	127	16.39	159	1.46	185	0.05	218	9.14	295	0.14
37	1.00	58	0.24	79	3.41	101	3.94	128	2.64	160	0.17	187	0.20	219	0.50	297	3.94
38	4.04	59	2.47	80	2.15	102	0.77	129	1.27	161	0.10	189	0.30	223	0.05	298	0.19
39	25.42	60	0.22	81	3.34	103	1.16	131	1.04	163	0.33	190	0.09	225	0.05	299	3.60
40	4.88	61	0.46	82	4.46	104	0.07	133	2.18	164	0.08	191	0.13	227	0.06	300	0.20
41	25.42	62	1.27	83	2.09	105	0.10	135	1.94	165	0.19	192	0.01	229	0.04		
42	1.44	63	3.62	84	0.92	107	1.27	137	0.54	166	0.08	193	0.08	233	0.18		
43	0.24	64	0.93	85	0.54	109	5.03	139	0.96	167	0.59	195	1.00	235	0.20		
44	0.82	65	13.34	86	0.11	110	0.49	140	0.10	168	0.18	197	14.50	237	0.27		
45	0.46	66	12.34	87	0.34	111	0.29	141	0.05	169	0.51	198	1.56	239	0.09		

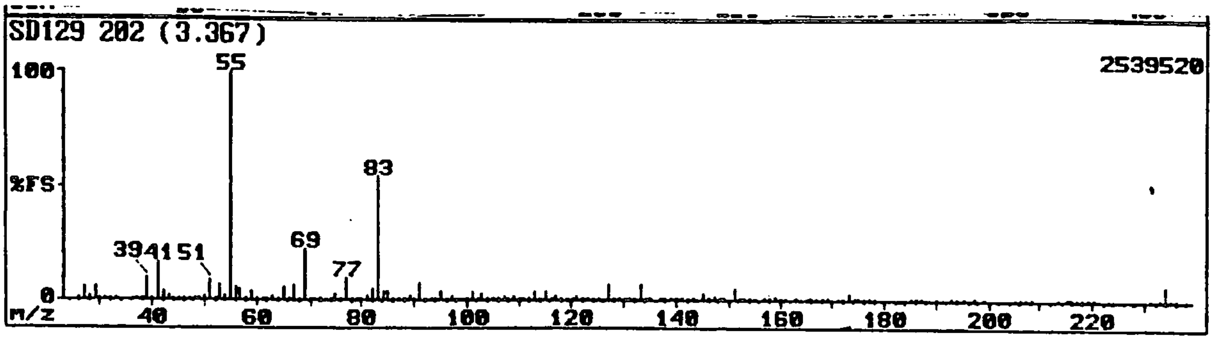
28. 1-(1,1,2,3,3,3-Hexafluoropropyl)-1,2-dibromocyclohexane (46)



SD158P 755 (12.584) 3801088

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.00	50	2.02	75	2.37	99	0.48	124	0.11	149	0.51	177	0.43	207	0.11	249	0.05
26	0.16	51	0.73	76	0.40	100	0.20	125	0.29	151	4.23	178	0.04	209	0.64	251	0.10
27	1.55	52	2.64	77	12.61	101	3.31	127	9.38	152	0.32	179	0.09	211	9.59	252	0.01
28	0.33	53	6.73	78	3.29	102	0.95	128	1.10	153	0.48	180	0.05	212	1.50	253	0.05
29	0.59	54	2.13	79	18.32	103	3.64	129	4.09	155	0.39	181	0.40	213	0.21	263	0.01
30	0.02	55	2.45	80	9.38	104	0.37	130	2.75	157	0.49	182	0.04	215	0.03	265	0.01
31	0.15	56	0.24	81	17.89	105	0.27	131	1.94	158	0.15	183	0.61	217	0.21	269	0.04
32	0.04	57	1.60	82	3.15	106	0.32	132	0.36	159	1.29	184	0.06	218	0.02	271	0.12
33	0.14	58	0.12	83	2.64	107	1.23	133	0.94	160	0.18	185	1.02	219	0.04	273	0.09
35	0.01	59	3.15	84	0.55	108	0.43	134	0.19	161	0.61	186	0.05	221	0.09	274	0.01
36	0.04	60	0.15	85	5.15	109	0.94	135	0.50	162	0.12	187	0.23	223	0.13	291	1.20
37	0.09	61	0.20	86	0.34	110	3.08	136	0.04	163	0.69	189	0.62	225	0.09	292	0.06
38	0.54	62	0.37	87	0.16	111	2.16	137	0.27	164	0.05	190	0.14	227	0.03	293	1.14
39	6.79	63	1.70	88	0.90	112	0.36	138	0.07	165	1.31	191	7.33	229	0.63	294	0.09
40	0.79	64	1.45	89	1.23	113	1.58	139	0.01	166	0.10	192	0.74	231	100.00	309	0.03
41	10.88	65	9.16	90	0.49	114	1.60	140	0.30	167	0.61	193	0.16	232	10.70	311	0.05
42	0.57	66	1.33	91	1.72	115	4.00	141	6.90	168	0.13	194	0.02	233	0.57	312	0.04
43	0.09	67	1.10	92	0.23	116	0.50	142	1.29	169	0.58	195	0.07	235	0.13	313	0.04
44	0.08	69	14.90	93	0.54	117	0.46	143	0.63	170	0.37	197	0.36	237	0.10	314	0.05
45	0.13	70	0.50	94	0.14	119	1.75	144	0.08	171	2.34	199	0.36	239	0.06		
46	0.10	71	0.51	95	2.75	120	0.40	145	2.21	172	0.25	201	0.23	241	0.06		
47	2.00	72	0.14	96	1.04	121	2.05	146	0.16	173	0.27	203	0.55	243	0.06		
48	0.07	73	0.59	97	1.43	122	0.54	147	1.97	175	0.11	204	0.17	245	0.03		
49	0.08	74	0.39	98	0.69	123	0.59	148	0.14	176	0.04	205	0.23	247	0.03		

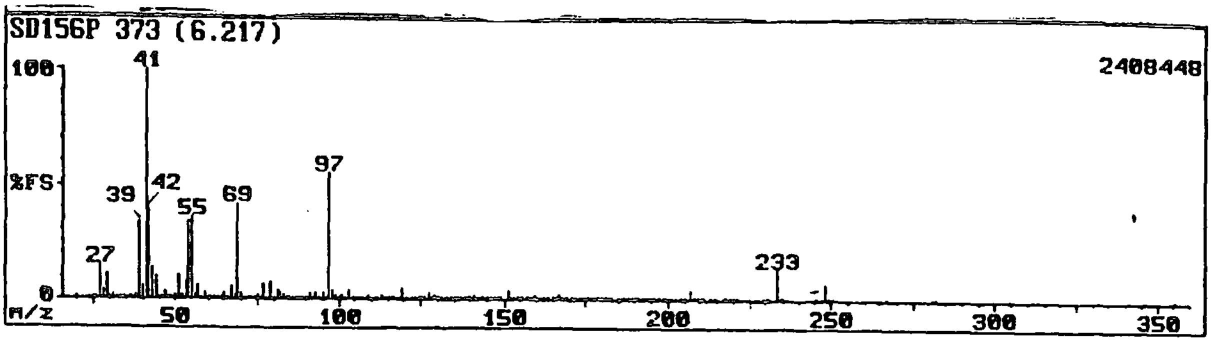
29. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclopentene oxide (47)



SD129 202 (3.367) 2539520

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.94	48	0.04	67	6.90	86	0.30	105	1.11	124	0.05	146	0.26	169	0.06	206	0.15
27	5.09	49	0.29	68	0.87	87	0.33	106	0.32	125	0.30	147	1.72	171	0.16	207	0.05
28	2.20	50	1.97	69	22.74	88	1.11	107	1.70	127	7.22	148	0.13	172	1.32	208	0.01
29	5.40	51	9.19	70	0.81	89	2.31	108	0.94	128	0.54	149	0.09	173	2.44	213	0.03
30	0.15	52	1.20	71	1.10	90	1.07	109	2.31	129	0.80	151	5.80	174	0.19	215	0.68
31	0.67	53	6.65	72	0.20	91	7.62	110	0.13	130	0.57	152	0.34	175	0.67	216	0.07
32	0.12	54	2.21	73	0.51	92	0.39	111	0.07	131	1.27	153	0.74	176	0.04	217	0.39
33	0.18	55	100.00	74	0.19	93	1.08	112	0.30	132	0.39	154	0.07	177	0.75	218	0.03
37	0.25	56	6.01	75	3.10	94	0.29	113	4.11	133	6.49	155	0.32	178	0.06	219	0.29
38	0.96	57	4.40	76	0.96	95	3.47	114	0.06	134	0.44	157	0.69	185	0.91	220	0.02
39	10.12	58	0.44	77	9.64	96	0.74	115	4.23	135	0.31	158	0.16	186	0.43	231	0.10
40	1.20	59	4.31	78	0.51	97	2.14	116	0.53	137	0.30	159	1.48	187	0.31	233	0.38
41	16.45	60	0.32	79	0.18	98	0.28	117	1.02	138	0.06	160	0.29	190	0.03	234	6.57
42	3.43	61	0.27	80	0.12	99	0.50	118	0.20	139	1.34	161	0.08	193	0.08	235	0.49
43	2.40	62	0.57	81	1.46	100	0.43	119	1.02	140	0.13	163	0.14	194	0.16	236	0.03
44	1.05	63	1.52	82	5.16	101	3.71	120	0.15	141	0.51	165	0.46	195	0.11		
45	0.37	64	0.96	83	54.04	102	0.66	121	1.06	142	0.03	166	0.05	197	0.23		
46	0.16	65	5.60	84	3.91	103	3.39	122	0.19	143	0.06	167	0.67	199	0.12		
47	0.89	66	0.83	85	3.55	104	0.79	123	0.43	145	3.15	168	0.05	205	0.10		

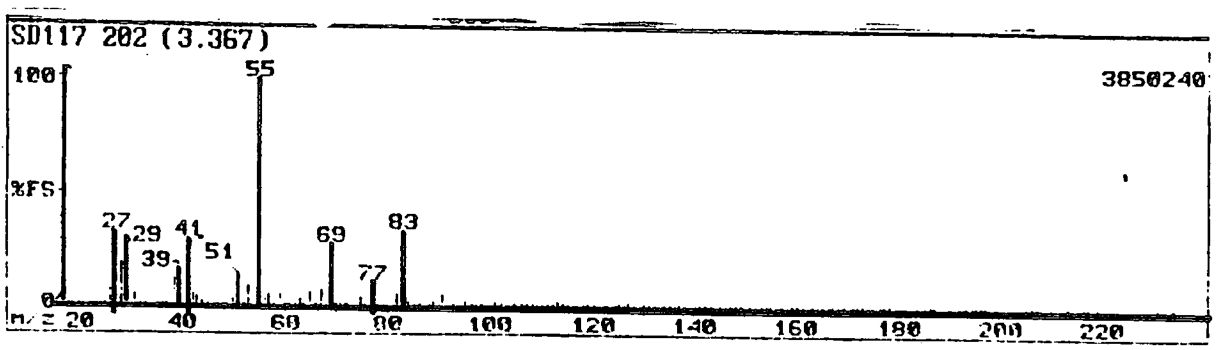
30. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene oxide (48)



SD156P 373 (6.217) 2408448

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.03	47	2.63	70	2.98	93	3.23	116	0.15	139	1.35	165	0.66	190	0.05	220	0.07
24	0.01	48	0.17	71	1.24	94	0.28	117	1.40	140	0.16	166	0.05	191	0.36	221	0.15
25	0.05	49	0.40	72	0.50	95	2.51	118	0.19	141	2.02	167	1.70	192	0.04	227	0.01
26	1.25	50	1.07	73	1.11	96	0.61	119	5.06	142	0.19	168	0.12	193	0.07	229	0.09
27	14.63	51	11.05	74	0.10	97	55.10	120	0.34	143	0.09	169	0.16	194	0.34	230	0.03
28	3.70	52	1.90	75	1.66	98	4.04	121	0.95	144	0.04	171	0.34	195	0.03	231	0.35
29	10.33	53	7.07	76	0.40	99	1.70	122	0.12	145	1.17	172	0.42	197	0.05	233	13.44
30	0.26	54	34.01	77	7.23	100	0.33	123	0.86	146	0.12	173	0.49	199	0.20	234	1.11
31	1.60	55	36.22	78	0.73	101	1.97	124	0.07	147	0.01	174	0.35	200	0.16	235	0.07
32	0.30	56	2.36	79	0.12	102	0.35	125	0.17	148	0.06	175	0.06	201	0.17	245	0.02
33	0.58	57	3.53	80	0.02	103	4.12	126	0.24	149	0.12	176	0.02	202	0.02	247	0.41
34	0.06	58	0.38	81	3.57	104	0.38	127	2.53	151	3.53	177	0.15	204	0.06	248	6.59
35	0.03	59	2.55	82	2.67	105	0.45	128	0.36	152	0.16	178	0.02	205	0.07	249	0.66
37	0.51	60	0.16	83	2.33	106	0.21	129	1.98	153	0.20	179	0.16	207	3.57	250	0.04
38	2.35	61	0.24	84	0.42	107	0.34	130	0.37	154	0.15	180	0.05	208	0.23	267	0.02
39	32.02	62	0.30	85	0.54	108	0.41	131	0.95	155	0.14	181	0.36	209	0.09	281	0.06
40	3.95	63	1.12	86	0.07	109	2.21	132	0.27	157	0.33	182	0.03	210	0.01	282	0.02
41	100.00	64	0.92	87	0.16	110	0.35	133	0.58	158	0.05	183	0.00	211	0.07	355	0.02
42	33.29	65	2.76	88	0.60	111	0.33	134	0.06	159	2.10	185	1.19	213	0.10		
43	13.61	66	0.05	89	1.23	112	0.16	135	0.28	160	0.18	186	0.13	214	0.01		
44	9.95	67	6.21	90	0.92	113	1.71	136	0.03	161	0.57	187	1.45	217	0.02		
45	1.01	68	1.97	91	3.36	114	0.28	137	0.19	162	0.05	188	0.10	218	0.05		
46	0.43	69	41.50	92	0.17	115	1.38	138	0.05	163	0.17	189	0.50	219	0.00		

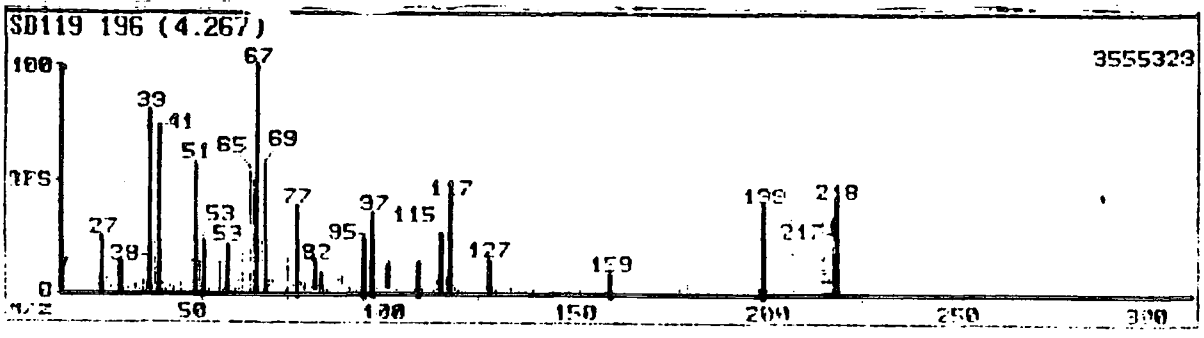
31. Epoxidation of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentene (41) using M.C.P.B.A. in an aqueous sytem.



SD117 202 (3.367) 3850240

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.40	67	7.23	116	0.22	158	0.07
24	0.35	69	26.91	117	0.47	159	0.05
25	0.96	70	0.66	118	0.12	160	0.05
26	7.23	71	1.37	119	0.31	161	0.01
27	32.34	72	0.12	120	0.11	163	0.03
28	10.30	73	0.52	121	0.42	164	0.02
29	25.96	74	0.10	122	0.06	165	0.10
31	5.08	75	3.91	123	0.10	166	0.03
32	1.25	76	0.27	124	0.02	167	0.14
33	0.80	77	10.53	125	0.10	168	0.01
35	0.09	78	0.35	126	0.22	169	0.01
36	0.24	79	0.17	127	1.62	171	0.05
37	0.67	82	4.92	128	0.14	172	0.25
38	11.81	83	32.77	129	0.08	173	0.42
39	15.85	84	1.89	130	0.25	174	0.07
40	0.30	85	2.21	131	0.38	175	0.12
41	29.36	86	0.16	132	0.38	176	0.03
42	5.32	88	0.47	133	1.24	177	0.16
43	3.70	89	2.07	134	0.10	178	0.02
44	1.99	91	4.76	135	0.07	185	0.19
45	0.45	93	0.98	136	0.02	186	0.10
46	0.18	95	2.34	137	0.09	187	0.06
47	1.26	96	0.32	138	0.05	193	0.02
48	0.06	97	1.02	139	0.32	194	0.02
49	0.57	98	0.16	140	0.06	195	0.05
50	2.87	99	0.27	141	0.10	196	0.02
51	11.70	101	2.21	142	0.01	197	0.06
52	1.28	102	0.51	143	0.03	199	0.02
53	8.94	103	1.12	144	0.09	205	0.03
55	100.00	105	0.15	145	0.67	206	0.02
56	4.34	105	0.32	146	0.10	207	0.01
57	4.79	106	0.20	147	0.33	213	0.01
58	0.32	107	0.34	148	0.03	215	0.11
59	4.76	108	0.45	149	0.02	217	0.06
60	0.28	109	0.59	151	1.24	217	0.09
61	0.29	110	0.05	152	0.07	219	0.07
62	0.62	111	0.07	153	0.13	231	0.04
63	3.01	112	0.40	154	0.01	234	0.71
64	1.24	113	1.49	155	0.06	234	0.54
65	6.25	114	0.50	156	0.02		
66	0.76	115	1.12	157	0.15		

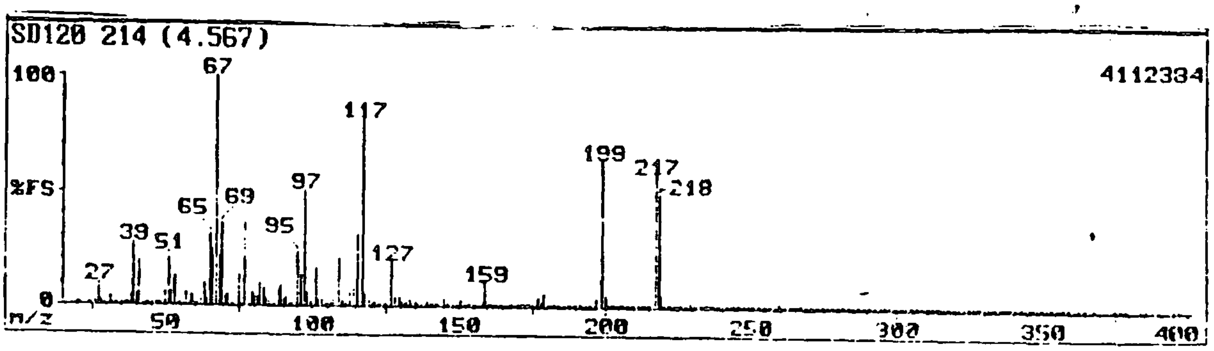
32. Failed epoxidation of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentene (41) using sodium hypochlorite dissolved in dioxane.



SD119

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.28	80	4.26	140	0.56	196	0.92
21	0.04	81	3.74	141	0.71	197	4.01
24	0.16	82	9.66	142	0.31	199	64.14
25	0.38	83	8.17	143	0.38	200	5.25
26	2.37	84	2.51	145	3.86	201	0.44
27	9.26	85	2.42	146	1.09	202	0.15
28	1.82	86	0.49	147	1.38	203	0.67
29	0.77	87	0.87	148	0.68	204	0.16
31	4.23	88	6.47	149	0.67	205	0.29
32	0.84	89	8.57	151	2.96	206	0.14
33	0.89	90	3.29	152	0.49	207	0.38
35	0.31	91	3.96	153	1.38	208	0.18
36	0.31	92	0.62	154	0.36	209	1.09
37	1.22	93	1.87	155	0.70	210	0.26
38	3.44	95	23.71	156	0.62	211	0.51
39	27.49	96	13.84	157	1.11	212	0.14
40	4.96	97	50.60	158	1.50	213	0.20
41	19.62	98	5.98	159	11.06	214	0.15
42	1.18	99	2.14	160	1.29	215	0.31
43	0.32	101	16.73	161	0.36	217	57.77
44	0.80	102	2.84	162	0.19	218	49.80
45	0.63	103	2.86	163	0.82	219	4.68
47	0.78	104	0.63	164	0.34	220	0.35
47	0.82	105	1.20	165	0.66	221	0.81
48	0.08	106	1.01	166	0.40		
50	5.43	107	2.76	167	0.83		
51	23.21	109	20.32	168	0.42		
52	3.68	110	2.29	169	0.58		
53	12.15	111	0.90	170	0.34		
54	0.75	113	7.37	171	0.89		
55	0.45	114	10.66	172	0.27		
56	0.62	115	30.68	173	0.29		
57	5.88	117	81.27	174	0.17		
58	0.42	118	5.10	175	0.21		
59	4.96	119	2.79	176	0.44		
60	0.46	120	0.85	177	3.54		
61	1.11	121	1.72	178	1.64		
62	2.71	122	0.35	179	6.10		
63	9.26	123	0.40	180	0.98		
64	3.24	124	0.22	181	0.34		
65	30.68	125	0.90	182	0.28		
66	24.60	127	19.52	183	0.54		
67	100.00	128	3.74	184	0.24		
68	21.02	129	3.46	185	0.44		
69	36.25	130	1.62	186	0.16		
70	3.78	131	1.13	187	0.19		
71	4.58	132	1.59	188	0.12		
72	0.88	133	3.31	189	0.42		
73	0.60	134	0.73	190	0.20		
75	13.15	135	1.56	191	0.46		
76	0.83	136	0.51	192	0.19		
77	35.46	137	0.96	193	0.21		
78	4.43	138	0.30	194	0.14		
79	5.00	139	2.13	195	0.51		

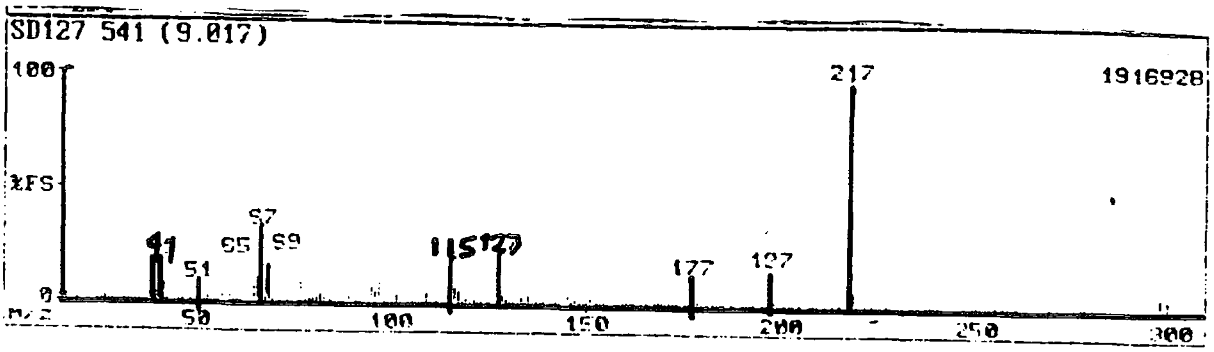
33. Failed epoxidation of 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentene (41) using sodium hypochlorite dissolved in anhydrous pyridine.



SD120 214 (4.567) 4112384

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.28	80	4.26	140	0.56	196	0.92
21	0.04	81	3.74	141	0.71	197	4.01
24	0.16	82	9.66	142	0.31	199	64.14
25	0.38	83	8.17	143	0.38	200	5.25
26	2.37	84	2.51	145	3.86	201	0.44
27	9.26	85	2.42	146	1.09	202	0.15
28	1.82	86	0.49	147	1.38	203	0.67
29	0.77	87	0.87	148	0.68	204	0.16
31	4.23	88	6.47	149	0.67	205	0.29
32	0.84	89	8.57	151	2.96	206	0.14
33	0.89	90	3.29	152	0.49	207	0.38
35	0.31	91	3.96	153	1.38	208	0.18
36	0.31	92	0.62	154	0.36	209	1.09
37	1.22	93	1.87	155	0.70	210	0.26
38	3.44	95	23.71	156	0.62	211	0.51
39	27.49	96	13.84	157	1.11	212	0.14
40	4.96	97	50.60	158	1.50	213	0.20
41	19.62	98	5.98	159	11.06	214	0.15
42	1.18	99	2.14	160	1.29	215	0.31
43	0.32	101	16.73	161	0.36	217	57.77
44	0.80	102	2.84	162	0.19	218	49.80
45	0.63	103	2.86	163	0.82	219	4.68
47	0.78	104	0.63	164	0.34	220	0.35
47	0.82	105	1.20	165	0.66	221	0.21
48	0.08	106	1.01	166	0.40		
50	5.43	107	2.76	167	0.83		
51	23.21	109	20.32	168	0.42		
52	5.68	110	2.29	169	0.58		
53	12.15	111	0.90	170	0.34		
54	0.75	113	7.37	171	0.89		
55	0.45	114	10.66	172	0.27		
56	0.62	115	30.68	173	0.29		
57	5.88	117	81.27	174	0.17		
58	0.42	118	5.10	175	0.21		
59	4.96	119	2.79	176	0.44		
60	0.46	120	0.85	177	3.54		
61	1.11	121	1.72	178	1.64		
62	2.71	122	0.35	179	6.10		
63	9.26	123	0.40	180	0.98		
64	3.24	124	0.22	181	0.34		
65	30.68	125	0.90	182	0.28		
66	24.60	127	19.52	183	0.54		
67	100.00	128	3.74	184	0.24		
68	21.02	129	3.46	185	0.44		
69	36.25	130	1.62	186	0.16		
70	3.78	131	1.13	187	0.19		
71	4.58	132	1.59	188	0.12		
72	0.88	133	3.31	189	0.42		
73	0.60	134	0.73	190	0.20		
75	13.15	135	1.56	191	0.46		
76	0.83	136	0.51	192	0.19		
77	35.46	137	0.96	193	0.21		
78	4.43	138	0.30	194	0.14		
[illegible]	[illegible]	139	2.19	195	0.51		

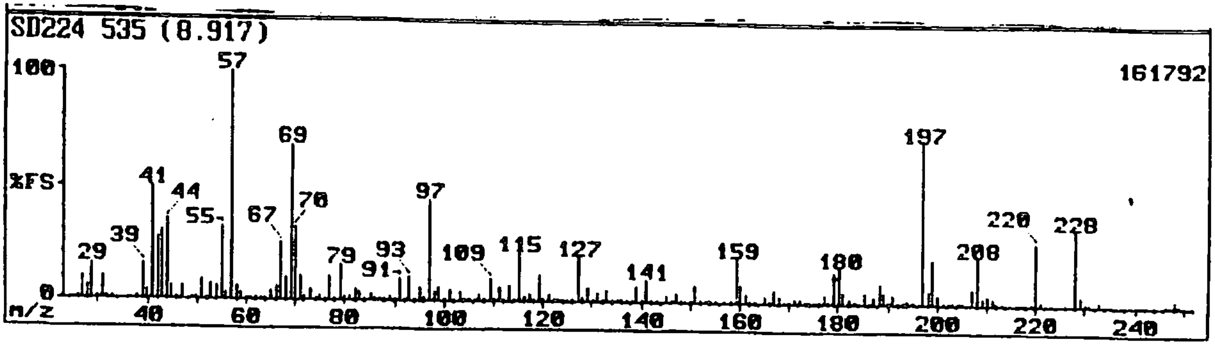
34. Attempted bromohydrin addition to 1-(1,1,2,3,3,3-hexafluoropropyl)-cyclopentene (41).



SD127 541 (9.017) 1916928

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.01	49	0.14	74	0.28	99	0.07	124	0.02	150	0.09	175	0.25	200	0.05	240	0.01
25	0.02	50	1.95	75	3.39	100	0.23	125	0.44	151	2.52	176	0.19	201	0.13	247	0.03
26	0.36	51	10.10	76	0.43	101	0.01	127	23.50	152	0.23	177	13.46	202	0.01	249	0.08
27	2.30	52	1.34	77	0.71	102	0.07	128	4.01	153	2.24	178	1.58	203	0.03	250	0.02
28	0.91	53	2.71	78	0.80	103	2.06	129	1.76	154	0.15	179	0.20	205	0.05	251	0.03
29	0.20	54	0.10	79	1.75	104	0.21	130	0.17	155	0.72	180	0.04	207	0.13	253	0.05
30	0.01	55	0.10	80	2.14	105	0.33	131	1.15	156	0.08	181	0.13	208	0.02	255	0.01
31	0.59	56	0.34	81	2.20	106	0.53	132	0.35	157	1.30	182	0.05	209	0.07	257	0.15
32	0.25	57	2.56	82	3.90	107	1.51	133	2.94	158	0.23	183	0.10	211	0.06	258	0.02
33	0.40	58	0.55	83	2.24	108	0.02	134	0.27	159	1.00	184	0.03	213	0.08	259	0.14
34	0.01	59	2.72	84	0.73	109	4.91	135	3.74	160	0.13	185	0.14	215	0.14	260	0.03
35	0.06	60	0.23	85	0.62	110	0.42	136	0.26	161	0.09	186	0.03	217	100.00	269	0.03
36	0.33	61	0.43	86	0.12	111	0.40	137	0.55	162	0.05	187	0.26	218	7.37	271	0.03
37	0.62	62	1.15	87	0.40	112	0.16	138	0.13	163	0.20	188	0.06	219	0.39	275	0.03
38	2.03	63	3.31	88	2.26	113	2.74	139	0.04	164	0.08	189	0.48	221	0.01	277	0.08
39	10.38	64	1.24	89	2.58	114	3.63	140	0.08	165	0.17	190	0.14	223	0.03	278	0.07
40	3.42	65	12.34	90	0.83	115	21.79	141	0.05	166	0.12	191	0.17	225	0.04	279	0.05
41	19.87	66	10.84	91	0.41	116	7.00	142	0.03	167	0.71	192	0.04	227	0.04	280	0.00
42	1.19	67	33.12	92	0.12	117	5.98	143	0.16	168	0.20	193	0.11	229	0.03	295	0.25
43	0.10	68	2.31	93	0.83	118	0.47	144	0.24	169	0.52	194	0.06	231	0.05	296	0.12
44	0.20	69	14.32	94	0.26	119	2.16	145	3.50	170	0.36	195	1.42	233	0.22	297	6.09
45	0.27	70	0.97	95	0.01	120	0.97	146	0.76	171	1.44	196	0.06	235	0.25	298	0.57
46	0.15	71	1.00	96	4.06	121	2.15	147	2.07	172	0.11	197	17.74	237	0.26	299	5.29
47	1.27	72	0.19	97	0.65	122	0.76	148	0.43	173	0.17	198	2.22	238	0.01	300	0.45
48	0.06	73	0.15	98	1.36	123	0.07	149	0.10	174	0.03	199	0.56	239	0.14	301	0.01

35. 1-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexane-1,2-diol (49)

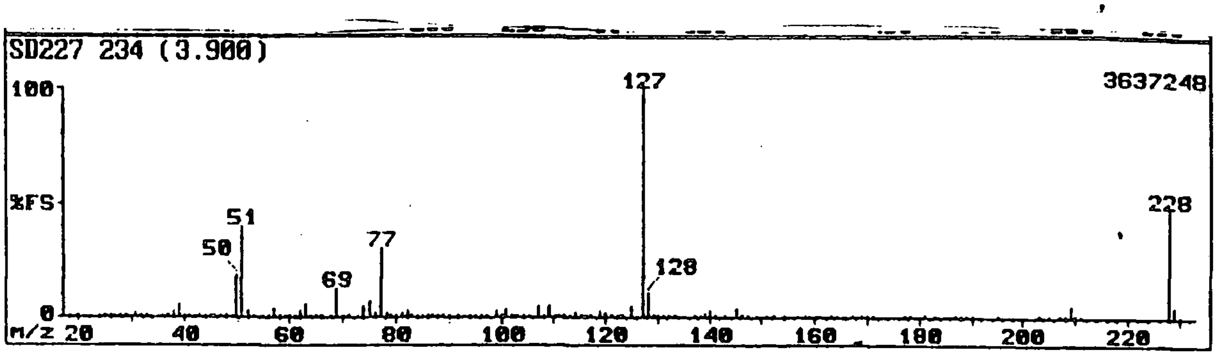


SD224 535 (8.917)

161792

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.74	53	6.45	75	2.31	97	44.30	119	11.71	141	9.73	166	0.78	189	4.75	213	1.14
27	10.05	54	5.34	76	0.51	98	3.76	120	1.12	142	0.96	167	5.66	190	0.72	219	0.80
28	5.66	55	32.20	77	10.76	99	5.74	121	2.57	143	0.96	168	2.09	191	3.40	220	27.22
29	15.02	56	3.16	78	1.33	100	0.80	122	0.85	145	2.57	169	1.11	192	0.40	221	2.21
30	1.45	57	100.00	79	15.51	101	4.67	123	0.86	146	0.43	170	1.45	193	0.35	226	0.33
31	9.45	58	6.17	80	2.12	102	0.67	124	0.21	147	4.31	171	1.60	194	1.64	228	33.23
32	1.00	59	3.32	81	2.31	103	3.56	125	1.34	148	0.29	172	1.50	195	1.07	229	3.64
33	0.60	60	0.84	82	4.55	104	0.56	126	0.76	149	1.42	173	0.75	197	70.09	230	0.34
38	0.78	61	0.67	83	3.96	105	0.67	127	19.46	150	0.06	174	0.90	198	6.17	231	1.10
39	15.51	62	0.42	84	0.98	106	0.06	128	2.10	151	7.59	175	0.41	199	19.46	233	2.02
40	3.56	63	1.35	85	3.13	107	3.09	129	5.54	152	0.59	176	0.93	200	3.52	246	0.66
41	49.37	64	0.79	86	0.86	108	1.89	130	0.70	153	0.55	177	4.15	201	0.40	247	0.65
42	27.06	65	3.08	87	0.61	109	10.13	131	3.52	154	0.54	178	1.06	202	1.32	248	2.57
43	29.75	66	6.17	88	0.61	110	1.12	132	0.95	155	1.26	179	13.29	203	0.30	249	0.23
44	34.49	67	25.47	89	1.76	111	5.74	133	4.63	157	1.44	180	15.02	204	0.25		
45	6.17	68	9.49	90	0.63	112	0.91	134	0.49	158	0.72	181	5.26	205	0.30		
46	0.53	69	67.72	91	9.73	113	6.84	135	1.23	159	19.15	182	2.20	207	6.41		
47	5.05	70	32.44	92	0.64	114	0.83	136	0.59	160	7.07	183	1.22	208	20.09		
49	1.32	71	10.44	93	10.60	115	21.20	137	1.11	161	3.64	185	4.59	209	2.97		
50	0.95	72	2.07	94	1.15	116	1.71	138	0.14	162	0.56	186	0.33	210	3.96		
51	0.47	73	3.02	95	5.70	117	2.61	139	6.76	163	0.52	187	2.53	211	2.69		
52	1.00	74	0.45	96	1.46	118	0.38	140	1.31	165	2.61	188	0.54	212	0.25		

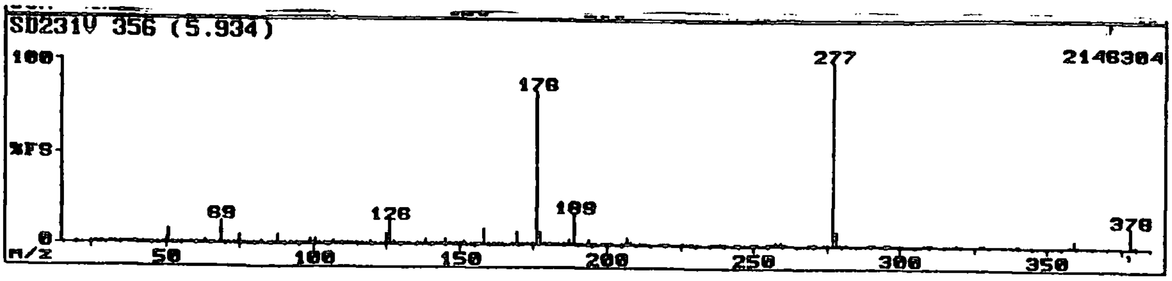
36. 1-(1,1,2,3,3,3-Hexafluoropropyl)-benzene(50)



SD227 234 (3.900) 3637248

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.01	43	0.07	60	0.16	78	2.80	95	0.64	113	0.91	132	0.29	158	1.18	189	0.70
24	0.01	44	0.25	61	1.30	79	0.29	96	0.68	114	1.06	133	0.03	159	0.47	190	0.12
25	0.04	45	0.16	62	3.07	80	0.52	97	0.08	115	0.15	137	0.39	160	0.07	195	0.02
26	0.42	46	0.04	63	5.00	81	2.14	99	2.51	116	0.09	138	1.09	161	0.05	203	0.02
27	1.33	47	0.03	64	0.99	82	2.48	100	1.06	117	0.17	139	1.77	163	0.08	205	0.02
28	0.27	48	0.06	65	0.12	83	1.30	101	4.28	119	3.01	140	3.32	164	0.02	207	0.31
29	0.01	49	1.09	66	0.02	84	0.12	102	0.34	120	2.25	141	0.29	167	0.06	208	0.11
31	1.94	50	18.02	68	0.63	85	0.31	103	0.07	121	0.63	143	0.16	169	1.37	209	4.45
32	0.40	51	39.64	69	12.16	86	0.42	104	0.15	122	0.04	145	3.49	170	0.16	210	0.41
33	0.16	52	2.65	70	0.93	87	0.54	105	0.37	123	0.32	146	0.36	171	0.06	211	0.02
36	0.04	53	0.10	71	0.07	88	1.86	107	4.76	125	4.76	147	0.04	177	0.54	228	47.75
37	0.07	55	0.16	73	0.74	89	1.09	108	0.96	127	100.00	149	0.11	178	0.05	229	4.73
38	2.51	56	0.65	74	4.65	90	0.20	109	5.10	128	10.70	151	0.51	181	0.02	230	0.23
39	5.46	57	3.66	75	6.95	92	0.26	110	0.42	129	0.53	152	0.03	183	0.01		
40	0.26	58	0.10	76	2.11	93	0.39	111	0.15	130	0.08	154	0.04	187	0.49		
41	0.03	59	0.36	77	29.73	94	0.52	112	0.60	131	0.17	157	0.31	188	0.06		

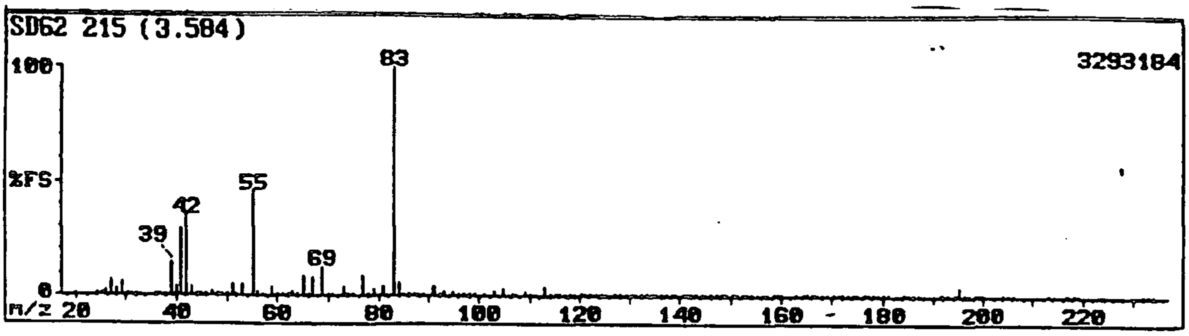
37. 1,4-di-(1,1,2,3,3,3-Hexafluoropropyl)-benzene (51)



SD231V 356 (5.934) 2146304

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.04	85	0.21	143	0.58	205	0.22
25	0.01	86	0.33	144	0.83	206	0.12
26	0.06	87	1.20	145	2.89	207	3.48
27	0.15	88	4.77	146	0.22	208	2.41
28	1.22	89	0.58	147	0.04	209	0.25
29	0.02	90	0.05	148	0.05	211	0.06
31	0.93	92	0.21	149	0.53	212	0.02
32	0.58	93	0.72	150	0.38	213	0.05
33	0.08	94	0.72	151	2.36	218	0.25
35	0.05	95	0.47	152	0.23	219	0.37
36	0.27	96	0.08	154	0.02	220	0.16
37	0.15	97	0.08	155	0.27	221	0.14
38	0.66	98	0.23	156	0.91	225	0.12
39	0.81	99	2.65	157	0.55	226	1.32
40	0.07	100	1.07	158	8.44	227	0.88
41	0.02	101	2.64	159	0.69	228	0.08
42	0.02	102	0.11	160	0.04	229	0.02
43	0.05	104	0.27	161	0.20	231	0.06
44	0.19	105	0.55	162	0.17	236	0.04
45	0.04	106	0.54	163	0.47	237	0.24
47	0.05	107	2.41	164	0.08	238	0.11
49	0.10	108	1.12	167	0.27	239	1.23
50	2.96	109	0.12	168	0.24	240	0.14
51	7.97	110	0.06	169	6.39	244	0.03
52	0.35	111	0.22	170	0.78	245	0.02
53	0.06	112	0.55	171	0.79	249	0.03
54	0.02	113	0.87	172	0.07	250	0.06
55	0.03	114	0.29	173	0.12	251	0.03
56	0.17	115	0.02	174	0.19	255	0.07
57	1.44	116	0.05	175	0.25	256	0.06
58	0.06	117	0.27	176	83.97	257	2.21
59	0.05	118	0.31	177	6.68	258	1.07
60	0.03	119	2.09	178	0.30	259	1.73
61	0.26	120	1.04	179	0.04	260	0.17
62	1.15	121	0.10	180	0.11	269	0.03
63	1.81	123	0.39	181	0.15	270	0.04
64	0.15	124	0.26	182	0.27	271	0.06
65	0.06	125	5.44	183	0.06	274	0.02
66	0.06	126	12.79	185	0.03	275	0.16
68	0.27	127	1.56	186	0.06	277	100.00
69	12.21	128	0.10	187	3.10	278	7.59
70	0.38	129	0.13	188	0.60	279	0.43
71	0.03	130	0.13	189	16.03	281	0.02
73	0.13	131	0.37	190	1.44	289	0.04
74	1.66	132	0.38	191	0.09	290	0.13
75	4.87	133	0.16	193	0.07	291	0.02
76	1.35	135	0.03	194	2.61	295	0.76
77	0.35	136	0.11	195	0.56	296	0.08
78	0.09	137	1.00	196	0.05	308	0.02
79	0.95	138	2.92	198	0.04	309	0.55
80	0.36	139	0.60	199	0.06	310	0.06
81	1.46	140	0.21	200	0.43	319	0.02
82	2.16	141	0.06	201	0.16	327	0.23
83	0.16	142	0.05	202	0.19	328	0.03
339	0.20	358	0.03	378	10.35		
340	0.04	359	4.20	379	1.19		
357	0.05	360	0.47	380	0.06		

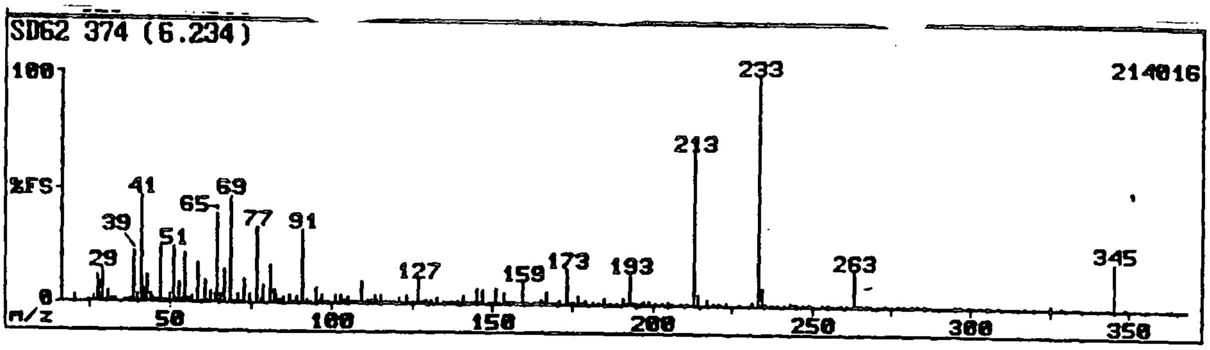
38. Gamma ray initiated formation of (1,1,2,3,3,3-hexafluoropropyl)-methylcyclopentanes (52) / (53)



SD62 215 (3.584) 3293184

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.32	70	0.47	122	0.09	167	0.31
24	0.10	71	1.20	123	0.15	168	0.01
25	0.31	73	4.04	124	0.02	169	0.02
26	1.87	74	0.36	125	0.08	170	0.00
27	7.12	75	1.38	127	1.03	171	0.03
28	2.89	77	8.71	128	0.10	172	0.10
29	5.78	78	0.74	129	0.14	173	0.28
30	0.10	79	2.80	130	0.05	174	0.08
31	1.16	81	3.89	131	0.17	175	0.17
32	0.31	83	100.00	132	0.21	176	0.02
33	0.46	84	6.16	133	0.50	177	0.11
36	0.08	85	0.66	134	0.08	178	0.02
37	0.54	86	0.17	135	0.26	179	0.12
38	1.29	87	0.26	136	0.03	180	0.02
39	14.80	88	0.35	137	0.03	181	0.01
40	4.07	89	1.29	138	0.03	184	0.01
41	29.23	91	4.32	139	0.20	185	0.03
42	34.83	91	3.73	140	0.03	186	0.06
43	4.23	92	0.30	141	0.13	187	0.02
44	0.51	93	1.46	142	0.03	191	0.02
45	0.34	95	1.80	143	0.02	192	0.12
46	0.24	96	0.34	144	0.04	193	0.08
47	2.08	97	1.14	145	0.49	194	0.38
48	0.08	98	0.21	146	0.06	195	3.76
49	0.14	99	0.18	147	0.16	196	0.35
50	1.27	101	1.30	148	0.01	197	0.04
51	5.16	103	1.50	149	0.10	198	0.06
52	0.86	105	3.26	150	0.13	199	0.61
53	5.10	106	0.09	151	0.81	200	0.06
55	45.77	107	0.11	152	0.05	204	0.02
56	2.24	109	1.56	153	0.17	205	0.02
57	1.19	110	0.16	154	0.11	206	0.05
59	3.73	111	0.19	155	0.54	213	0.25
60	0.37	113	4.07	156	0.03	214	0.05
61	0.85	114	0.48	157	0.05	217	0.01
62	0.26	115	0.75	158	0.05	218	0.01
63	1.46	116	0.11	159	0.51	219	0.01
64	1.08	117	0.23	160	0.06	232	0.02
65	8.71	118	0.06	163	0.04	233	0.08
66	1.14	119	0.17	164	0.01	234	0.01
67	7.77	120	0.07	165	0.08		
69	12.31	121	0.38	166	0.03		

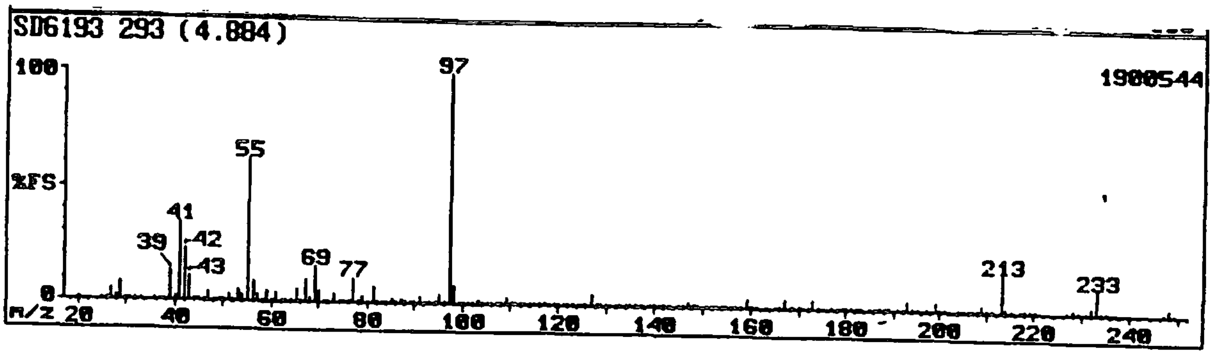
39. Gamma ray initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-methylcyclopentanes (54)



SD62 374 (6.234) 214016

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	3.11	83	3.44	141	4.25	203	1.17
24	0.26	84	1.52	142	0.60	205	2.42
25	0.52	85	2.93	143	0.55	206	0.72
26	2.78	87	3.83	144	0.51	209	0.51
27	11.36	88	0.58	145	7.09	211	0.42
28	8.49	89	3.26	146	1.08	213	66.99
29	14.11	91	31.58	147	5.59	214	5.29
30	0.43	92	1.70	148	0.25	217	3.20
31	4.75	93	0.65	149	0.79	219	0.52
32	1.94	95	6.46	150	0.83	221	0.25
33	1.76	96	1.72	151	6.73	223	1.69
36	0.32	97	3.74	152	0.81	227	0.76
37	1.05	98	0.60	153	4.64	231	2.06
38	2.27	99	0.49	154	0.27	233	100.00
39	22.49	101	3.77	155	1.14	234	7.48
40	4.13	102	1.17	156	0.07	235	1.28
41	46.41	103	4.19	157	0.51	237	0.19
42	5.92	104	2.00	158	1.06	239	0.13
43	12.08	105	2.90	159	10.05	241	0.77
44	3.47	106	0.13	160	0.77	243	2.36
45	1.65	107	0.45	161	0.58	244	0.24
46	1.17	108	1.39	162	0.10	245	0.41
47	22.97	109	9.81	163	1.03	247	0.39
48	0.68	110	0.68	164	0.19	249	0.15
49	0.36	111	2.33	165	1.97	253	0.19
50	3.44	112	2.00	166	0.27	255	0.29
51	23.80	113	4.04	167	5.53	259	0.71
52	2.21	114	1.56	168	0.36	261	0.27
53	9.09	115	4.16	169	1.28	263	15.55
54	2.33	116	0.82	170	0.13	264	1.39
55	21.05	117	1.44	171	1.72	265	0.41
56	1.70	118	0.16	173	15.79	267	0.33
57	2.60	119	0.85	174	1.28	273	0.16
59	17.94	120	0.32	175	0.10	277	0.26
60	1.20	121	3.29	176	0.14	279	0.99
61	9.69	122	0.81	177	3.44	281	0.39
62	0.93	123	3.50	178	0.33	283	0.27
63	5.05	124	0.24	179	1.50	285	0.89
64	4.01	125	0.58	181	0.26	295	0.19
65	39.23	126	1.04	183	0.87	297	0.41
66	3.59	127	11.00	185	2.90	299	0.33
67	14.11	128	1.09	186	0.24	303	0.18
69	46.89	129	2.27	187	0.52	305	1.01
70	0.87	130	0.36	189	0.39	309	0.32
71	4.37	131	1.70	191	3.38	317	0.24
72	0.59	133	2.63	192	0.66	325	2.33
73	10.41	134	0.22	193	13.76	329	0.22
75	3.65	135	1.43	194	1.31	345	20.45
77	33.01	136	0.11	195	1.14	349	0.73
78	1.91	137	0.25	196	0.16	363	0.25
79	7.66	138	0.19	197	1.94		
81	16.51	139	1.82	199	2.12		
82	6.22	140	0.84	201	0.31		

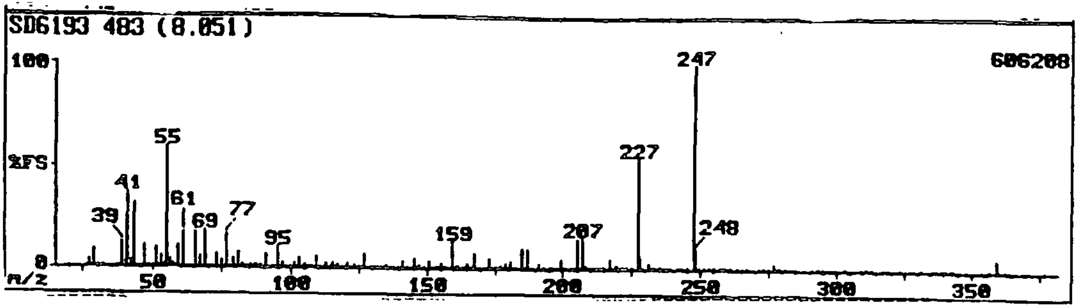
40. Gamma ray initiated formation of (1,1,2,3,3,3-hexafluoropropyl)-methylcyclohexanes (55) / (56)



SD6193 293 (4.884) 1900544

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.02	74	0.26	122	0.09	177	0.53
25	0.01	75	0.92	123	1.04	178	0.04
26	0.28	76	0.16	124	0.15	179	0.53
27	5.17	77	10.78	125	0.11	180	0.05
28	1.72	78	0.69	126	0.04	181	0.38
29	7.44	79	2.49	127	4.74	182	0.03
30	0.18	80	0.61	128	0.38	183	0.02
31	0.17	81	6.57	129	0.53	185	0.82
32	0.12	82	1.35	130	0.07	186	0.17
33	0.26	83	1.16	131	0.36	187	1.02
36	0.02	84	0.41	132	0.09	188	0.07
37	0.09	85	1.47	133	0.71	189	0.14
38	0.41	86	0.13	134	0.06	191	0.84
39	12.45	87	1.87	135	0.43	192	0.06
40	2.32	88	0.32	136	0.04	193	3.66
41	33.62	89	0.86	137	0.10	194	0.34
42	21.98	90	0.89	139	0.36	195	0.03
43	10.24	91	2.57	140	0.14	197	0.04
44	0.41	92	0.26	141	0.73	199	3.66
45	0.21	93	0.36	142	0.06	200	0.31
46	0.25	94	0.17	143	0.06	201	0.05
47	4.36	95	4.26	145	1.32	204	0.03
48	0.06	96	0.48	146	0.08	205	0.60
49	0.04	97	100.00	147	2.02	206	0.12
50	0.40	98	8.24	148	0.14	207	0.20
51	2.69	99	0.84	149	0.56	208	0.03
52	0.82	100	0.14	151	1.43	209	2.99
53	5.17	101	1.16	152	0.06	210	0.29
54	2.67	102	0.20	153	1.19	211	0.04
55	62.07	103	2.03	154	0.10	213	16.38
56	8.57	104	0.37	155	0.55	214	1.51
57	2.52	105	0.64	156	0.02	215	0.07
58	0.12	106	0.08	157	0.07	217	0.08
59	4.96	107	0.90	158	0.04	218	0.26
60	0.33	108	0.21	159	3.66	219	0.20
61	4.04	109	2.61	160	0.22	220	0.07
62	0.25	110	0.27	161	0.12	227	0.55
63	0.56	111	0.32	163	0.11	228	1.76
64	0.85	112	0.47	165	0.46	229	0.20
65	5.39	113	0.84	166	0.03	231	0.07
66	0.77	114	0.22	167	3.61	232	3.02
67	10.08	115	1.04	168	0.25	233	10.24
68	1.70	116	0.15	169	0.60	234	0.88
69	15.73	117	0.55	170	0.04	235	0.03
70	5.23	118	0.10	171	0.23	247	0.45
71	0.94	119	0.32	172	0.18	248	2.51
72	0.21	120	0.04	173	4.26	249	0.24
73	3.41	121	0.86	174	0.32		

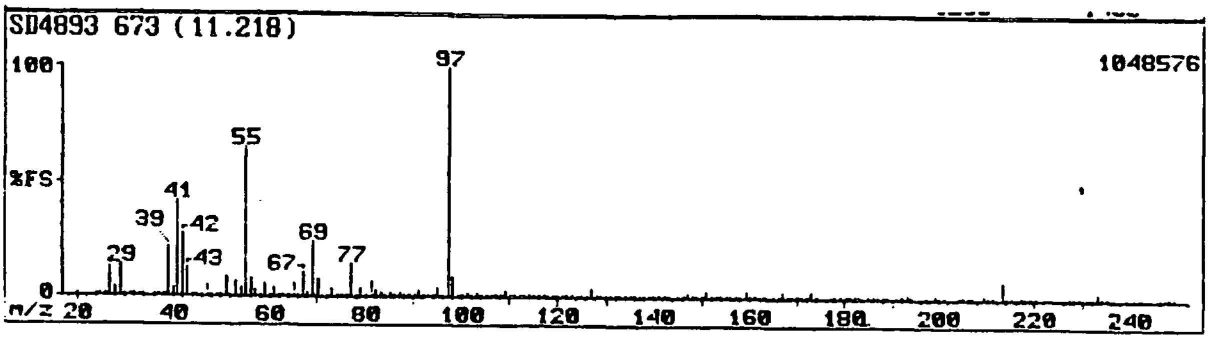
41. Gamma ray initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-methylcyclohexanes (57)



SD6193 483 (8.051) 606208

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.08	81	7.94	135	2.06	192	0.24
26	0.19	82	1.92	136	0.21	193	0.50
27	3.67	83	2.09	137	0.92	195	0.46
28	1.44	84	0.94	138	0.18	196	0.05
29	8.57	85	2.39	139	1.35	197	0.98
30	0.09	86	0.26	140	0.34	198	0.10
31	0.34	87	2.25	141	4.14	199	4.43
32	0.40	88	0.53	142	0.32	200	0.39
33	0.61	89	1.85	143	0.71	201	0.15
36	0.04	90	1.45	144	0.09	203	0.23
37	0.09	91	6.59	145	5.24	204	0.08
38	0.17	92	0.50	146	0.42	205	14.53
39	12.33	93	1.16	147	2.34	206	1.05
40	2.58	94	1.13	148	0.23	207	15.54
41	37.16	95	10.26	149	0.69	208	1.62
42	4.14	96	1.40	151	4.14	209	0.63
43	31.08	97	2.68	152	0.25	210	0.11
44	1.27	98	0.57	153	1.27	211	0.59
45	0.37	99	1.02	154	0.14	212	0.08
46	0.22	100	0.26	155	2.57	213	0.75
47	11.15	101	3.38	156	0.23	214	0.10
48	0.15	102	0.55	157	0.36	215	0.23
49	0.05	103	4.48	158	0.16	217	4.56
50	0.53	104	1.18	159	13.18	218	0.40
51	9.42	105	1.64	160	0.79	219	1.97
52	0.90	106	0.49	161	1.85	220	0.18
53	5.57	107	0.42	162	0.16	221	0.09
54	2.06	108	0.27	163	0.79	222	0.02
55	59.46	109	6.17	164	0.14	223	0.39
56	3.84	110	0.70	165	2.63	225	0.09
57	1.78	111	1.02	166	0.21	227	54.05
58	0.28	112	0.16	167	7.85	228	5.36
59	10.98	113	2.45	168	0.57	229	0.57
60	0.57	114	0.65	169	0.51	231	2.61
61	17.23	115	2.87	170	0.04	232	0.27
62	0.78	116	0.49	171	0.72	233	0.18
63	0.81	117	1.54	172	0.22	235	0.94
64	0.99	118	0.21	173	5.32	236	0.06
65	17.06	119	0.68	174	0.35	237	0.96
66	1.27	120	0.09	175	0.12	238	0.14
67	5.83	121	2.96	176	0.11	239	0.07
68	1.21	122	0.32	177	2.23	241	0.21
69	18.92	123	2.13	178	0.20	242	0.07
70	0.58	124	0.32	179	3.21	243	0.06
71	1.31	125	0.63	180	0.27	245	1.08
72	0.40	126	0.63	181	3.46	247	100.00
73	6.84	127	6.38	182	0.34	248	10.05
74	0.37	128	0.57	183	0.41	249	0.74
75	3.80	129	0.84	185	9.63	251	0.06
76	0.37	130	0.20	186	0.88	253	0.13
77	16.72	131	0.62	187	9.80	255	0.16
78	1.19	132	0.50	188	0.84	257	0.73
79	4.43	133	1.43	189	0.33	258	0.12
80	0.95	134	0.20	191	2.96	259	0.21
261	0.08	279	0.20	311	0.15	340	0.11
263	0.06	281	0.07	313	0.13	343	0.11
265	0.05	291	0.15	317	1.11	357	0.05
267	0.07	293	0.18	318	0.10	359	5.41
271	0.04	295	0.07	319	0.35	360	0.67
273	0.16	297	0.21	323	0.08	363	0.50
275	0.09	299	0.36	331	0.20	364	0.07
277	3.00	303	0.05	337	0.07	377	0.17
278	0.34	309	0.05	339	0.83		

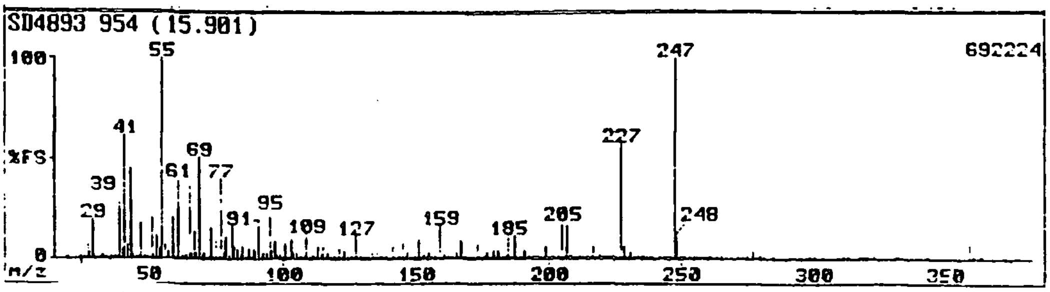
42. D.T.B.P. initiated formation of (1,1,2,3,3,3-hexafluoropropyl)-methylcyclohexanes (55) / (56)



SD4893 673 (11.218) 1048576

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.02	73	3.83	122	0.11	174	0.25
24	0.02	74	0.31	123	0.89	177	0.39
25	0.03	75	1.37	124	0.13	178	0.03
26	0.79	76	0.28	125	0.11	179	0.34
27	12.60	77	14.84	126	0.05	180	0.03
28	3.71	78	1.09	127	4.35	181	0.33
29	13.57	79	3.42	128	0.36	182	0.04
30	0.35	80	0.82	129	0.43	183	0.02
31	0.46	81	6.45	130	0.07	185	0.56
32	0.19	82	2.51	131	0.42	186	0.16
33	0.65	83	1.78	132	0.13	187	0.87
34	0.01	84	0.65	133	0.68	188	0.07
36	0.01	85	1.98	134	0.08	189	0.12
37	0.17	86	0.20	135	0.33	191	0.59
38	0.79	87	1.78	136	0.04	192	0.05
39	21.29	88	0.46	137	0.10	193	2.12
40	3.78	89	1.13	138	0.03	194	0.22
41	41.41	90	1.23	139	0.38	197	0.04
42	26.95	91	3.15	140	0.14	199	2.05
43	12.30	92	0.31	141	0.70	200	0.19
44	0.51	93	0.48	142	0.07	201	0.04
45	0.27	94	0.25	143	0.07	204	0.03
46	0.31	95	3.64	145	1.37	205	0.37
47	4.47	96	0.67	146	0.11	206	0.10
48	0.13	97	100.00	147	1.61	207	0.14
49	0.05	98	8.59	148	0.14	209	2.42
50	0.85	99	0.87	149	0.43	210	0.27
51	8.30	100	0.27	150	0.08	211	0.03
52	1.20	101	1.64	151	2.76	213	7.71
53	6.84	102	0.29	152	0.11	214	0.75
54	3.49	103	2.29	153	0.87	215	0.05
55	65.23	104	0.51	154	0.11	217	0.05
56	7.32	105	0.71	155	0.42	218	0.13
57	2.47	106	0.11	156	0.04	219	0.11
58	0.24	107	0.98	157	0.04	220	0.06
59	5.44	108	0.28	158	0.05	227	0.31
60	0.37	109	2.51	159	2.95	228	0.15
61	3.61	110	0.27	160	0.21	229	0.03
62	0.30	111	0.35	161	0.11	231	0.05
63	0.80	112	0.39	163	0.11	232	0.55
64	1.09	113	1.13	165	0.38	233	2.86
65	5.93	114	0.31	166	0.04	234	0.30
66	1.03	115	1.12	167	3.13	235	0.02
67	10.35	116	0.17	168	0.26	246	0.01
68	1.86	117	0.50	169	0.48	247	0.29
69	24.02	118	0.10	170	0.05	248	1.29
70	7.42	119	0.32	171	0.18	249	0.15
71	1.30	120	0.06	172	0.18		
72	0.31	121	0.79	173	3.22		

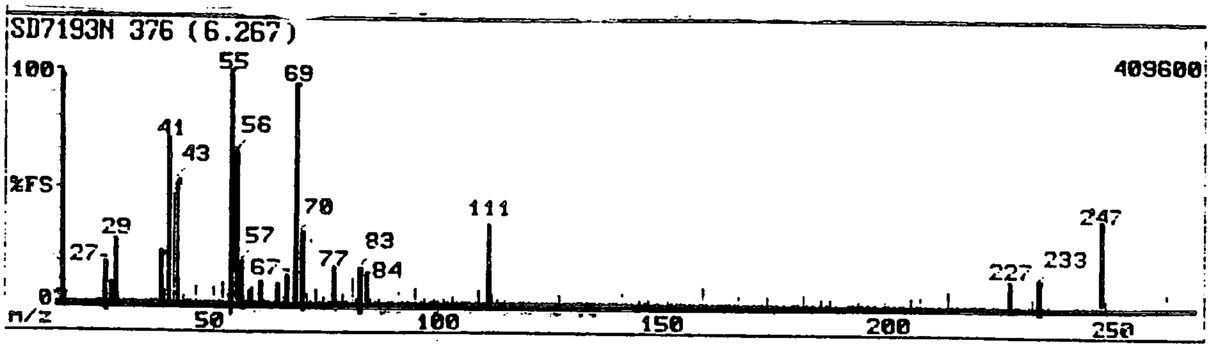
43. D.T.B.P. initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-methylcyclohexanes (57)



SD4893 954 (15.901) 692224

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.10	78	3.18	132	1.27	186	1.20
24	0.02	79	10.50	133	2.59	187	11.54
25	0.05	80	2.37	134	0.36	188	1.05
26	0.64	81	16.86	135	3.03	189	0.47
27	11.03	82	5.58	136	0.33	190	0.08
28	3.10	83	5.25	137	1.34	191	3.05
29	19.67	84	2.36	138	0.33	192	0.20
30	0.51	85	5.47	139	2.40	193	0.67
31	1.04	86	0.66	140	0.64	194	0.10
32	0.41	87	4.66	141	5.81	195	0.62
33	1.55	88	1.37	142	0.50	196	0.12
34	0.03	89	4.62	143	0.99	197	1.23
36	0.04	90	4.11	144	0.15	198	0.08
37	0.17	91	16.12	145	8.17	199	5.73
38	0.74	92	1.24	146	0.74	200	0.53
39	25.44	93	2.85	147	3.37	201	0.12
40	4.96	94	2.51	148	0.35	202	0.06
41	60.95	95	24.70	149	0.89	203	0.28
42	7.06	96	3.40	150	0.23	204	0.16
43	44.38	97	8.69	151	9.76	205	18.49
44	1.83	98	1.53	152	0.55	206	1.45
45	0.68	99	2.13	153	1.70	207	16.42
46	0.69	100	0.72	154	0.22	208	1.90
47	17.90	101	7.66	155	3.37	209	0.08
48	0.47	102	1.34	156	0.32	210	0.13
49	0.06	103	9.76	157	0.62	211	0.72
50	1.14	104	2.81	158	0.29	212	0.11
51	20.86	105	3.25	159	16.86	213	1.16
52	1.99	106	0.94	160	1.19	214	0.16
53	12.13	107	1.03	161	2.37	215	0.29
54	4.44	108	0.71	162	0.22	216	0.06
55	100.00	109	12.57	163	1.14	217	5.62
56	7.06	110	1.49	164	0.23	218	0.55
57	3.70	111	2.19	165	3.25	219	2.14
58	0.55	112	0.38	166	0.31	220	0.25
59	20.27	113	5.51	167	0.91	221	0.16
60	1.16	114	1.53	168	0.76	222	0.03
61	20.11	115	6.14	169	0.70	223	0.52
62	1.34	116	1.04	170	0.12	224	0.06
63	1.71	117	3.18	171	0.99	225	0.17
64	2.40	118	0.43	172	0.44	227	56.00
65	35.00	119	1.52	173	6.92	228	6.25
66	3.07	120	0.29	174	0.50	229	0.67
67	13.46	121	5.18	175	0.13	230	0.08
68	3.25	122	0.68	176	0.14	231	3.11
69	50.09	123	3.66	177	2.92	232	0.37
70	1.65	124	0.55	178	0.26	233	0.45
71	3.33	125	1.17	179	3.55	234	0.07
72	1.04	126	1.08	180	0.35	235	1.08
73	15.24	127	11.24	181	4.33	236	0.12
74	0.91	128	1.10	182	0.49	237	1.23
75	0.47	129	1.51	183	0.49	238	0.16
76	1.04	130	0.35	184	0.08	239	0.09
77	40.24	131	1.28	185	11.54	241	0.25
242	0.07	260	0.05	293	0.20	332	0.04
243	0.07	261	0.09	295	0.08	337	0.07
244	0.03	263	0.07	297	0.25	339	0.08
245	1.13	265	0.04	298	0.03	340	0.14
246	0.20	267	0.07	299	0.43	343	0.12
247	100.00	269	0.05	300	0.06	357	0.06
248	10.80	271	0.04	303	0.07	359	6.77
249	0.85	273	0.17	309	0.06	360	0.92
250	0.07	275	0.10	311	0.15	361	0.08
251	0.07	277	3.48	313	0.15	363	0.53
253	0.14	278	0.40	317	1.29	364	0.08
255	0.18	279	0.20	318	0.15	377	0.15
256	0.04	280	0.02	319	0.38	378	0.03
257	0.79	281	0.06	320	0.06		
258	0.13	285	0.03	323	0.07		
259	0.25	291	0.16	331	0.23		

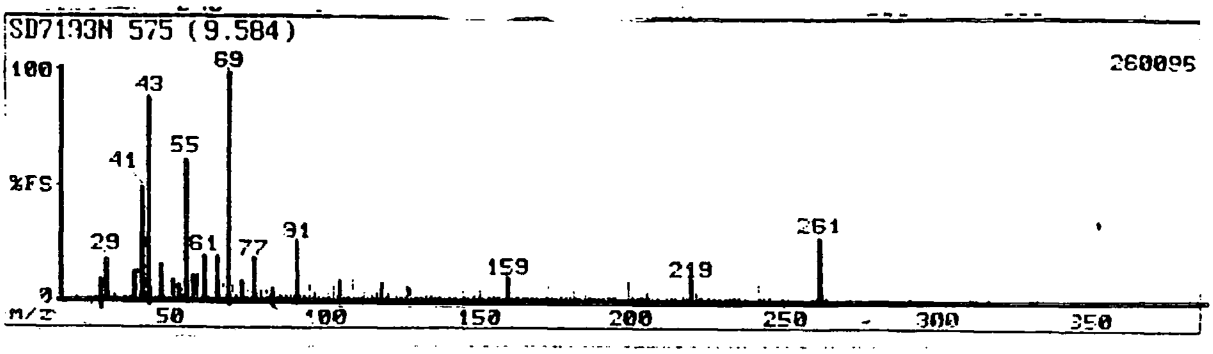
44. D.T.B.P. initiated formation of (1,1,2,3,3,3-hexafluoropropyl)-1,2-dimethylcyclohexanes (58) / (59)



SD7193N 376 (6.267) 40960

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.11	77	16.00	128	0.30	183	0.20
25	0.07	78	1.16	129	0.53	185	2.92
26	0.82	79	3.80	130	0.15	186	0.54
27	16.75	80	0.85	131	0.54	187	3.20
28	8.38	81	10.81	132	0.19	188	0.28
29	27.75	82	1.97	133	0.93	191	1.09
30	0.75	83	15.44	134	0.13	192	0.11
31	0.38	84	10.75	135	0.70	193	1.58
32	1.59	85	2.17	136	0.10	194	0.17
33	0.64	86	0.21	137	0.44	195	0.24
36	0.15	87	2.31	138	0.12	197	0.11
37	0.17	88	0.43	139	0.67	199	2.00
38	0.67	89	1.25	140	0.27	200	0.55
39	21.50	90	1.06	141	5.00	201	1.00
40	4.38	91	4.50	142	0.48	202	0.07
41	71.00	92	0.44	143	0.24	203	0.07
42	46.75	93	1.27	145	2.41	205	3.88
43	52.00	94	0.73	146	0.21	206	0.46
44	3.28	95	6.63	147	1.55	207	3.83
45	0.39	96	1.02	148	0.15	208	0.43
46	0.38	97	1.97	149	0.43	211	0.06
47	6.31	98	0.57	151	1.94	213	7.00
48	0.21	99	2.20	152	0.13	214	0.68
49	0.04	100	0.29	153	0.93	215	0.06
50	0.73	101	2.20	154	0.12	217	0.39
51	7.25	102	0.42	155	0.70	218	0.80
52	1.23	103	2.94	156	0.06	219	0.88
53	8.94	104	0.73	157	0.14	220	0.87
54	3.84	105	1.19	158	0.08	221	0.17
55	100.00	106	0.36	159	7.50	223	0.90
56	65.00	107	0.36	160	0.48	224	0.12
57	17.75	108	0.25	161	1.05	227	12.94
58	0.94	109	5.81	162	0.09	228	1.39
59	7.19	110	0.70	163	0.39	229	0.08
60	0.55	111	38.00	164	0.07	231	0.18
61	9.81	112	3.69	165	1.02	232	3.66
62	0.49	113	1.63	166	0.10	233	10.69
63	0.70	114	0.42	167	4.31	234	1.44
64	0.88	115	1.94	168	0.34	235	0.05
65	8.56	116	0.36	169	0.35	241	0.20
66	1.20	117	1.45	170	0.04	242	0.36
67	11.94	118	0.24	171	0.24	243	0.06
68	3.08	119	1.14	172	0.17	245	0.25
69	95.00	120	0.15	173	3.92	246	1.80
70	30.25	121	2.84	174	0.25	247	36.75
71	4.00	122	0.32	175	0.03	248	3.95
72	0.41	123	1.39	177	0.86	249	0.23
73	5.50	124	0.25	179	1.09	260	0.15
74	0.45	125	0.19	180	0.14	261	0.35
75	2.75	126	0.29	181	4.44	262	6.69
76	0.27	127	3.64	182	0.42	263	0.80

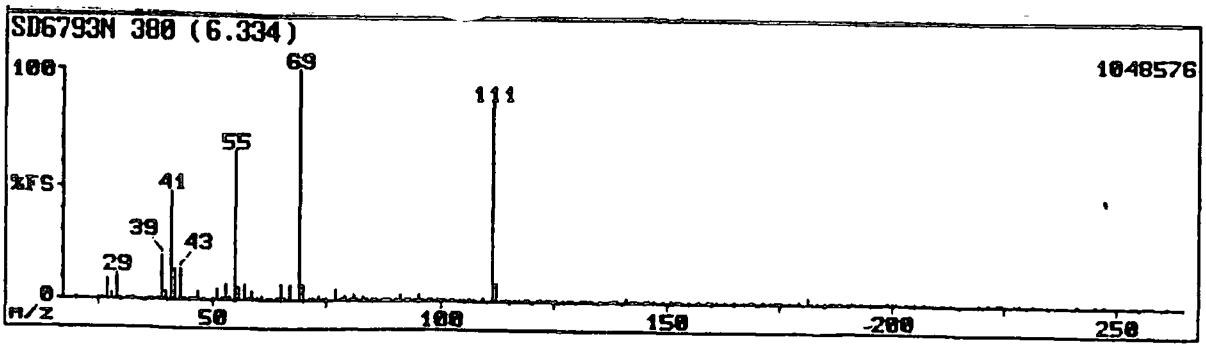
45. D.T.B.P. initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-1,2-dimethylcyclohexanes (60)



SD7133N 575 (9.584)

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.27	80	1.06	134	0.24	194	0.16
25	0.07	81	3.86	135	1.09	195	0.47
26	0.47	82	1.75	136	0.25	197	0.24
27	8.66	83	4.55	137	0.54	199	7.69
28	7.50	84	1.13	138	0.15	200	2.34
29	20.57	85	1.09	139	1.21	201	1.0[illegible]
30	0.59	86	0.31	140	0.53	202	0.11
31	0.49	87	1.80	141	3.17	203	0.13
32	2.12	88	0.47	142	0.31	204	0.17
33	0.92	89	2.09	143	0.55	205	2.51
35	0.05	90	1.60	145	3.72	206	0.27
36	0.20	91	26.38	146	0.36	207	0.31
37	0.12	92	1.46	147	0.86	209	0.29
38	0.29	93	1.02	148	0.09	211	0.23
39	11.61	94	0.63	149	1.77	213	0.27
40	2.53	95	7.03	150	0.21	214	0.12
41	40.02	96	1.09	151	3.47	217	1.54
42	25.90	97	2.63	152	0.24	218	0.14
43	83.37	98	0.81	153	1.09	219	9.25
44	5.17	99	1.99	154	0.20	220	2.00
45	0.44	100	0.34	155	2.07	221	2.46
46	0.40	101	2.63	156	0.20	222	[illegible]
47	14.67	102	0.50	157	0.73	223	0.27
49	0.39	103	5.54	158	0.17	225	0.11
50	0.46	104	1.62	159	10.93	227	0.16
51	7.68	105	8.76	160	0.82	229	0.11
52	0.82	106	0.68	161	1.05	231	1.37
53	6.25	107	0.62	162	0.12	232	0.16
54	2.14	108	0.74	163	0.55	233	0.46
55	63.39	109	8.37	165	0.97	234	0.13
56	3.96	110	0.97	166	0.13	235	0.15
57	9.84	111	1.07	167	1.67	237	0.14
58	0.66	112	0.31	168	0.16	241	6.59
59	10.83	113	2.76	169	0.51	242	0.77
60	0.35	114	0.62	171	0.44	243	0.13
61	14.67	115	3.13	172	1.25	245	0.47
62	0.62	116	0.51	173	5.63	249	0.20
63	0.60	117	2.61	174	0.41	251	0.14
64	1.02	118	0.66	175	0.19	259	0.31
65	13.49	119	7.29	177	1.53	260	0.06
66	1.30	120	0.68	178	0.14	261	29.13
67	7.13	121	2.90	179	2.02	262	3.40
68	2.24	122	0.44	180	0.60	263	0.36
69	100.00	123	1.57	181	3.67	271	0.33
70	5.01	124	0.16	182	0.27	291	0.56
71	1.33	125	0.44	183	0.21	311	0.13
72	0.60	126	0.09	185	1.93	313	0.06
73	7.97	127	5.71	186	0.54	317	0.17
74	0.68	128	0.40	187	1.30	331	0.47
75	4.11	129	0.76	188	0.11	333	0.08
76	0.38	130	0.11	189	0.15	353	0.09
77	10.41	131	0.92	191	0.08	373	0.43
78	1.35	132	0.42	192	0.53	377	0.10
79	3.86	133	1.57	193	1.10		

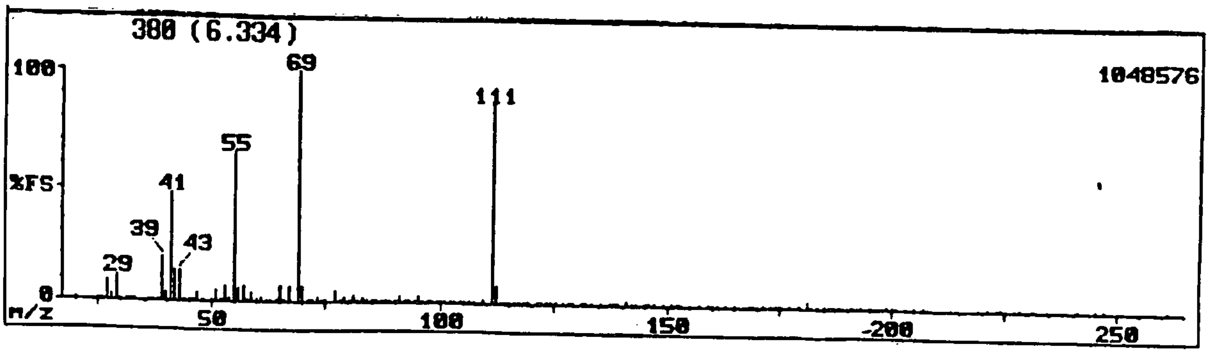
46. Gamma ray initiated formation of (1,1,2,3,3,3-hexafluoropropyl)-1,3-dimethylcyclohexanes (61) / (62)



SD6793N 380 (6.334)

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.03	67	6.84	111	85.94	165	0.23
25	0.04	69	100.00	112	7.32	167	0.74
26	0.43	70	6.45	113	0.92	168	0.06
27	8.59	71	0.86	114	0.14	169	0.10
28	2.47	72	0.22	115	0.67	171	0.06
29	11.72	73	1.86	116	0.11	173	0.46
30	0.28	74	0.13	117	0.34	174	0.04
31	0.28	75	0.79	118	0.11	175	0.03
32	0.24	77	4.88	119	0.21	177	0.18
33	0.42	78	0.57	121	0.96	179	0.17
36	0.03	79	2.08	122	0.14	181	2.49
37	0.14	80	0.48	123	0.27	182	0.18
38	0.57	81	2.66	124	0.04	183	0.11
39	19.14	82	1.19	125	0.08	185	0.40
40	3.71	83	1.64	127	0.90	186	0.11
41	47.66	84	0.35	128	0.10	187	0.33
42	13.18	85	0.57	129	0.13	188	0.03
43	13.57	86	0.10	131	0.16	191	0.14
44	0.55	87	0.60	132	0.19	193	0.06
45	0.26	88	0.18	133	0.30	195	0.16
46	0.26	89	0.57	135	0.21	199	0.28
47	3.44	90	0.33	137	0.10	200	0.04
48	0.11	91	2.81	138	0.02	201	0.09
50	0.59	92	0.23	139	0.23	203	0.04
51	4.88	93	0.74	141	1.56	205	0.42
52	0.95	94	0.32	142	0.14	207	0.24
53	7.23	95	2.56	143	0.07	213	0.06
54	2.20	96	0.40	145	0.73	219	0.15
55	64.84	97	0.79	146	0.07	221	0.04
56	5.47	98	0.19	147	0.17	223	0.86
57	6.54	99	0.63	149	0.08	224	0.09
58	0.31	100	0.12	151	1.18	227	0.45
59	3.71	101	0.75	152	0.05	228	0.05
60	0.24	102	0.15	153	0.13	231	0.03
61	2.39	103	0.91	155	0.18	241	0.09
62	0.23	104	0.32	157	0.05	245	0.03
63	0.61	105	0.38	159	1.39	247	0.05
64	0.47	106	0.07	160	0.06	261	0.09
65	6.93	107	0.14	161	0.27		
66	0.72	109	1.64	163	0.19		

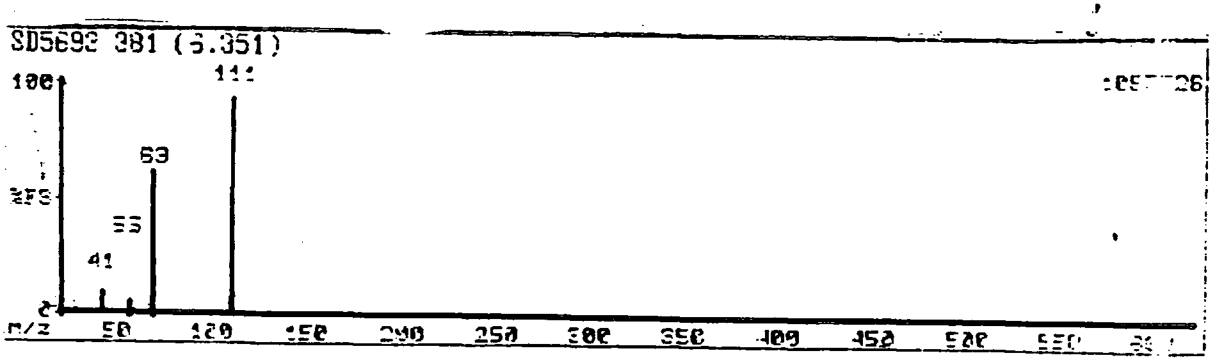
47. D.T.B.P. initiated formation of (1,1,2,3,3,3-hexafluoropropyl)-1,3-dimethylcyclohexanes (61) / (62)



380 (6.334)

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.03	67	6.84	111	85.94	165	0.23
25	0.04	69	100.00	112	7.32	167	0.74
26	0.43	70	6.45	113	0.92	168	0.06
27	8.59	71	0.86	114	0.14	169	0.10
28	2.47	72	0.22	115	0.67	171	0.06
29	11.72	73	1.86	116	0.11	173	0.46
30	0.28	74	0.13	117	0.34	174	0.04
31	0.28	75	0.79	118	0.11	175	0.03
32	0.24	77	4.88	119	0.21	177	0.18
33	0.42	78	0.57	121	0.96	179	0.17
36	0.03	79	2.08	122	0.14	181	2.49
37	0.14	80	0.48	123	0.27	182	0.18
38	0.57	81	2.66	124	0.04	183	0.11
39	19.14	82	1.19	125	0.08	185	0.40
40	3.71	83	1.64	127	0.90	186	0.11
41	47.66	84	0.35	128	0.10	187	0.33
42	13.18	85	0.57	129	0.13	188	0.03
43	13.57	86	0.10	131	0.16	191	0.14
44	0.55	87	0.60	132	0.19	193	0.06
45	0.26	88	0.18	133	0.30	195	0.16
46	0.26	89	0.57	135	0.21	199	0.28
47	3.44	90	0.33	137	0.10	200	0.04
48	0.11	91	2.81	138	0.02	201	0.09
50	0.59	92	0.23	139	0.23	203	0.04
51	4.88	93	0.74	141	1.56	205	0.42
52	0.95	94	0.32	142	0.14	207	0.24
53	7.23	95	2.56	143	0.07	213	0.06
54	2.20	96	0.40	145	0.73	219	0.15
55	64.84	97	0.79	146	0.07	221	0.04
56	5.47	98	0.19	147	0.17	223	0.86
57	6.54	99	0.63	149	0.08	224	0.09
58	0.31	100	0.12	151	1.18	227	0.45
59	3.71	101	0.75	152	0.05	228	0.05
60	0.24	102	0.15	153	0.13	231	0.03
61	2.39	103	0.91	155	0.18	241	0.09
62	0.23	104	0.32	157	0.05	245	0.03
63	0.61	105	0.38	159	1.39	247	0.05
64	0.47	106	0.07	160	0.06	261	0.09
65	6.93	107	0.14	161	0.27		
66	0.72	109	1.64	163	0.15		

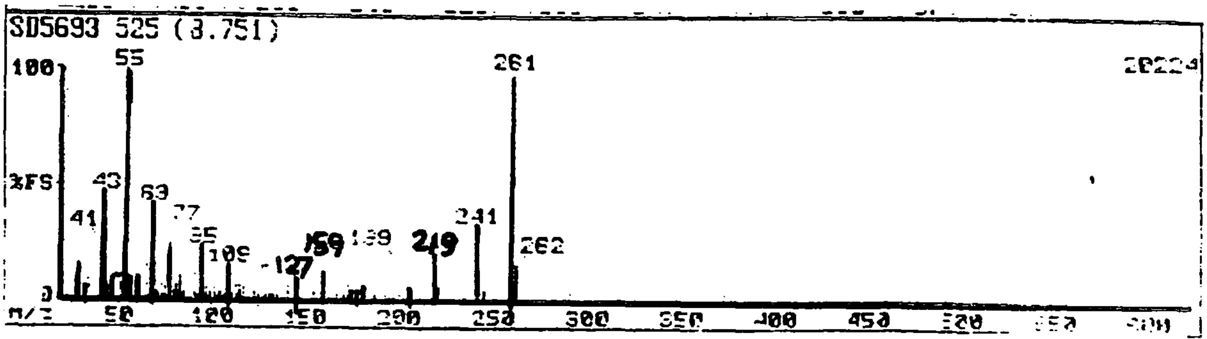
48. Gamma ray initiated formation of 1-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dimethylcyclohexane (63)



SD5693 381 (6.351) 1097728

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.01	73	1.18	120	0.05	168	0.07
25	0.02	74	0.07	121	1.11	169	0.12
26	0.23	75	0.73	122	0.16	171	0.08
27	4.41	76	0.13	123	0.41	173	0.78
28	1.59	77	4.10	124	0.07	174	0.07
29	6.34	78	0.47	125	0.11	175	0.04
30	0.16	79	0.83	126	0.09	177	0.28
31	0.11	80	0.23	127	1.11	179	0.24
32	0.21	81	2.75	128	0.11	180	0.03
33	0.17	82	0.76	129	0.15	181	2.64
36	0.02	83	1.54	130	0.04	182	0.22
37	0.05	84	0.31	131	0.18	183	0.13
38	0.20	85	0.55	132	0.10	185	0.65
39	6.72	86	0.08	133	0.32	186	0.17
40	1.41	87	0.64	134	0.05	187	0.54
41	18.75	88	0.08	135	0.25	188	0.04
42	5.97	89	0.48	136	0.03	191	0.24
43	6.55	90	0.10	137	0.14	192	0.02
44	0.33	91	2.52	138	0.03	193	0.11
45	0.12	92	0.22	139	0.28	195	0.17
46	0.15	93	0.66	140	0.06	197	0.02
47	1.59	94	0.27	141	1.91	199	0.38
48	0.07	95	2.49	142	0.19	200	0.04
49	0.02	96	0.37	143	0.08	201	0.06
50	0.30	97	0.65	145	0.92	203	0.03
51	2.19	98	0.16	146	0.08	205	0.69
52	0.49	99	0.66	147	0.30	206	0.04
53	3.59	100	0.11	148	0.02	207	0.40
54	1.43	101	0.76	149	0.10	208	0.05
55	33.96	102	0.14	150	0.03	213	0.15
56	2.70	103	0.83	151	0.93	217	0.03
57	3.52	104	0.37	152	0.05	219	0.21
58	0.23	105	0.71	153	0.19	221	0.04
59	2.12	106	0.16	154	0.04	223	0.85
60	0.16	107	0.21	155	0.24	224	0.10
61	1.91	108	0.09	156	0.03	227	0.02
62	0.14	109	1.84	157	0.07	228	0.10
63	0.32	110	0.25	158	0.02	231	0.03
64	0.31	111	100.00	159	1.90	241	0.11
65	4.24	112	9.61	160	0.13	242	0.02
66	0.55	113	1.04	161	0.34	245	0.03
67	4.17	114	0.19	162	0.03	247	0.11
68	2.05	115	0.71	163	0.17	260	0.05
69	64.55	116	0.11	164	0.03	261	0.14
70	5.10	117	0.37	165	0.31		
71	0.61	118	0.06	166	0.02		
72	0.13	119	0.22	167	0.92		

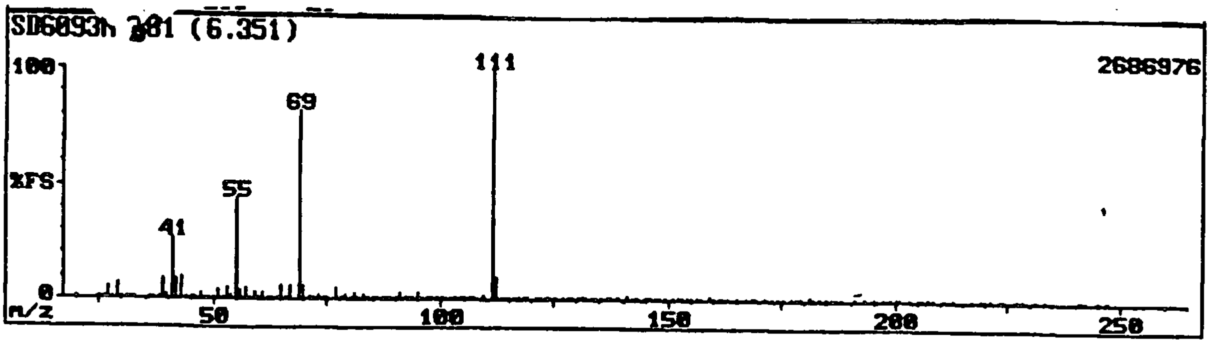
49. Gamma ray initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dimethylcyclohexanes (64)



SD5693 525 (3.751)

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.59	77	25.00	114	1.68	185	4.11
27	5.54	78	2.55	115	6.09	187	2.29
28	10.68	79	6.49	116	1.13	191	2.83
29	12.10	80	2.87	117	4.98	193	2.06
32	5.22	81	5.38	119	2.42	195	1.[illegible]
39	8.70	82	2.95	121	5.38	197	1.10
40	2.35	83	9.34	123	3.78	199	15.17
41	22.15	84	1.82	125	1.54	200	1.94
42	16.06	85	2.57	127	11.87	201	2.04
43	46.20	87	2.16	128	1.03	203	5.70
44	4.59	89	3.26	129	2.18	207	1.38
47	8.54	90	1.84	131	2.39	211	1.36
51	7.04	91	13.61	132	1.52	213	1.85
52	1.23	92	1.40	133	3.82	217	4.87
53	6.09	93	3.70	135	1.70	219	22.15
54	2.23	94	1.07	139	2.93	220	2.31
55	100.00	95	11.39	141	6.01	221	6.09
56	9.10	96	2.16	143	1.36	231	8.86
57	3.73	97	4.39	145	8.47	233	1.17
59	6.96	98	1.08	147	1.34	235	0.85
61	10.60	99	3.26	151	6.17	241	20.89
63	1.11	101	4.61	153	2.53	242	2.05
64	1.15	102	1.29	155	2.87	243	3.50
65	17.41	103	6.80	159	20.89	259	1.90
66	1.68	104	2.85	161	2.06	261	100.00
67	6.49	105	3.26	163	1.31	262	12.50
68	3.32	106	1.42	165	1.70	263	0.74
69	42.09	107	2.33	167	2.97	271	3.14
70	2.55	108	1.60	171	1.56	317	1.20
71	2.16	109	15.27	173	8.62	331	2.20
73	9.02	110	2.14	177	3.72	373	2.95
74	0.75	111	2.45	179	4.09	377	1.52
75	5.22	113	5.93	181	6.25		

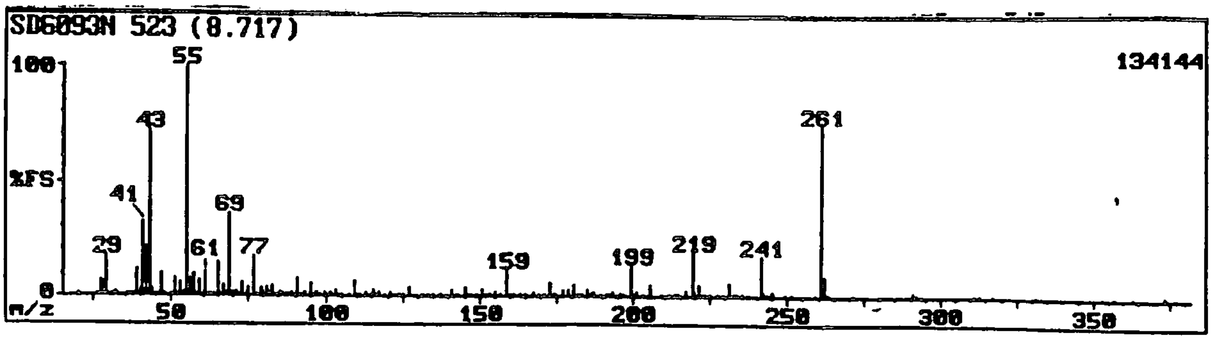
50. D.T.B.P. initiated formation of 1-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dimethylcyclohexane (63)



SD6093N 381 (6.351) 2686976

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.01	71	0.75	118	0.07	173	0.68
25	0.02	72	0.14	119	0.22	174	0.05
26	0.25	73	2.12	121	1.09	175	0.02
27	4.73	74	0.14	122	0.14	177	0.22
28	1.41	75	0.82	123	0.38	178	0.01
29	6.78	77	4.84	124	0.05	179	0.21
30	0.16	78	0.45	125	0.09	181	2.42
31	0.12	79	1.96	127	1.08	182	0.17
32	0.09	80	0.37	128	0.08	183	0.11
33	0.18	81	3.05	129	0.13	185	0.63
36	0.01	82	0.80	130	0.02	186	0.13
37	0.06	83	1.71	131	0.17	187	0.52
38	0.25	84	0.33	132	0.15	188	0.04
39	8.84	85	0.63	133	0.27	191	0.22
40	1.86	86	0.08	134	0.02	193	0.11
41	25.76	87	0.71	135	0.21	195	0.16
42	8.61	88	0.16	136	0.01	197	0.03
43	9.64	89	0.56	137	0.11	199	0.42
44	0.37	90	0.23	139	0.23	200	0.03
45	0.18	91	2.90	141	1.58	201	0.10
46	0.22	92	0.20	142	0.14	203	0.04
47	2.59	93	0.74	143	0.06	205	0.77
48	0.09	94	0.25	145	0.72	206	0.05
49	0.02	95	2.59	146	0.05	207	0.45
50	0.48	96	0.38	147	0.24	208	0.04
51	3.43	97	0.76	148	0.02	211	0.01
52	0.71	98	0.16	149	0.08	213	0.17
53	5.22	99	0.71	151	0.89	217	0.05
54	1.99	100	0.10	152	0.03	219	0.23
55	43.90	101	0.84	153	0.15	220	0.02
56	3.58	102	0.13	154	0.02	221	0.05
57	4.65	103	0.94	155	0.19	223	0.97
58	0.28	104	0.38	156	0.01	224	0.10
59	2.71	105	0.72	157	0.05	227	1.01
60	0.18	106	0.11	159	1.57	228	0.09
61	2.44	107	0.14	160	0.09	231	0.04
62	0.17	109	1.83	161	0.29	233	0.01
63	0.42	111	100.00	162	0.02	241	0.14
64	0.45	112	9.41	163	0.14	242	0.02
65	5.72	113	1.03	165	0.29	245	0.02
66	0.68	114	0.17	167	0.81	247	0.14
67	5.41	115	0.73	168	0.06	261	0.16
69	81.71	116	0.11	169	0.10		
70	6.06	117	0.38	171	0.07		

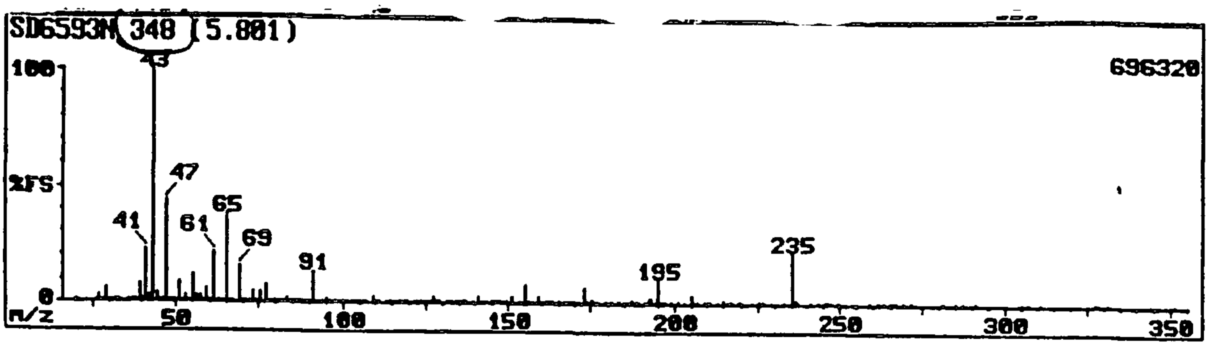
51. D.T.B.P. initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dimethylcyclohexanes (64)



SD6093N 523 (8.717) 134144

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.26	74	0.49	128	0.45	200	0.85
26	0.27	75	3.67	129	0.75	201	1.65
27	6.44	77	17.18	131	0.94	203	0.35
28	5.58	78	1.17	132	0.50	205	4.58
29	17.18	79	3.48	133	1.46	209	0.52
30	0.49	80	1.71	135	1.35	211	0.80
31	0.48	81	3.44	137	0.46	213	1.35
32	2.29	82	1.57	139	1.15	214	0.22
33	0.67	83	5.25	141	2.53	217	3.39
36	0.20	84	1.01	142	0.29	219	19.27
37	0.16	85	1.49	143	0.51	220	1.53
38	0.41	86	0.22	145	3.72	221	5.06
39	11.55	87	0.76	146	0.37	222	0.64
40	2.66	88	0.27	147	0.89	223	0.45
41	32.25	89	1.92	149	0.93	225	0.34
42	21.18	90	0.88	151	3.10	227	0.49
43	71.76	91	7.78	152	0.25	229	0.29
44	2.73	92	0.67	153	1.20	231	5.77
45	0.37	93	1.87	155	1.97	232	0.59
46	0.31	95	6.20	157	0.41	233	0.34
47	10.02	96	0.91	159	11.98	235	0.65
48	0.27	97	2.14	160	0.74	237	0.19
50	0.56	98	0.59	161	1.16	241	17.75
51	7.63	99	1.51	163	0.61	242	2.08
52	0.85	100	0.26	165	1.28	243	0.39
53	6.11	101	2.19	167	1.69	245	1.97
54	1.96	102	0.47	169	0.50	249	0.80
55	100.00	103	3.34	171	0.51	251	0.26
56	8.02	104	0.85	173	5.68	259	0.92
57	10.07	105	1.29	174	0.47	261	74.81
58	0.62	107	0.59	175	0.25	262	8.49
59	6.97	109	7.01	177	2.46	263	0.67
60	0.75	110	0.97	179	3.10	271	0.66
61	10.35	111	1.16	181	4.77	291	1.84
62	0.49	113	2.42	182	0.43	292	0.30
63	0.60	114	0.51	183	0.41	311	0.35
64	0.83	115	2.50	185	2.91	313	0.26
65	14.89	116	0.40	186	0.51	317	0.45
66	1.17	117	1.86	187	1.62	331	1.12
67	5.20	119	1.20	189	0.35	353	0.41
68	2.10	121	2.06	191	1.12	357	0.27
69	35.69	122	0.33	192	0.08	363	0.33
70	1.75	123	1.17	193	1.94	373	1.96
71	1.55	124	0.17	195	0.40	374	0.30
72	0.29	125	0.36	197	0.28	377	0.69
73	6.15	127	4.29	199	13.36		

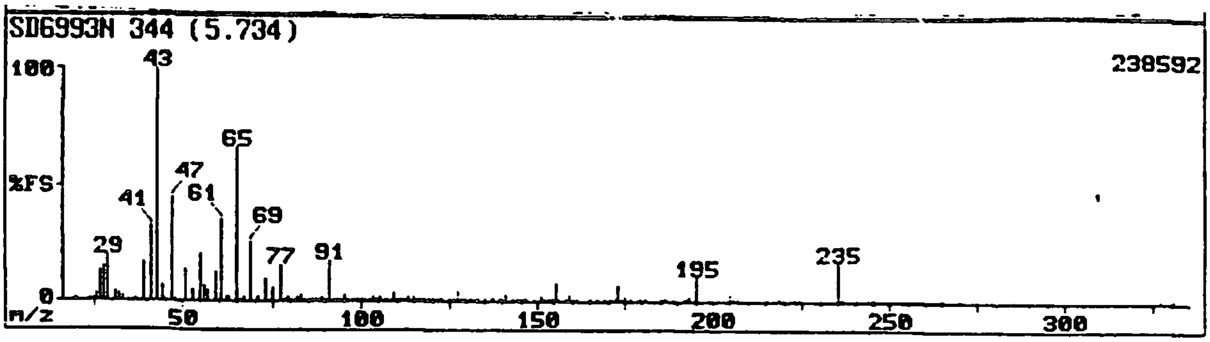
52. Gamma ray initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-2-methylpentanes (65)



BD6593N 348 (5.801) 696320

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.02	79	1.27	133	1.01	199	0.28
26	0.09	80	0.11	134	0.07	201	0.10
27	2.46	81	0.28	135	0.97	203	0.09
28	0.85	82	0.97	136	0.09	205	3.42
29	5.85	83	1.65	137	0.25	206	0.27
30	0.16	84	0.40	139	0.46	207	0.19
31	0.25	85	0.55	141	2.54	209	0.18
32	0.26	86	0.09	142	0.18	210	0.04
33	0.57	87	0.82	143	0.93	211	0.11
36	0.04	88	0.23	145	1.17	213	0.04
37	0.08	89	1.08	146	0.08	215	1.67
38	0.28	90	0.30	147	0.83	216	0.17
39	7.57	91	13.38	148	0.05	217	0.09
40	1.54	92	0.95	149	0.32	219	0.76
41	22.06	93	0.58	151	2.61	220	0.08
42	2.87	94	0.24	153	1.05	223	0.28
43	100.00	95	1.99	155	7.68	225	0.84
44	3.64	96	0.21	156	0.49	226	0.05
45	0.48	97	0.58	157	0.11	227	0.03
46	0.36	98	0.13	159	2.76	229	0.02
47	44.12	99	0.25	160	0.23	233	0.05
48	1.01	100	0.13	161	0.83	235	22.21
49	0.03	101	0.97	162	0.04	236	2.11
50	0.36	102	0.17	163	0.12	237	0.18
51	8.42	103	1.08	165	0.40	241	0.08
52	0.45	104	0.25	167	0.95	243	0.04
53	2.76	105	1.35	168	0.08	245	0.75
54	0.39	106	0.12	169	0.37	246	0.09
55	12.06	107	0.12	170	0.04	247	0.06
56	3.20	109	2.83	171	0.18	249	0.06
57	2.50	110	0.17	173	6.91	259	0.03
58	0.20	111	0.26	174	1.22	261	0.06
59	6.07	113	1.28	175	1.74	263	0.10
60	0.33	114	0.22	176	0.16	265	0.39
61	21.76	115	1.00	177	0.38	266	0.05
62	0.76	116	0.10	179	0.31	267	0.10
63	0.32	117	0.23	181	0.29	269	0.05
64	0.58	118	0.11	183	0.07	271	0.03
65	38.24	119	0.26	185	0.95	281	0.07
66	1.08	121	0.92	186	0.10	285	0.07
67	1.04	122	0.08	187	1.66	287	0.11
69	15.15	123	1.01	188	0.13	291	0.05
70	0.44	124	0.09	189	0.08	305	0.05
71	1.18	125	0.10	191	0.76	307	0.14
72	0.25	126	0.07	192	1.93	311	0.09
73	5.33	127	3.27	193	2.72	327	0.30
74	0.38	128	0.18	194	0.13	328	0.04
75	4.49	129	0.39	195	11.03	331	0.23
77	8.24	131	0.33	196	1.05	351	0.15
78	0.71	132	0.20	197	0.12		

53 .D.T.B.P. initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-2-methylpentanes (65)



SD6993N 344 (5.734) 238592

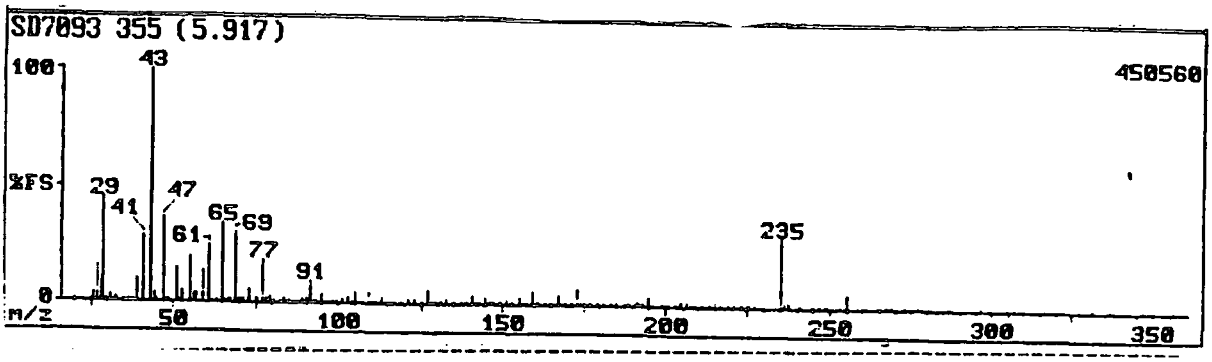
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.26	78	1.23	114	0.42	159	3.14
24	0.11	79	1.72	115	1.48	160	0.24
25	0.24	80	0.21	116	0.12	161	0.90
26	2.60	81	0.75	117	0.40	165	0.52
27	12.88	82	2.15	118	0.16	167	1.11
28	14.16	83	3.14	119	0.41	169	0.47
29	18.99	84	0.69	120	0.11	171	0.20
31	4.13	85	1.12	121	1.36	172	0.27
32	2.52	86	0.22	122	0.19	173	7.19
33	2.01	87	1.21	123	1.25	174	1.05
37	0.49	88	0.53	125	0.12	175	1.98
39	16.95	89	1.72	126	0.22	177	0.37
41	31.76	90	1.35	127	3.84	179	0.29
43	100.00	91	17.70	128	0.31	181	0.27
44	6.49	92	1.40	129	0.46	185	1.03
45	1.24	93	1.04	131	0.49	186	0.11
47	44.64	94	0.40	132	0.35	187	1.06
48	0.82	95	2.95	133	1.38	192	0.84
51	13.95	96	0.41	135	1.19	193	2.39
53	4.64	97	0.88	137	0.27	195	10.52
55	20.49	98	0.11	139	0.47	199	0.22
56	6.63	99	0.43	140	0.15	205	3.08
57	4.48	100	0.34	141	2.76	206	0.11
59	12.34	101	1.41	143	0.95	207	0.12
61	34.76	102	0.30	144	0.11	215	1.07
62	1.49	103	1.74	145	1.39	219	0.49
63	2.23	104	0.48	146	0.21	223	0.15
65	65.67	105	2.15	147	0.93	225	0.35
66	1.21	106	0.21	149	0.25	235	16.85
67	1.80	107	0.17	151	1.77	236	0.96
69	25.32	108	0.37	152	0.09	245	0.61
71	2.41	109	4.08	153	1.24	265	0.28
73	9.76	110	0.23	154	0.36	327	0.19
74	1.38	111	0.43	155	7.83	331	0.21
75	6.25	112	0.26	156	0.20		
77	15.45	113	2.20	158	0.14		

54. Gamma ray initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-3-methylpentanes (66)

SD6493N 356 (5.934) 761856

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.03	83	1.38	146	0.28	219	0.45
26	0.32	84	0.45	147	0.85	220	0.05
27	4.94	85	1.00	148	0.05	221	0.10
28	2.39	86	0.15	149	0.10	223	0.38
29	19.35	87	0.43	151	2.07	224	0.03
30	0.51	88	0.21	152	0.10	225	1.21
31	0.30	89	1.56	153	0.66	226	0.10
32	0.29	90	0.45	155	2.65	227	0.20
33	0.56	91	7.09	156	0.18	228	0.02
36	0.05	92	0.35	157	0.16	229	0.03
37	0.06	93	0.21	159	4.67	233	0.19
38	0.21	95	2.62	160	0.30	235	34.95
39	5.14	96	0.29	161	0.64	236	3.23
40	0.95	97	0.75	162	0.06	237	3.33
41	19.89	98	0.14	163	0.20	238	0.28
42	1.84	99	0.22	165	0.57	239	0.04
43	100.00	100	0.16	167	3.13	241	0.12
44	4.10	101	1.18	168	0.24	243	0.03
45	0.46	102	0.25	169	0.08	245	1.22
46	0.27	103	1.87	171	1.00	246	0.14
47	31.99	104	0.50	173	6.25	247	0.09
48	0.72	105	3.63	174	0.39	249	0.07
49	0.04	106	0.28	175	0.38	251	0.04
50	0.37	107	0.12	177	1.09	253	0.13
51	9.01	109	3.39	178	0.09	255	6.22
52	0.54	110	0.37	179	0.15	256	0.58
53	3.02	111	0.14	181	0.73	257	0.11
54	0.64	113	1.56	182	0.08	259	0.07
55	10.75	114	0.24	183	0.14	261	0.08
56	1.60	115	1.07	185	0.80	263	0.03
57	2.02	116	0.12	187	6.25	265	0.57
58	0.21	117	0.26	188	0.47	266	0.05
59	6.96	118	0.02	189	0.22	267	0.12
60	0.40	119	0.36	191	2.86	269	0.53
61	14.11	121	1.47	192	0.50	270	0.05
62	0.54	122	0.17	193	0.30	271	0.04
63	0.32	123	1.40	195	3.66	273	0.05
64	1.44	124	0.07	196	0.37	277	0.11
65	17.34	125	0.41	197	0.21	279	0.04
66	0.63	127	4.84	199	0.26	281	0.12
67	0.97	128	0.27	201	0.26	285	0.07
69	18.68	129	0.27	203	0.16	287	0.16
70	0.88	131	0.25	205	3.49	291	0.08
71	0.92	132	0.16	206	1.03	297	0.16
72	0.17	133	0.92	207	2.13	299	0.05
73	3.26	134	0.11	208	0.18	305	0.10
74	0.21	135	0.76	209	0.45	307	0.17
75	1.32	136	0.07	210	0.04	311	0.03
77	10.75	137	0.24	211	0.67	317	0.32
78	0.67	139	0.60	212	0.05	318	0.03
79	2.15	141	3.29	213	0.08	319	0.02
80	0.14	142	0.21	215	1.94	327	0.53
81	0.19	143	0.97	216	0.20	328	0.07
82	1.14	145	2.42	217	0.44	331	0.08
337	0.51	339	0.12	347	0.06	356	0.07
338	1.20	345	0.04	351	0.03		

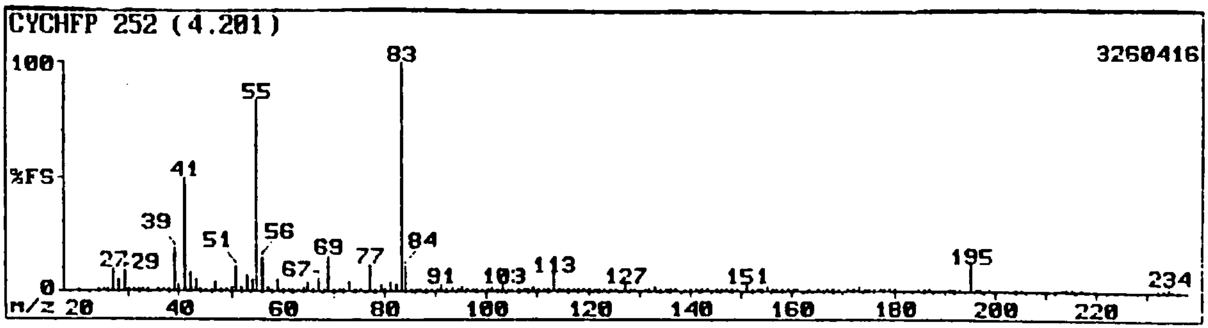
55. D.T.B.P. initiated formation of di-(1,1,2,3,3,3-hexafluoropropyl)-3-methylpentanes (66)



SD7093 355 (5.917) 450560

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.39	80	0.17	139	0.91	205	1.86
24	0.15	82	1.29	141	4.09	207	1.52
25	0.40	83	2.17	142	0.24	207	1.14
26	3.55	84	0.74	143	1.04	209	0.40
27	15.91	85	1.26	145	3.21	211	0.36
28	8.58	86	0.21	146	0.64	213	0.12
29	44.32	87	0.73	147	1.01	215	2.07
30	0.77	88	0.58	149	0.16	217	0.39
31	2.90	89	2.13	151	2.13	219	0.31
32	1.01	90	1.62	153	1.07	221	0.12
33	1.62	91	9.32	155	3.25	223	0.40
35	0.10	92	0.29	156	0.19	225	0.66
36	0.24	93	0.48	157	0.18	225	0.45
37	0.39	95	4.03	159	6.08	227	0.09
38	1.05	96	0.50	160	0.31	234	0.09
39	9.55	97	1.04	161	0.71	235	30.23
41	28.18	98	0.15	163	0.28	236	2.05
43	100.00	99	0.17	165	0.86	237	2.20
44	3.64	101	1.59	167	3.81	241	0.03
45	1.18	103	3.20	168	0.17	245	0.62
47	35.91	104	0.88	169	0.14	247	0.07
48	0.60	105	4.66	171	1.34	249	0.05
51	14.77	106	0.38	173	7.10	253	0.15
52	0.37	107	0.16	174	0.23	255	5.34
53	4.77	109	4.89	175	0.40	261	0.09
55	19.77	110	0.42	177	1.39	265	0.59
56	2.80	111	0.11	179	0.16	267	0.11
57	4.26	113	2.43	181	0.83	269	0.35
59	13.69	114	0.35	183	0.16	273	0.07
61	24.55	115	1.38	185	1.02	277	0.11
62	1.28	116	0.10	187	3.69	281	0.14
63	1.45	117	0.42	188	0.20	287	0.09
65	33.86	119	0.48	189	0.13	297	0.10
66	0.81	121	2.17	191	1.24	305	0.03
67	1.62	123	1.86	191	1.86	307	0.17
69	30.45	125	0.39	192	0.25	317	0.18
70	1.59	127	5.51	193	0.18	327	0.59
71	1.65	128	0.32	195	3.69	331	0.07
73	5.68	129	0.28	196	0.16	337	0.33
75	2.06	131	0.36	199	0.19	338	1.28
77	18.18	133	1.65	199	0.12	347	0.06
78	1.46	135	1.02	201	0.12	356	0.07
79	2.74	137	0.25	203	0.21		

56. Gamma ray initiated formation of (1,1,2,3,3,3-hexaflouoropropyl)-cyclohexane (13)

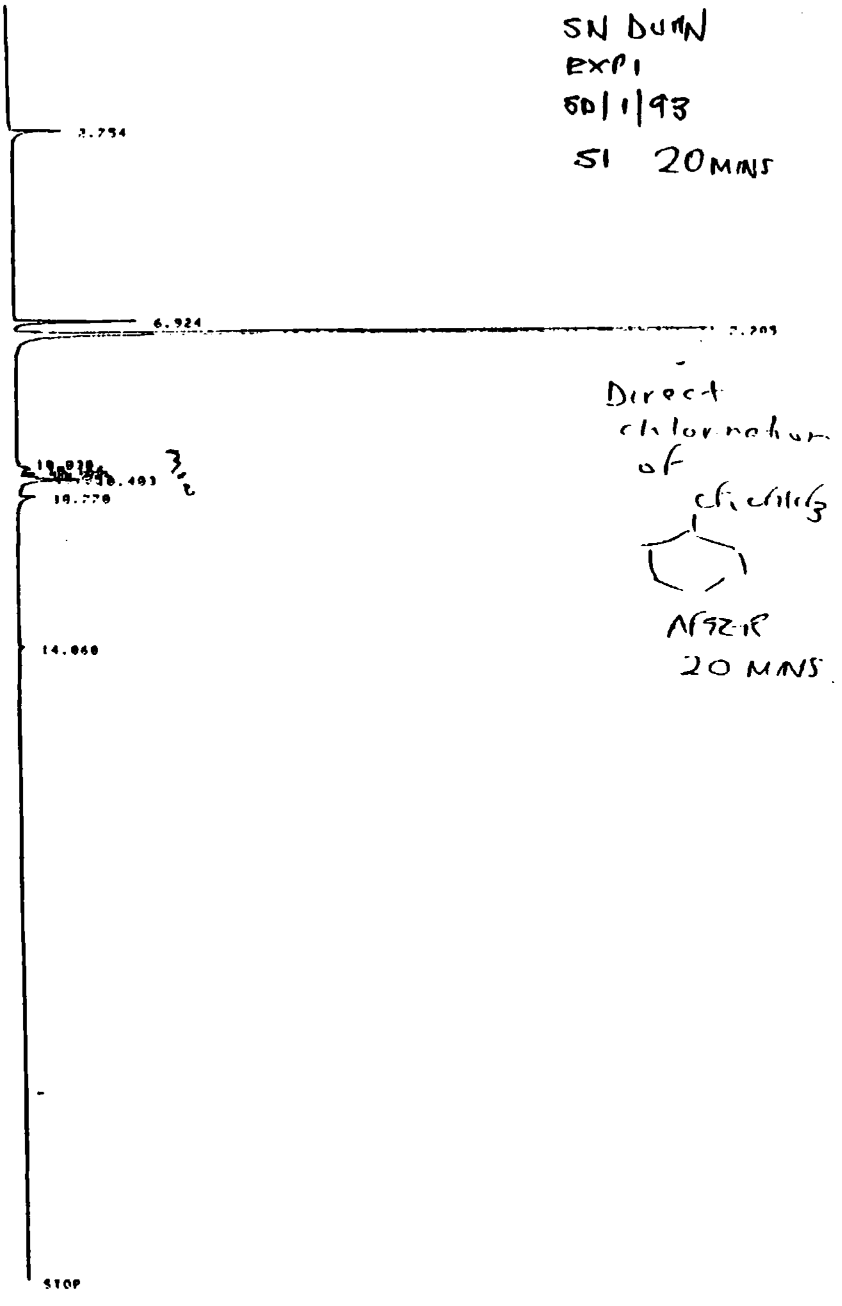


CYCHFP 252 (4.201)

3260416

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.02	43	5.34	62	0.20	82	3.36	101	1.01	120	0.06	142	0.04	165	0.16	193	0.30
24	0.01	44	0.42	63	0.05	83	100.00	102	0.28	121	0.09	143	0.04	167	0.05	195	12.05
25	0.03	45	0.35	64	1.49	84	10.43	103	2.54	122	0.12	145	1.34	168	0.06	196	1.01
26	0.92	46	0.43	65	4.00	85	1.32	104	0.61	123	0.53	146	0.09	169	0.11	197	0.07
27	10.05	47	3.58	66	0.78	86	0.13	105	0.65	124	0.10	147	0.52	171	0.10	199	0.09
28	5.21	48	0.09	67	5.46	87	0.43	106	0.09	125	0.14	148	0.04	172	0.93	204	0.02
29	0.54	49	0.07	68	1.18	88	0.35	107	0.16	127	2.58	149	0.31	173	1.67	205	0.05
30	0.21	50	1.46	69	15.06	89	1.00	108	0.18	128	0.17	151	2.70	174	0.10	213	1.01
31	0.52	51	10.93	70	0.60	90	1.23	109	2.32	129	0.33	152	0.10	175	0.50	214	0.27
32	0.27	52	1.62	71	1.33	91	2.73	110	0.22	131	0.39	153	0.47	176	0.04	215	0.03
33	0.58	53	7.00	72	0.31	92	0.22	111	0.30	132	0.12	154	0.03	177	0.16	217	0.02
34	0.01	54	4.62	73	3.09	93	1.03	112	0.10	133	1.01	155	1.51	178	0.01	232	0.02
36	0.02	55	83.92	74	0.28	94	0.45	113	0.04	134	0.13	156	0.11	179	0.04	233	0.25
37	0.19	56	14.45	75	1.26	95	1.66	114	0.02	135	0.60	157	0.08	180	0.01	234	2.73
38	0.89	57	2.36	77	12.06	96	0.40	115	1.18	136	0.02	158	0.05	185	0.14	235	0.21
39	10.47	58	0.26	78	0.83	97	0.97	116	0.17	137	0.08	159	0.90	186	0.03		
40	3.30	59	4.77	79	2.58	98	0.17	117	0.28	139	0.37	160	0.06	187	0.10		
41	49.25	60	0.33	80	0.59	99	0.24	118	0.03	140	0.17	161	0.02	191	0.16		
42	7.32	61	1.25	81	3.64	100	0.22	119	0.36	141	0.37	163	0.07	192	0.02		

57. G.C. to show direct chlorination of (1,1,2,3,3,3-hexafluoropropyl)-cyclohexane (13) using chlorine gas.



SN DUNN
EXP1
30/1/93
51 20MINS

Direct chlorination of CF_2CFHCF_3

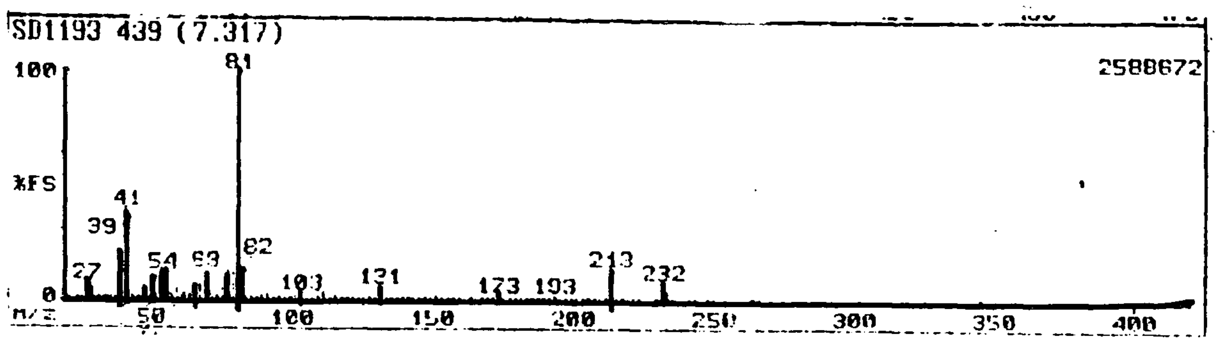
AF92 1R
20 MINS

```
RUN#      4            JAN  1, 1991  06:20:44

AREA%
      RT          AREA TYPE   WIDTH       AREA%
   2.754         25606   PB    .045     1.89371
   6.924         54027   VB    .041     4.05476
   7.205       1171044   PB    .041    86.60520
  10.038          2216   BV    .054      .16336
  10.166         11103   VV    .070      .82113
  10.269          9340   VV    .046      .69134
  10.353          8002   VV    .034      .59179
  10.403         47955   VV    .069     3.54694
  10.770         18029   VB    .090     1.33340
  14.060          4021   PB    .057      .29738

TOTAL AREA=1352162
MUL FACTOR=1.0000E+00
```

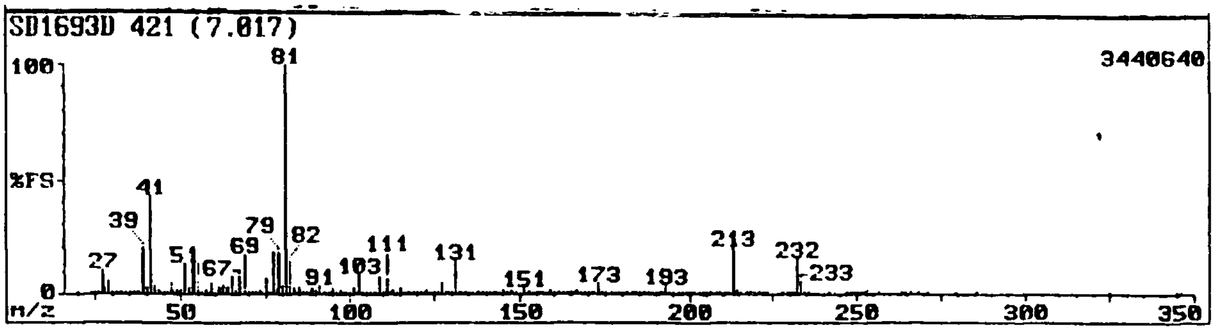
58. Formation of 1-(1,1,2,3,3,3-hexafluoropropyl)-chloro-cyclohexanes (67) / (68) / (69) using chlorine gas and carbon disulphide as a solvating solvent



SD1193 439 (7.317) 2588672

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.03	75	4.83	127	2.27	184	0.04
24	0.01	76	0.90	128	0.22	185	0.51
25	0.03	77	12.50	129	0.54	186	0.05
26	0.64	78	1.43	130	0.27	187	0.08
27	7.59	79	12.82	131	6.88	188	0.01
28	2.03	80	4.51	132	0.61	189	0.05
29	4.71	81	100.00	133	0.64	190	0.02
30	0.12	82	11.23	134	0.08	191	0.08
31	0.46	83	1.92	135	0.31	192	0.05
32	0.19	84	0.54	136	0.03	193	3.05
33	0.51	85	1.68	137	0.12	194	0.20
34	0.01	86	0.23	138	0.04	195	0.07
35	0.09	87	0.81	139	0.28	197	0.20
36	0.31	88	0.63	140	0.17	198	0.03
37	0.27	89	1.79	141	0.65	199	0.28
38	1.13	90	1.20	142	0.12	200	0.03
39	19.62	91	2.61	143	0.27	201	0.01
40	2.61	92	0.34	145	1.09	203	0.05
41	39.56	93	0.36	146	0.08	204	0.34
42	3.20	94	0.13	147	1.23	205	0.25
43	1.50	95	1.75	148	0.11	206	0.04
44	0.31	96	0.55	149	0.22	207	0.03
45	0.34	97	1.09	151	1.81	208	0.01
46	0.43	98	0.23	152	0.11	209	0.04
47	4.59	99	0.28	153	0.97	211	0.15
48	0.16	100	0.24	154	0.08	212	0.30
49	1.42	101	1.80	155	0.10	213	14.24
50	1.81	102	0.41	156	0.02	214	1.33
51	11.71	103	4.31	157	0.08	215	0.07
52	2.28	104	0.59	158	0.06	217	0.07
53	12.18	105	0.36	159	1.18	218	0.08
54	12.50	106	0.09	160	0.08	219	0.02
55	12.50	107	0.19	161	0.07	221	0.01
56	0.86	108	0.21	163	0.18	223	0.02
57	1.80	109	3.04	164	0.02	229	0.06
58	0.26	110	0.66	165	0.34	230	0.01
59	4.83	111	3.48	167	1.32	231	0.01
60	0.35	112	0.72	168	0.10	232	8.94
61	2.00	113	0.89	169	0.23	233	3.72
62	3.05	114	0.39	170	0.03	234	0.31
63	2.20	115	1.47	171	0.33	235	0.02
64	2.37	116	0.24	172	0.70	241	0.01
65	6.57	117	0.36	173	3.01	243	0.01
66	1.85	118	0.05	174	0.26	248	0.02
67	6.33	119	0.31	175	0.02	250	0.01
69	13.45	120	0.08	177	0.41	263	0.07
70	0.52	121	0.66	178	0.04	264	0.01
71	0.97	122	0.15	179	0.03	266	0.01
72	0.33	123	0.99	180	0.02	325	0.01
73	1.81	124	0.20	181	0.03	345	0.02
74	0.30	125	0.21	183	0.05	346	0.01

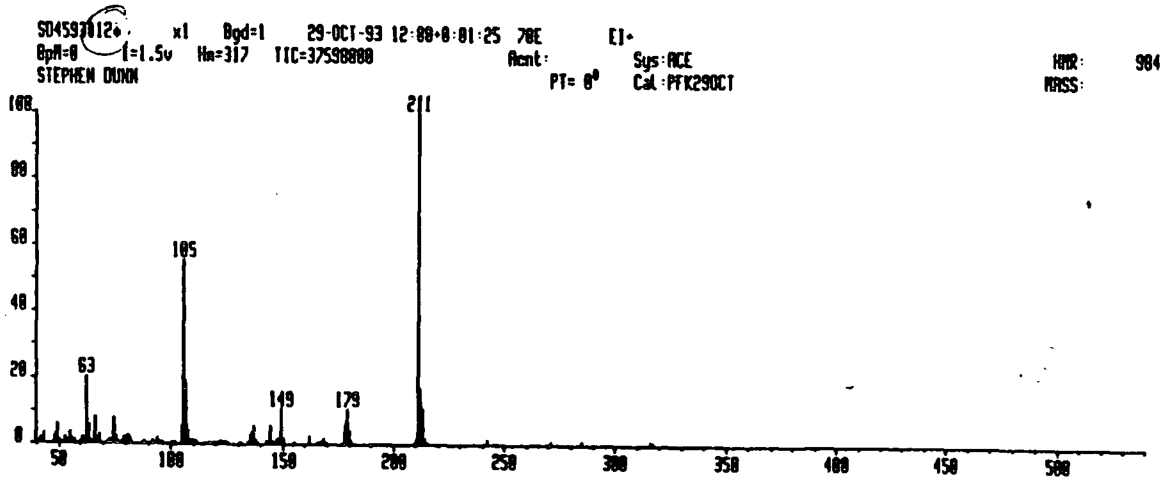
59. Formation of a mixture of 1-(1,1,2,3,3,3-hexafluoropropyl)-3-chlorocyclohexane (68) and 4-chloro-(1,1,2,3,3,3-hexafluoropropyl)-cyclohexane (67) using sulphuryl chloride.



SD1693D 421 (7.017) 3440640

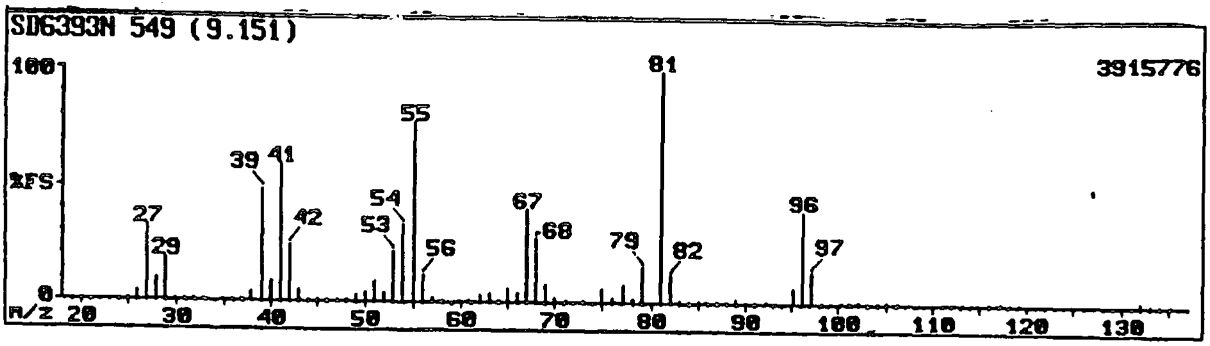
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.03	48	0.16	74	0.32	99	0.49	124	0.32	149	0.40	175	0.04	204	0.51	241	0.01
24	0.01	49	1.68	75	6.79	100	0.36	125	0.41	151	3.07	177	0.60	205	0.36	243	0.01
25	0.04	50	2.11	76	1.00	101	3.39	126	0.10	152	0.14	178	0.05	206	0.06	247	0.01
26	0.92	51	13.93	77	10.33	102	0.60	127	4.46	153	1.60	179	0.13	207	0.04	248	0.04
27	10.60	52	2.50	78	1.90	103	0.45	128	0.40	154	0.13	180	0.02	208	0.02	249	0.01
28	2.95	53	12.45	79	18.01	104	1.10	129	1.10	155	0.17	181	0.04	209	0.06	250	0.02
29	6.19	54	13.45	80	3.57	105	0.66	130	0.20	156	0.02	183	0.08	211	0.22	256	0.02
30	0.16	55	13.33	81	100.00	106	0.15	131	14.76	157	0.14	184	0.05	212	0.56	263	0.07
31	0.62	56	1.00	82	14.52	107	0.37	132	1.10	158	0.08	185	0.76	213	20.36	264	0.01
32	0.22	57	2.11	83	2.62	108	0.27	133	1.17	159	1.09	186	0.07	214	1.71	266	0.01
33	0.60	58	0.27	84	0.74	109	7.29	134	0.12	160	0.12	187	0.13	215	0.09	268	0.01
34	0.01	59	3.27	85	2.47	110	1.12	135	0.61	161	0.11	188	0.01	217	1.36	271	0.01
35	0.11	60	0.43	86	0.33	111	6.79	136	0.05	162	0.02	189	0.09	218	0.11	279	0.01
36	0.34	61	2.47	87	1.22	112	1.32	137	0.26	163	0.29	190	0.03	219	0.02	285	0.01
37	0.28	62	3.66	88	0.97	113	1.71	138	0.06	164	0.03	191	1.02	221	0.01	325	0.02
38	1.20	63	2.62	89	2.95	114	0.69	139	0.50	165	0.53	192	0.07	222	0.01	345	0.09
39	20.24	64	2.86	90	2.02	115	2.74	140	0.31	166	0.04	193	4.32	223	0.01	346	0.01
40	2.00	65	0.10	91	4.35	116	0.46	141	1.27	167	1.99	194	0.39	227	0.01		
41	42.38	66	2.26	92	0.54	117	0.60	142	0.20	168	0.14	195	0.04	229	0.12		
42	3.60	67	0.21	93	0.64	118	0.08	143	0.54	169	0.37	197	0.42	230	0.01		
43	1.90	69	17.26	94	0.14	119	0.62	144	0.07	170	0.03	198	0.03	231	0.94		
44	0.50	70	0.67	95	2.95	120	0.12	145	1.99	171	0.49	199	0.43	232	15.40		
45	0.41	71	1.29	96	0.09	121	1.32	146	0.12	172	1.00	200	0.04	233	5.45		
46	0.48	72	0.42	97	1.75	122	0.26	147	2.17	173	4.64	201	0.01	234	0.40		
47	5.09	73	2.41	98	0.41	123	1.83	148	0.17	174	0.35	203	0.06	235	0.03		

60. Attempted nucleophilic substitution of 1-(1,1,2,3,3,3-hexafluoropropyl)-chlorocyclohexanes (67) / (68) using thiophenol.



```
SD45938128*        x1    Bgd=1     29-OCT-93 12:00+0:01:25  70E         EI+          1.1
BpM=0      I=1.5v   Hm=317   TIC=37598000                   Acnt:               Sys:ACE
STEPHEN DUNN                                                       PT= 0      Cal:PFK290CT
           Mass        % Base                          Mass       % Base
           40.62         0.36                          135.46        2.81
           41.59         1.48                          136.44        5.28
           42.48         1.28                          137.42        1.05
           43.45         2.57                          138.37        0.45
           48.33         1.92                          142.30        0.69
           49.30         5.84                          144.23        5.20
           50.28         0.58                          145.21        0.60
           51.26         0.37                          147.18        1.24
           53.21         1.55                          148.13        1.13
           54.18         0.83                          149.13       10.40
           55.07         0.62                          150.12        1.28
           55.16         3.24                          161.70        2.16
           56.05         1.00                          165.56        0.33
           57.03         0.59                          167.53        0.86
           60.92         1.77                          168.51        1.20
           61.81         0.52                          178.20        5.56
           61.89         0.39                          179.18       10.40
           62.97        19.96                          180.15        3.87
           63.85         5.20                          181.13        0.82
           64.82         0.77                          209.25        0.42
           66.70         7.55                          210.23        1.63
           67.66         0.52                          211.20      100.00
           67.75         1.25                          212.18       16.53
           68.63         0.79                          213.14       10.13
           68.72         2.36                          214.13        1.41
           71.56         0.49                          242.29        1.06
           72.53         0.61                          270.64        0.58
           73.43         0.45                          285.12        0.57
           73.51         0.86                          316.25        0.83
           74.48         7.08                          317.23        0.39
           75.46         2.17
           76.43         0.43
           78.30         0.43
           78.39         0.77
           79.27         1.72
           79.36         0.37
           80.29         1.52
           81.22         2.02
           81.30         0.38
           82.28         1.02
           88.06         0.57
           91.95         0.53
           92.84         0.47
           93.85         1.26
           95.85         0.47
          101.60         0.36
          104.46         5.20
          105.44        55.22
          106.41        18.88
          107.39         3.63
          108.35         0.86
          108.45         0.49
          109.43         1.16
          111.30         0.70
          117.08         0.34
          121.07         0.37
          121.93         0.54
          123.90         0.41
          124.88         0.30
          134.58         0.54
```

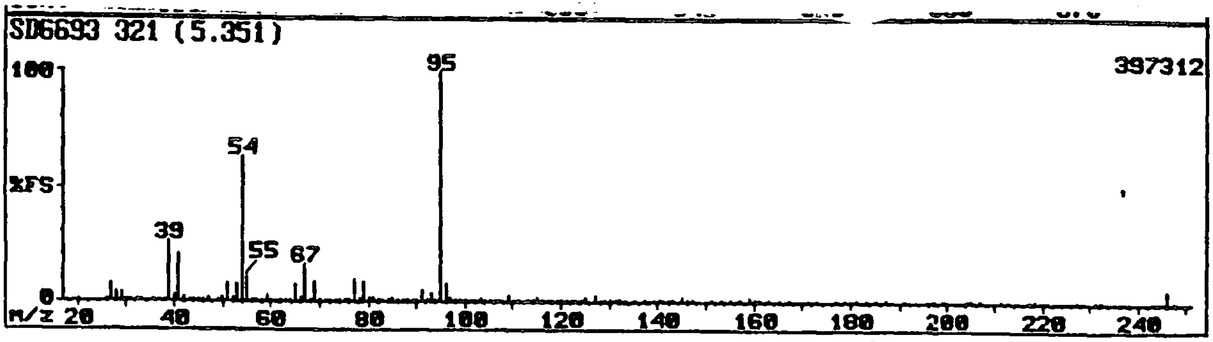
61. A Gamma ray initiated attempted addition of 1-methyl-4-chlorocylohexane to hexafluoropropene



SD6393N 549 (9.151) 3915776

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.01	46	0.86	69	7.32	95	6.69
24	0.02	47	0.38	70	1.86	96	39.75
25	0.12	48	0.24	71	0.10	97	13.91
26	3.74	49	2.93	73	0.55	98	0.93
27	31.80	50	3.71	75	6.12	99	0.08
28	9.31	51	8.79	76	2.30	100	0.02
29	18.31	52	3.63	77	7.32	101	0.07
30	0.43	53	20.92	78	1.73	102	0.06
31	0.06	54	33.47	79	15.48	103	0.27
32	0.03	55	77.82	81	100.00	104	0.14
33	0.09	56	11.19	82	11.92	105	0.09
35	0.25	57	2.09	83	0.79	106	0.02
36	0.55	58	0.11	84	0.07	112	0.01
37	1.19	60	0.13	85	0.08	113	0.02
38	3.74	61	1.15	86	0.06	116	0.06
39	48.95	62	3.11	87	0.15	117	0.12
40	8.47	63	3.63	88	0.34	118	0.03
41	59.41	64	1.12	89	1.49	119	0.04
42	23.85	65	5.99	90	1.02	132	2.38
43	5.33	66	4.18	91	1.45	133	0.15
44	0.27	67	40.17	92	0.37	134	0.78
45	0.56	68	26.78	93	0.68	135	0.06

62. A D.T.B.P. initiated attempted addition of 1-methyl-4-chlorocylohexane to hexafluoropropene



SD6693 321 (5.351) 397312

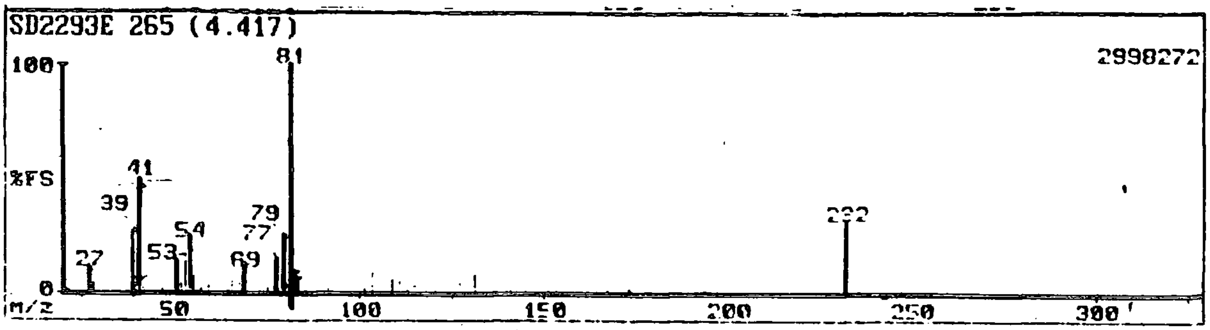
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.04	65	7.86	102	0.23	146	0.17
26	0.64	66	1.50	103	1.98	147	0.38
27	7.93	67	16.75	104	0.46	151	1.11
28	3.87	68	1.24	105	0.47	153	0.22
29	4.12	69	8.83	106	0.17	155	0.17
30	0.12	70	0.36	107	0.20	157	0.11
31	0.37	71	0.61	109	2.50	159	1.58
32	0.43	72	0.27	110	0.62	160	0.11
33	0.47	73	0.81	111	0.34	161	0.17
36	0.11	74	0.19	113	0.77	163	0.15
37	0.26	75	0.97	114	0.43	165	0.57
38	1.26	76	0.21	115	1.51	167	0.57
39	26.03	77	9.92	116	0.25	171	0.22
40	3.13	78	1.85	117	1.22	173	0.35
41	20.62	79	8.51	118	0.10	177	0.28
42	1.61	80	2.38	119	0.21	179	0.14
43	1.02	81	1.66	120	0.04	181	0.34
44	0.22	82	1.18	121	0.66	183	0.08
45	0.29	83	1.06	122	0.05	185	0.84
46	0.28	84	0.39	123	0.78	187	0.39
47	2.37	85	2.03	124	0.22	191	0.31
49	0.08	86	0.22	125	1.68	197	0.16
50	1.63	87	0.11	127	2.53	199	0.14
51	7.67	88	0.33	128	0.29	204	0.13
52	2.24	89	0.81	129	0.70	205	0.22
53	7.67	90	0.24	130	0.24	207	0.41
54	63.40	91	5.03	131	0.13	211	0.33
55	10.89	92	0.46	132	0.16	217	0.14
56	0.54	93	3.93	133	0.33	218	0.11
57	1.03	94	0.63	135	0.31	227	0.16
58	0.15	95	100.00	137	0.22	231	1.16
59	2.53	96	7.73	139	0.33	232	0.10
60	0.19	97	2.01	140	0.15	246	5.61
61	1.06	98	0.32	141	1.06	247	0.30
62	0.43	99	0.48	142	0.15		
63	1.32	100	0.16	143	0.18		
64	0.72	101	1.27	145	2.05		

63. 4-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene (71)

SD3093A 250 (4.167) 3178496

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.03	44	0.46	64	1.39	85	1.95	105	0.11	127	4.93	148	0.10	173	1.68	197	0.72
24	0.01	45	0.35	65	6.44	86	0.86	106	0.08	128	0.58	149	0.15	174	0.15	198	0.06
25	0.04	46	0.31	66	3.35	87	0.16	107	0.36	129	0.93	151	1.96	175	0.03	199	0.03
26	0.98	47	2.65	67	5.51	88	0.71	108	0.22	130	0.30	152	0.10	177	0.71	203	0.04
27	9.66	48	0.07	69	14.30	89	1.23	109	7.02	131	0.63	153	1.06	178	0.06	204	0.43
28	7.25	49	0.17	70	0.69	90	1.22	110	1.86	132	0.77	154	0.09	179	0.03	205	0.04
29	2.16	50	3.54	71	0.73	91	2.55	111	6.12	133	0.08	155	0.06	181	0.03	209	0.03
30	0.07	51	14.02	72	0.35	92	0.33	112	0.08	134	0.09	157	0.12	183	0.06	211	0.14
31	0.68	52	4.32	73	0.64	93	0.41	113	1.43	135	0.72	158	0.18	184	0.04	212	0.08
32	1.15	53	15.21	74	0.51	94	0.19	114	0.90	136	0.06	159	0.69	185	0.32	213	1.55
33	0.51	54	25.90	75	2.38	95	2.71	115	3.64	137	0.10	160	0.05	186	0.03	214	0.14
34	0.01	55	7.10	76	0.52	96	1.25	116	0.60	138	0.06	161	0.03	187	0.02	217	1.35
36	0.03	56	0.65	77	22.16	97	1.43	117	0.15	139	0.39	163	0.19	189	0.06	218	0.11
37	0.32	57	2.06	78	3.40	98	0.34	119	0.45	140	0.34	164	0.02	190	0.05	231	0.38
38	1.50	58	0.21	79	35.05	99	0.47	120	0.14	141	1.10	165	0.24	191	0.38	232	28.40
39	22.94	59	2.04	80	5.48	100	0.32	121	0.05	142	0.20	167	1.00	192	0.03	233	2.61
40	2.58	60	0.19	81	100.00	101	3.09	122	0.28	143	0.35	168	0.07	193	1.22	234	0.19
41	44.85	61	0.25	82	12.76	102	0.56	123	1.24	145	1.06	169	0.11	194	0.10	235	0.01
42	2.22	62	0.48	83	11.08	103	11.60	124	0.23	146	0.08	171	0.35	195	0.44	281	0.03
43	0.47	63	1.79	84	1.17	104	0.71	125	0.18	147	1.15	172	0.29	196	0.03		

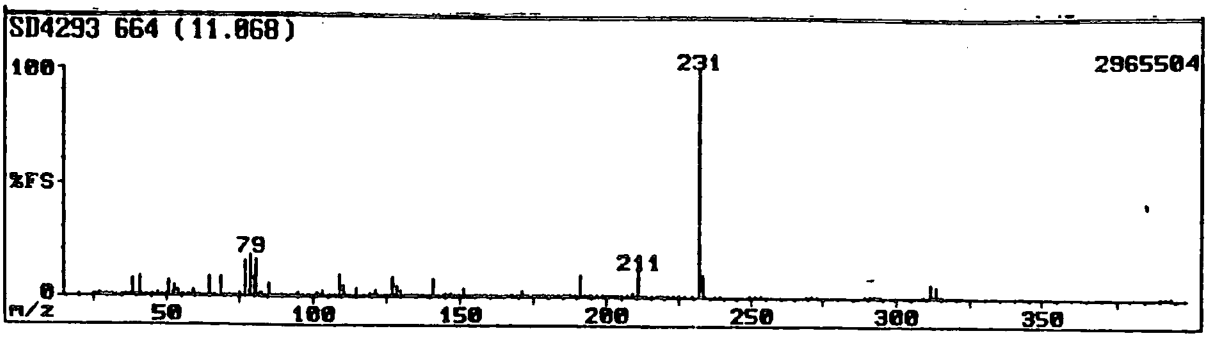
64. 4-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene (71)



SD2293E 265 (4.417) 2998272

Pk#	Mass	Abs Int	Rel Int	Pk#	Mass	Abs Int	Rel Int	Pk#	Mass	Abs Int	Rel Int	Pk#	Mass	Abs Int	Rel Int	Pk#	Mass	Abs Int	Rel Int
1	26	34560	1.15	13	52	111616	3.72	25	75	47360	1.58	37	103	248832	8.30	49	153	33024	1.10
2	27	331776	11.07	14	53	393216	13.11	26	77	446464	14.89	38	109	164864	5.50	50	167	34048	1.14
3	28	105472	3.52	15	54	712704	23.77	27	78	68608	2.29	39	111	143360	4.78	51	173	54528	1.82
4	29	72704	2.42	16	55	202752	6.76	28	79	688128	22.95	40	113	34816	1.16	52	193	38400	1.28
5	38	54272	1.81	17	57	53760	1.79	29	80	103424	3.45	41	115	89088	2.97	53	213	47360	1.58
6	39	815104	27.19	18	59	79872	2.66	30	81	2998272	100.00	42	123	31488	1.05	54	217	45568	1.52
7	40	86016	2.87	19	63	45056	1.50	31	82	227328	7.58	43	127	129024	4.30	55	232	901376	30.07
8	41	1523712	50.82	20	64	33792	1.13	32	83	215040	7.17	44	131	230400	7.68	56	233	73728	2.46
9	42	68608	2.29	21	65	150528	5.02	33	85	34816	1.16	45	141	31232	1.04				
10	47	68608	2.29	22	66	74752	2.49	34	91	50688	1.69	46	145	30976	1.03				
11	50	96256	3.21	23	67	120832	4.03	35	95	50944	1.70	47	147	34816	1.16				
12	51	401408	13.39	24	69	307200	10.25	36	101	63744	2.13	48	151	60928	2.03				

65. 1-(1,1,2,3,3,3-Hexafluoropropyl)-3,4-dibromocyclohexane (73)

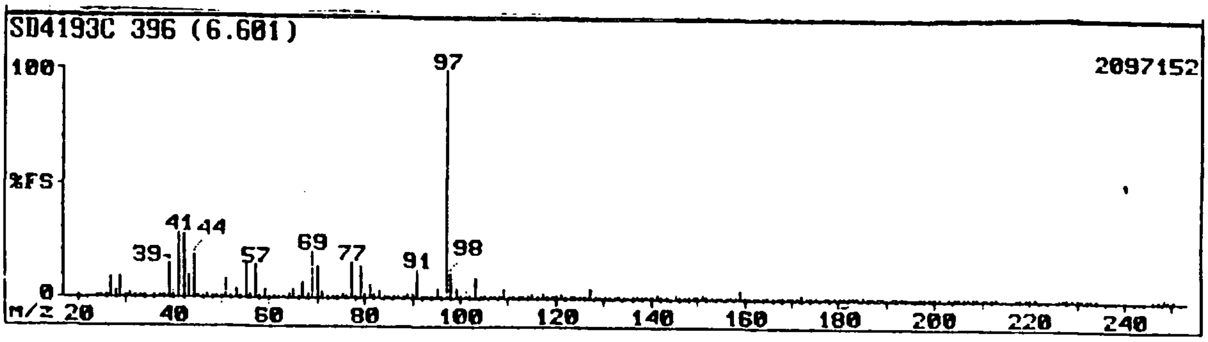


SD4293 664 (11.868)

2965504

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
24	0.00	50	1.42	76	0.39	101	2.30	126	0.07	151	4.11	177	0.37	204	0.10	269	0.02
25	0.01	51	7.01	77	15.33	102	0.62	127	0.53	152	0.30	178	0.04	205	0.14	271	0.07
26	0.10	52	1.09	78	3.35	103	2.07	128	0.92	153	0.29	179	0.05	207	0.07	273	0.04
27	1.93	53	5.32	79	18.63	104	0.35	129	5.10	154	0.02	180	0.05	209	1.52	289	0.02
28	0.42	54	3.00	80	9.12	105	0.53	130	2.94	155	0.10	181	0.34	210	0.13	291	0.46
29	0.52	55	0.05	81	16.05	106	0.49	131	0.96	156	0.03	182	0.03	211	11.46	292	0.03
30	0.02	56	0.09	82	2.42	107	1.22	132	0.30	157	0.19	183	0.45	212	1.30	293	0.44
31	0.16	57	0.06	83	1.04	108	0.36	133	0.74	158	0.12	184	0.06	213	0.11	294	0.04
32	0.06	58	0.00	84	0.49	109	9.94	134	0.22	159	1.29	185	1.13	215	0.02	309	0.07
33	0.10	59	2.66	85	5.77	110	4.65	135	0.35	160	0.10	186	0.10	217	0.16	311	5.59
35	0.01	60	0.12	86	0.39	111	1.70	136	0.04	161	0.30	187	0.16	218	0.02	312	0.30
36	0.05	61	0.15	87	0.10	112	0.21	137	0.20	162	0.09	188	0.03	219	0.02	313	5.28
37	0.11	62	0.21	88	0.49	113	1.15	138	0.06	163	0.49	189	0.37	221	0.05	314	0.43
38	0.56	63	1.05	89	0.99	114	0.90	139	0.55	164	0.05	190	0.10	223	0.05	315	0.02
39	7.77	64	1.22	90	0.00	115	2.65	140	0.35	165	1.33	191	9.33	225	0.01	390	0.02
40	0.03	65	0.98	91	1.41	116	0.37	141	7.49	166	0.10	192	0.93	227	0.01	392	0.03
41	0.70	66	1.23	92	0.17	117	0.41	142	1.17	167	0.60	193	0.09	229	1.15	394	0.01
42	0.36	67	0.00	93	0.60	118	0.04	143	0.30	168	0.08	194	0.01	231	100.00		
43	0.94	69	0.70	94	0.13	119	2.20	144	0.04	169	0.27	195	0.04	232	9.25		
44	0.09	70	0.30	95	2.35	120	0.23	145	1.91	170	0.15	197	0.10	233	0.42		
45	0.13	71	0.50	96	0.77	121	2.73	146	0.15	171	2.69	199	0.12	237	0.03		
46	0.10	72	0.10	97	1.27	122	0.62	147	1.06	172	0.20	200	0.01	239	0.03		
47	2.10	73	0.31	98	0.74	123	0.66	148	0.14	173	0.16	201	0.07	249	0.02		
48	0.06	74	0.32	99	0.34	124	0.10	149	0.74	175	0.06	202	0.01	251	0.04		
49	0.07	75	1.46	100	0.21	125	0.22	150	0.08	176	0.02	203	0.54	253	0.03		

66. 4-(1,1,2,3,3,3-Hexafluoropropyl)-cyclohexene oxide (75)



SD4193C 396 (6.601)

2097152

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.01	47	2.36	70	13.20	93	0.30	116	0.27	139	1.20	163	0.19	187	0.23	218	0.29
24	0.01	48	0.08	71	2.04	94	0.10	117	1.67	140	0.29	164	0.04	188	0.04	219	0.21
25	0.03	49	0.20	72	0.63	95	3.91	118	0.17	141	2.21	165	0.72	189	0.12	220	0.06
26	0.71	50	0.94	73	1.32	96	1.16	119	1.16	142	0.21	166	0.10	191	1.05	221	0.16
27	0.30	51	7.91	74	0.19	97	100.00	120	0.13	143	0.10	167	0.30	192	0.13	226	0.06
28	2.59	52	0.98	75	1.84	98	10.25	121	1.66	145	2.14	168	0.03	193	0.05	227	0.06
29	0.59	53	4.10	76	0.40	99	3.71	122	0.23	146	0.24	169	0.13	197	0.32	228	0.02
30	0.19	54	1.26	77	15.43	100	0.44	123	0.29	147	0.73	170	0.03	198	0.05	229	0.04
31	1.78	55	14.84	78	1.22	101	2.73	124	0.03	148	0.07	171	0.62	199	0.56	230	0.05
32	0.16	56	2.19	79	14.06	102	0.55	125	0.23	149	0.13	172	1.66	200	0.26	231	0.40
33	0.49	57	15.04	80	1.54	103	9.13	126	0.14	150	0.04	173	0.40	201	0.05	232	0.05
34	0.01	58	0.70	81	5.91	104	0.79	127	3.52	151	1.07	174	0.03	203	0.02	233	0.72
36	0.01	59	3.71	82	2.12	105	0.60	128	0.45	152	0.14	175	0.01	204	0.29	234	0.06
37	0.24	60	0.22	83	3.13	106	0.21	129	1.17	153	0.52	177	0.43	205	0.52	246	0.04
38	1.10	61	0.20	84	0.03	107	0.29	130	0.19	154	0.12	178	0.06	206	0.06	247	0.77
39	14.63	62	0.32	85	1.00	108	0.45	131	0.59	155	0.17	179	1.33	207	0.10	248	1.72
40	2.99	63	0.92	86	0.13	109	3.01	132	0.25	156	0.02	180	0.10	208	0.04	249	0.21
41	20.13	64	1.62	87	0.16	110	0.55	133	0.99	157	0.50	181	0.74	209	0.03	250	0.02
42	27.54	65	0.25	88	0.70	111	0.54	134	0.12	158	0.16	182	0.07	210	0.05		
43	10.16	66	1.12	89	2.12	112	0.17	135	0.66	159	3.06	183	0.07	211	0.14		
44	18.75	67	6.54	90	1.79	113	1.43	136	0.07	160	0.31	184	0.02	212	0.02		
45	0.96	68	1.67	91	12.70	114	0.44	137	0.15	161	0.66	185	2.03	213	0.11		
46	0.44	69	20.12	92	0.63	115	2.09	138	0.04	162	0.06	186	0.50	217	0.08		

APPENDIX 4
RESEARCH COLLOQUIA, SEMINARS, LECTURES AND CONFERENCES

Appendix 4
Colloquia, Induction Courses and Conferences

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing:-

a) all research colloquia, seminars and lectures arranged by the Department of Chemistry during the period of the author's residence as a postgraduate student.

b) lectures organised by Durham University Chemical Society.

c) details of the postgraduate induction course.

d) all research conferences attended and papers presented by the author during the period when research for the thesis was carried out.

*a) Colloquia, Lectures and Seminars From Invited Speakers **1992 - 1995***

1992

October 15 Dr M. Glazer & Dr. S. Tarling (Oxford University & Birbeck College, London),
'It Pays to be British! - The Chemist's Role as an Expert Witness in Patent Litigation'

October 20 Dr. H. E. Bryndza (Du Pont Central Research),
'Synthesis, Reactions and Thermochemistry of Metal (Alkyl) Cyanide Complexes and Their Impact on Olefin Hydrocyanation Catalysis'

October 22 Prof. A. Davies* (University College London),
'The Ingold-Albert Lecture The Behaviour of Hydrogen as a Pseudometal'

October 28 Dr. J. K . Cockcroft (University of Durham),
'R'ecent Developments in Powder Diffraction'

October 29 Dr. J. Emsley (Imperial College, London),
'The Shocking History of Phosphorus'

November 4 Dr. T. P. Kee (University of Leeds),
'Synthesis and Co-ordination Chemistry of Silylated Phosphites'

November 5 Dr. C. J. Ludman (University of Durham),
'Explosions, A Demonstration Lecture'

November 11 Prof. D. Robins†* (Glasgow University),
Pyrrolizidine Alkaloids : Biological Activity, Biosynthesis and Benefits

November 12 Prof. M. R. Truter (University College, London)
'Luck and Logic in Host - Guest Chemistry'

November 18 Dr. R. Nix†* (Queen Mary College, London),
'Characterisation of Heterogeneous Catalysts'

November 25 Prof. Y. Vallee. (University of Caen),
'Reactive Thiocarbonyl Compounds'

November 25 Prof. L. D. Quin† (University of Massachusetts, Amherst),
'Fragmentation of Phosphorous Heterocycles as a Route to Phosphoryl Species with Uncommon Bonding'

November 26 Dr. D. Humber (Glaxo, Greenford),
'AIDS - The Development of a Novel Series of Inhibitors of HIV'

December 2 Prof. A. F. Hegarty (University College, Dublin),
'Highly Reactive Enols Stabilised by Steric Protection'

December 2 Dr. R. A. Aitken† (University of St. Andrews),
'The Versatile Cycloaddition Chemistry of $Bu_3P.CS_2$*'*

December 3 Prof. P. Edwards (Birmingham University),
'The SCI Lecture - What is Metal?'

December 9 Dr. A. N. Burgess† (ICI, Runcorn)
'The Structure of Perfluorinated Ionomer Membranes'

1993

January 20 Dr. D. C. Clary† (University of Cambridge),
'Energy Flow in Chemical Reactions'

January 21 Prof. L. Hall (Cambridge),
'NMR - Window to the Human Body'

January 27 Dr. W. Kerr (University of Strathclyde),
'Development of the Pauson-Khand Annulation Reaction : Organocobalt Mediated Synthesis of Natural and Unnatural Products'

January 28 Prof. J. Mann (University of Reading),
'Murder, Magic and Medicine'

February 3 Prof. S. M. Roberts (University of Exeter),
'Enzymes in Organic Synthesis'

February 10 Dr. D. Gillies† (University of Surrey),
'NMR and Molecular Motion in Solution'

February 11 Prof. S. Knox (Bristol University),
'The Tilden Lecture Organic Chemistry at Polynuclear Metal Centres'

February 17 Dr. R. W. Kemmitt† (University of Leicester),
'Oxatrimethylenemethane Metal Complexes'

February 18 Dr. I. Fraser (ICI, Wilton),
'Reactive Processing of Composite Materials'

February 22 Prof. D. M. Grant (University of Utah),
'Single Crystals, Molecular Structure, and Chemical-Shift Anisotropy'

February 24 Prof. C. J. M. Stirling† (University of Sheffield),
'Chemistry on the Flat-Reactivity of Ordered Systems'

March 10 Dr. P. K. Baker (University College of North Wales, Bangor),
'Chemistry of Highly Versatile 7-Coordinate Complexes'

March 11 Dr. R. A. Y. Jones* (University of East Anglia),
'The Chemistry of Wine Making'

March 17 Dr. R. J. K. Taylor†*(University of East Anglia),
'Adventures in Natural Product Synthesis'

March 24	Prof. I. O. Sutherland† (University of Liverpool), *'Chromogenic Reagents for Cations'*
May 13	Prof. J. A. Pople (Carnegie-Mellon University, Pittsburgh, USA), *'The Boys-Rahman Lecture Applications of Molecular Orbital Theory'*
May 21	Prof. L. Weber (University of Bielefeld), *'Metallo-phospha Alkenes as Synthons in Organometallic Chemistry'*
June 1	Prof. J. P. Konopelski (University of California, Santa Cruz), *'Synthetic Adventures with Enantiomerically Pure Acetals'*
June 2	Prof. F. Ciardelli* (University of Pisa), *'Chiral Discrimination in the Stereospecific Polymerisation of Alpha Olefins'*
June 7	Prof. R. S. Stein* (University of Massachusetts), *'Scattering Studies of Crystalline and Liquid Crystalline Polymers'*
June 16	Prof. A. K. Covington (University of Newcastle), *'Use of Ion Selective Electrodes as Detectors in Ion Chromatography'*
June 17	Prof. O. F. Nielsen, H. C. Δrsted Institute (University of Copenhagen), *'Low-Frequency IR - and Raman Studies of Hydrogen Bonded Liquids'*
September 13	Prof. Dr. A.D. Schlüter (Freie Universität Berlin, Germany), *'Synthesis and Characterisation of Molecular Rods and Ribbons'*
September 13	Dr. K.J. Wynne* (Office of Naval Research, Washington, USA), *'Polymer Surface Design for Minimal Adhesion'*
September 14	Prof. J.M. DeSimone (University of North Carolina, Chapel Hill, USA), *'Homogeneous and Heterogeneous Polymerisations in Environmentally Responsible Carbon Dioxide'*
September 28	Prof. H. Ila* (North Eastern Hill University, India), *'Synthetic Strategies for Cyclopentanoids via Oxoketene Dithioacetals'*

October 4	Prof. F.J. Feher[†] (University of California, Irvine, USA), *'Bridging the Gap between Surfaces and Solution with Sessilquioxanes'*
October 14	Dr. P. Hubberstey (University of Nottingham), *'Alkali Metals: Alchemist's Nightmare, Biochemist's Puzzle and Technologist's Dream'*
October 20	Dr. P. Quayle[†*] (University of Manchester), *'Aspects of Aqueous ROMP Chemistry'*
October 21	Prof. R. Adams[†] (University of South Carolina, USA), *'Chemistry of Metal Carbonyl Cluster Complexes : Development of Cluster Based Alkyne Hydrogenation Catalysts'*
October 27	Dr. R.A.L. Jones[†*] (Cavendish Laboratory, Cambridge), *'Perambulating Polymers'*
November 10	Prof. M.N.R. Ashfold[†] (University of Bristol), *'High Resolution Photofragment Translational Spectroscopy : A New Way to Watch Photodissociation'*
November 17	Dr. A. Parker[†] (Rutherford Appleton Laboratory, Didcot), *'Applications of Time Resolved Resonance Raman Spectroscopy to Chemical and Biochemical Problems'*
November 24	Dr. P.G. Bruce[†] (University of St. Andrews), *'Structure and Properties of Inorganic Solids and Polymers'*
November 25	Dr. R.P. Wayne (University of Oxford), *'The Origin and Evolution of the Atmosphere'*
December 1	Prof. M.A. McKervey[†*] (Queen's University, Belfast), *'Synthesis and Applications of Chemically Modified Calixarenes'*
December 8	Prof. O. Meth-Cohn[†*] (University of Sunderland), *'Friedel's Folly Revisited - A Super Way to Fused Pyridines'*
December 16	Prof. R.F. Hudson (University of Kent), *'Close Encounters of the Second Kind'*

1994

January 26	Prof. J. Evans† (University of Southampton), *'Shining Light on Catalysts'*
February 2	Dr. A. Masters†* (University of Manchester), *'Modelling Water Without Using Pair Potentials*
February 9	Prof. D. Young†* (University of Sussex), *'Chemical and Biological Studies on the Coenzyme Tetrahydrofolic Acid'*
February 16	Prof. K.H. Theopold (University of Delaware, USA), *'Paramagnetic Chromium Alkyls : Synthesis and Reactivity'*
February 23	Prof. P.M. Maitlis†* (University of Sheffield), *'Across the Border : From Homogeneous to Heterogeneous Catalysis'*
March 2	Dr. C. Hunter†* (University of Sheffield), *'Noncovalent Interactions between Aromatic Molecules'*
March 9	Prof. F. Wilkinson (Loughborough University of Technology) *'Nanosecond and Picosecond Laser Flash Photolysis'*
March 10	Prof. S.V. Ley* (University of Cambridge), *'New Methods for Organic Synthesis'*
March 25	Dr. J. Dilworth (University of Essex), *'Technetium and Rhenium Compounds with Applications as Imaging Agents'*
April 28	Prof. R. J. Gillespie (McMaster University, Canada), *'The Molecular Structure of some Metal Fluorides and Oxofluorides: Apparent Exceptions to the VSEPR Model.'*
May 12	Prof. D. A. Humphreys (McMaster University, Canada), *'Bringing Knowledge to Life'*
October 5	Prof. N. L. Owen* (Brigham Young University, Utah, USA), *'Determining Molecular Structure - the INADEQUATE NMR way'*

October 19	Prof. N. Bartlett* (University of California), *'Some Aspects of Ag(II) and Ag(III) Chemistry'*
November 2	Dr P. G. Edwards (University of Wales, Cardiff), *'The Manipulation of Electronic and Structural Diversity in Metal Complexes - New Ligands'*
November 3	Prof. B. F. G. Johnson (Edinburgh University), *'Arene-metal Clusters'*
November 9	Dr G. Hogarth* (University College, London), *'New Vistas in Metal-imido Chemistry'*
November 10	Dr M. Block* (Zeneca Pharmaceuticals, Macclesfield), *'Large-scale Manufacture of ZD 1542, a Thromboxane Antagonist Synthase Inhibitor '*
November 16	Prof. M. Page* (University of Huddersfield), *'Four-membered Rings and b-Lactamase'*
November 23	Dr J. M. J. Williams* (University of Loughborough), *'New Approaches to Asymmetric Catalysis'*
December 7	Prof. D. Briggs* (ICI and University of Durham), *'Surface Mass Spectrometry'*

1995

January 11	Prof. P. Parsons* (University of Reading), *'Applications of Tandem Reactions in Organic Synthesis'*
January 18	Dr G. Rumbles (Imperial College, London), *'Real or Imaginary Third Order Non-linear Optical Materials'*
January 25	Dr D. A. Roberts* (Zeneca Pharmaceuticals), *'The Design and Synthesis of Inhibitors of the Renin-angiotensin System'*
February 1	Dr T. Cosgrove* (University of Bristol), *'Polymers do it at Interfaces'*

February 8 Dr D. O'Hare (University of Oxford),
'Synthesis and Solid-state Properties of Poly-, Oligo- and Multidecker Metallocenes'

February 22 Prof. E. Schaumann* (University of Clausthal),
'Silicon- and Sulphur-mediated Ring-opening Reactions of Epoxide'

March 1 Dr M. Rosseinsky (University of Oxford),
'Fullerene Intercalation Chemistry'

March 22 Dr M. Taylor (University of Auckland, New Zealand),
'Structural Methods in Main-group Chemistry'

April 26 Dr M. Schroder (University of Edinburgh),
'Redox-active Macrocyclic Complexes : Rings, Stacks and Liquid Crystals'

May 4 Prof. A. J. Kresge* (University of Toronto),
'The Ingold Lecture Reactive Intermediates : Carboxylic-acid Enols and Other Unstable Species'

October 11 Prof. P. Lugar (Frei Univ Berlin, FRG),
'Low Temperature Crystallography'

October 13 Prof. R. Schmultzer (Univ Braunschweig, FRG.),
'Calixarene-Phosphorus Chemistry: A New Dimension in Phosphorus Chemistry'

October 18 Prof. A. Alexakis* (Univ. Pierre et Marie Curie, Paris),
'Synthetic and Analytical Uses of Chiral Diamines'

October 25 Dr.D.Martin Davies (University of Northumbria),
'Chemical reactions in organised systems.'

November 1 Prof. W. Motherwell* (UCL London),
'New Reactions for Organic Synthesis'

November 3 Dr B. Langlois (University Claude Bernard-Lyon),
'Radical Anionic and Psuedo Cationic Trifluoromethylation'

November 8 Dr. D. Craig (Imperial College, London),
'New Stategies for the Assembly of Heterocyclic Systems'

November 15 Dr Andrea Sella* (UCL, London),
'Chemistry of Lanthanides with Polypyrazoylborate Ligands'

November 17 Prof. David Bergbreiter (Texas A&M, USA),
'Design of Smart Catalysts, Substrates and Surfaces from Simple Polymers'

November 22 Prof. I Soutar (University of Lancaster),
'A Water of Glass? Luminescence Studies of Water-Soluble Polymers.'

November 29 Prof. Dennis Tuck (University of Windsor, Ontario, Canada),
'New Indium Coordination Chemistry'

† Invited specially for the graduate training programme.
* Seminars attended

b) First Year Induction Course

This course consists of a series of one hour lectures on the services available in the department.

Departmental Organisation - Dr. E.J.F. Ross
Safety Matters - Dr. G.M. Brooke
Electrical Appliances - Mr. B.T. Barker
Chromatography and Microanalysis - Mr. T.F. Holmes
Atomic Absorptiometry and Inorganic Analysis - Mr. R. Coult
Library Facilities - Mr. R.B. Woodward
Mass Spectroscopy - Dr. M. Jones
Nuclear Magnetic Resonance Spectroscopy - Dr. R.S. Matthews
Glass-blowing Techniques - Mr. R. Hart / Mr. G. Haswell
X-Ray Crystallography Prof. J.A.C. Howard
Polymers Prof. J. Feast
Inorganic Chemistry Prof. V. Gibson / Prof. D. Parker

c) Research Conference Attended

July 1993	2nd Anglo-Russian-Ukranian Symposium on Fluorine Chemistry, Durham.

REFERENCES

1. J. Fossey, D. Lefort and J. Sorba, *Free Radicals in Organic Chemistry,* John Wiley & Sons, New York, 1995.

2. P. Sykes, *Mechanism in Organic Chemistry,* Longman Scientific & Technical, New York, 1986.

3. A. K. Joel, Ph.D. Thesis, Univ. of Durham, 1992.

4. O. Paleta, Z. Budkova, J. Kvicala and H. J. Timpe, *Tetrahedron Lett.,* 1993, **32**, 251.

5. O. Paleta, J. Kvicala, Z. Budkova and H. J. Timpe, *Collect. Czech. Chem. Commun.,* 1995, **60**, 636.

6. B. Giese, *Angew Chem., Int. Ed. Engl.,* 1983, **22**, 753.

7. J. M. Tedder and J. C. Walton, *Acc. Chem. Res.,* 1976, **9**, 183.

8. J. M. Tedder and J. C. Walton, *Tetrahedron,* 1980, **36**, 701.

9. G. Costa and S. Russo, *J. Macromol. Sci., Chem.,* 1982, **A18**, 299.

10. R. N. Haszeldine, R. Rowland, R. P. Sheppard and A. E. Tipping, *J. Fluorine Chem.,* 1985, **28**, 291.

11. J. D. Lazerte and R. J. Koshar, *J. Am. Chem. Soc.,* 1955, **77**, 910.

12. O. Paleta, A. Danda and V. Dedek, Czech. Pat., 1987; 246 495.

13. O. Paleta, J. Kvicala and V. Dedek, Czech. Pat., 1987; 245 149.

14. O. Paleta, A. Danda and V. Dedek, Czech. Pat., 1989; 254 747.

15. O. Paleta, V. Dedek, S. Neuenfeld and H. J. Joachim, Czech. Pat., 1990; 268 247.

16. W. H. Urry, F. W. Stacey, O. O. Juveland and C. H. McDonnell, *J. Am. Chem. Soc.* , 1953, **75**, 250.

17. R. N. Haszeldine, US Pat., 1974; 3 816 286.

18. R. N. Haszeldine, US Pat., 1975; 3 917 725.

19. R. N. Haszeldine, A. J. Mitchinson, R. Rowland and A. E. Tipping, *J. Chem. Soc., Perkin Trans. 1,* 1976, 517.

20. R. N. Haszeldine, C. M. Raynor and A. E. Tipping, *J. Chem. Soc., Perkin Trans. 1,* 1982, 2219.

21. R. N. Haszeldine, R. Rowland, A. E. Tipping and G. Tyrrell, *J. Fluorine Chem.,* 1982, **21**, 253.

22. R. N. Haszeldine, C. M. Raynor and A. E. Tipping, *J. Chem. Soc., Perkin Trans. 1,* 1983, 2801.

23. O. Paleta, V. Cirkva and J. Kvicala, *Macromol. Symp.,* 1994, **82**, 111.

24. R. D. Chambers, N. Kelly and J. W. Emsley, *J. Fluorine Chem.,* 1978, **12**, 49.

25. H. Kimoto, H. Muramatsu and K. Inukai, *Bull. Chem. Soc. Jpn.,* 1977, **50**, 2815.

26. F. Liska and V. Kubelka, *Collect. Czech. Chem. Commun.,* 1972, **37**, 1381.

27. H. Muramatsu, S. Moriguchi and K. Inukai, *Bull. Chem. Soc. Japan,* 1966, **39**, 1482.

28. H. Muramatsu, S. Moriguchi and K. Inukai, *Bull. Chem. Soc. Japan,* 1969, **42**, 1684.

29. H. Muramatsu, S. Moriguchi and K. Inukai, *J. Org. Chem.*, 1966, **31**, 1306.

30. C. Walling and E. S. Huyser, *Org. React.*, 1963, **13**, 91.

31. R. F. Stockel and M. T. Beachem, *J. Org. Chem,* 1967, **32**, 1658.

32. E. D. W. Lewiston and H. L. Schlichting, US Pat.; 1967, 3 322 837.

33. H. Muramatsu, K. Inukai and T. Ueda, *J. Org. Chem,* 1965, **30**, 2546.

34. H. Muramatsu, *J. Org. Chem.*, 1962, **27**, 2325.

35. A. Fontana, S. Modena and G. Moggi, GB Pat., 1985; 0 163 533.

36. A. Fontana, S. Modena and G. Moggi, *J. Fluorine Chem.*, 1985, **30**, 109.

37. R. W. Fuss, Ph.D. Thesis, Univ. of Durham, 1989.

38. T. Davies, R. N. Haszeldine, R. Rowland and A. E. Tipping, *J. Chem. Soc., Perkin Trans. 1,* 1983, 109.

39. A. T. Podkhaluyzin and M. P. Nazarova, *Khim. Uys Energ.*, 1979, **13**, 130.

40. B. Atkinson and P. B. Stockwell, *J. Chem. Soc., B,* 1966, 740.

41. A. H. Fainberg and M. Braid, *J. Am. Chem. Soc.*, 1958, **80**, 842.

42. H. C. Brown, *J. Org. Chem.*, 1957, **22**, 1256.

43. J. M. Birchall, R. Fields, R. N. Haszeldine and N. T. Kendall, *J. Chem. Soc., Perkin Trans 1,* 1973, 1773.

44. W. A. Lalande, M. Hauptschein and R. B. Hager, Ger. Offen, 1973, 2 218 552.

45. I. L. Knunyants and E. Y. Pervova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1966, 1623.

46. R. D. Chambers, *Fluorine in Organic Chemistry,* John Wiley and Sons, New York, 1973.

47. H. G. Viehe, R. Merenyi, L. Stella and Z. Janousek, *Angew. Chem., Int. Ed. Engl.,* 1979, **18**, 917.

48. R. D. Chambers, B. Grievson and N. M. Kelly, *J. Chem. Soc., Perkin Trans. 1,* 1985, 2209.

49. T. S. Everett, in *Chemistry of Organic Fluorine Compounds II,* ed. M. Hudlicky and A. E. Pavlath, American Chemical Society, Washington DC, 1995, p. 1037-1086.

50. M. Hudlicky, *Chemistry of Organic Fluorine Compounds,* Halstead Press, New York, 1976.

51. A. L. Henne and S. Kaye, *J. Am. Chem. Soc.,* 1950, **72**, 3369.

52. Y. Kobayashi, T. Nagai, I. Kumadaki, M. Takahashi and T. Yamau, *Chem. Pharm. Bull.,* 1984, **32**, 4382.

53. C. Krespan, US Pat., 1993; 5 185 477.

54. P. C. Myhre and G. D. Andrews, *J. Am. Chem. Soc.*, 1970, **92**, 7595.

55. P. C. Myhre and G. D. Andrews, *J. Am. Chem. Soc.*, 1970, **92**, 7596.

56. V. A. Petrov, *J. Org. Chem.*, 1995, **60**, 3423.

57. C. G. Swain and R. E. T. Spalding, *J. Am. Chem. Soc.,* 1960, **82**, 6104.

58. C. Coudures, R. Pastor and A. Cambon, *J. Fluorine Chem.*, 1984, **24**, 93.

59. E. Moller, in *Methoden der organishen Chemie,* ed. G. T. Verlag, Houben-Weyl, Stuttgart, 1962, vol. 5, p. 469-476.

60. M. A. McClinton and D. A. McClinton, *Tetrahedron,* 1992, **48**, 6555.

61. R. E. Banks, *Organofluorine chemicals and their industrial applications,* Ellis Harwood Ltd, New York, 1979.

62. R. E. Banks, *Preparation, Properties and Industrial Applications of Organofluorine compounds,* Ellis Harwood Ltd, New York, 1982.

63. J. B. Dickey, E. B. Towne, G. J. Taylor, H. M. Hill, R. A. Corbitt, M. A. McCall, W. H. Moore and D. G. Hedberg, *Ind. Eng. Chem.*, 1953, **45**, 1730.

64. J. H. Simons and C. J. Lewis, *J. Am. Chem. Soc.*, 1938, **60**, 492.

65. A. J. Bloodworth, K. J. Bowyer and J. C. Mitchell, *Tetrahedron Lett.*, 1987, **28**, 5347.

66. A. L. Henne and M. S. Newman, *J. Am. Chem. Soc.*, 1938, **60**, 1697.

67. J. Riera, J. Castaner, J. Carilla and A. Robert, *Tetrahedron Lett.*, 1989, **30**, 3825.

68. J. Riera, J. Castaner, J. Carilla, A. Robert, E. Molins and C. Miravitlles, *J. Org. Chem.*, 1991, **56**, 103.

69. G. E. Carr, R. D. Chambers, T. F. Holmes and D. G. Parker, *J. Chem. Soc., Perkin Trans 1,* 1988, 921.

70. Q. Y. Chen and S. Wu, *J. Chem. Soc., Perkin Trans 1,* 1989, 2385.

71. Y. Kobayashi, I. Kumadaki, S. Sato, N. Hara and E. Chikami, *Chem. Pharm. Bull.,* 1970, **18**, 2334.

72. V. C. R. McLoughlin and J. Thrower, *Tetrahedron,* 1969, **25**, 5921.

73. J. M. Paratian, S. Sibille and J. Perichon, *J. Chem. Soc., Chem. Commun.*, 1992, 53.

74. D. B. Su, J. X. Duan and Q. Y. Chen, *Tetrahedron Lett.,* 1991, **32**, 7689.

75. H. Urata and T. Fuchikami, *Tetrahedron Lett.,* 1991, **32**, 91.

76. Q. Y. Chen and S. W. Wu, *J. Chem. Soc., Chem. Commun.*, 1989, 705.

77. Y. Kobayashi, I. Kumadaki, A. Ohsawa and T. Yamada, *Chem. Pharm. Bull.,* 1972, **20**, 1839.

78. K. Matsui, E. Tobita, M. Ando and K. Kondo, *Chem. Lett.,* 1981, 1719.

79. T. Umemoto and A. Ando, *Bull. Chem. Soc. Jpn.,* 1986, **59**, 447.

80. J. H. Clark, M. A. McClinton and R. J. Blade, *J. Chem. Soc., Chem. Commun.,* 1988, 638.

81. J. H. Clark, M. A. McClinton, C. W. Jones, P. Landon, D. Bishop and R. J. Blade, *Tetrahedron Lett.,* 1989, **30**, 2133.

82. J. H. Clark, J. E. Denness, M. A. McClinton and A. J. Wynd, *J. Fluorine Chem.,* 1990, **50**, 411.

83. C. A. Heaton and R. L. Powell, *J. Fluorine Chem.,* 1989, **45**, 86.

84. Y. Kobayashi and I. Kumadaki, *J. Chem. Soc., Perkin Trans 1,* 1980, 661.

85. J. M. Birchall, G. P. Irvin and R. A. Boyson, *J. Chem. Soc., Perkin Trans. 2,* 1975, 435.

86. Y. Girard, J. G. Atkinson, P. C. Belanger, J. J. Fuentes, J. Rokach, C. S. Rooney, D. C. Remy and C. A. Hunt, *J. Org. Chem.,* 1983, **48**, 3220.

87. H. Kimoto, S. Fujii and L. A. Cohen, *J. Org. Chem.,* 1982, **47**, 2867.

88. H. Kimoto, S. Fujii and L. A. Cohen, *J. Org. Chem.,* 1984, **49**, 1060.

89. Y. Kobayashi, I. Kumadaki, A. Ohsawa, S. I. Murakami and T. Nakano, *Chem. Pharm. Bull.,* 1978, **26**, 1247.

90. D. Naumann, B. Wilkes and J. J. Kischkewitz, *J. Fluorine Chem.,* 1985, **30**, 73.

91. D. Naumann and J. J. Kischkewitz, *J. Fluorine Chem.,* 1990, **47**, 283.

92. M. Nishida, H. Kimoto, S. Fujii, Y. Hayakawa and L. A. Cohen, *Bull. Chem. Soc. Jpn.,* 1991, **64**, 2255.

93. D. Naumann and J. J. Kischkewitz, *J. Fluorine Chem.,* 1990, **46**, 265.

94. A. P. Stefani, L. Herk and M. Szwarc, *J. Am. Chem. Soc.,* 1961, **83**, 4732.

95. A. P. Stefani and M. Szwarc, *J. Am. Chem. Soc.,* 1962, **84**, 3661.

96. T. Umemoto and O. Miyano, *Tetrahedron Lett.,* 1982, **23**, 3929.

97. I. M. Whittlemore, A. P. Stefani and M. J. Szwarc, *J. Am. Chem. Soc.,* 1962, **84**, 3799.

98. C. P. Andrieux, L. Gelis and J. M. Saveant, *Tetrahedron Lett.,* 1989, **30**, 4961.

99. L. Hein and D. Z. Cech, *Chem.,* 1977, **17**, 415.

100. J. H. P. Utley and R. J. Holman, *Electrochim. Acta,* 1976, **21**, 987.

101. S. W. Charles and E. Wittle, *Trans. Faraday Soc.,* 1960, **56**, 794.

102. S. W. Charles, J. T. Pearson and E. Wittle, *Trans. Faraday Soc.,* 1963, **59**, 1156.

103. A. B. Cowell and C. Tamborski, *J. Fluorine Chem.,* 1981, **17**, 345.

104. J. L. Holmes and K. O. Kutscheke, *Trans. Faraday Soc.,* 1962, **58**, 333.

105. E. S. Huyser and E. J. Bedard, *J. Org. Chem.,* 1964, **29**, 1588.

106. A. Sekiya and T. Umemoto, *Chem. Lett.,* 1982, 1519.

107. J. H. Tobin, US Pat., 1977; 4 038 331.

108. J. H. Tobin, US Pat., 1978; 4 101 554.

109. A. Gregorcic and M. Zupan, *J. Org. Chem.,* 1979, **44**, 4120.

110. B. R. Langlois, E. Laurent and N. Roidot, *Tetrahedron Lett.,* 1991, **32**, 7525.

111. H. Sawada, M. Nakayama, M. Yoshida, T. Yoshida and N. Kamigata, *J. Fluorine Chem.,* 1990, **46**, 423.

112. Y. Tanabe, N. Matsuo and N. Ohno, *J. Org. Chem.,* 1988, **53**, 4582.

113. M. Tordeux, B. Langlois and C. Wakselman, *J. Chem. Soc., Perkin Trans. 1,* 1990, 2293.

114. M. Yoshida, T. Yoshida, M. Kobayashi and N. Kamigata, *J. Chem. Soc., Perkin Trans. 1,* 1989, 909.

115. T. Akiyama, K. Kato, M. Kajitani, Y. Sakaguchi, J. Nakamura, H. Hayashi and A. Sugimori, *Bull. Chem. Soc. Jpn.,* 1988, **61**, 3531.

116. A. Schwartz and P. Madan, *J. Org. Chem.*, 1986, **51**, 5463.

117. J. L. Gaston, M. F. Grundon and K. J. James, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1136.

118. W. S. Allen and S. Bernstein, *J. Am. Chem. Soc.*, 1955, **77**, 1028.

119. M. S. Newman and S. Otsuka, *J. Org. Chem.*, 1958, **23**, 797.

120. P. B. Baker and B. C. Saunders, *Tetrahedron*, 1974, **30**, 3303.

121. O. Grummitt and E. I. Becker, *Org. Synth.*, 1963, **4**, 771.

122. H. Adkins and W. Zartman, *Org. Synth.*, 1943, **2**, 606.

123. T. W. Abbott and J. R. Johnson, *Org. Synth.*, 1941, **1**, 430.

124. G. B. Bachman and L. L. Lewis, *J. Am. Chem. Soc.*, 1947, **69**, 2022.

125. N. Campbell and D. Kidd, *J. Chem. Soc.*, 1954, **2**, 2154.

126. H. R. Snyder and L. A. Brooks, *Org. Synth.*, 1943, **2**, 171.

127. C. S. T. Lee, I. M. Mathai and S. I. Miller, *J. Am. Chem. Soc.*, 1970, **92**, 4602.

128. P. L. Julian, W. Cole, A. Magnani and E. W. Meyer, *J. Am. Chem. Soc.*, 1945, **67**, 1728.

129. P. P. Fu and R. G. Harvey, *Chem. Rev.*, 1978, **78**, 317-361.

130. F. Camps, J. Coll, A. Messeguer and M. A. Pericas, *Tetrahedron Lett.*, 1981, **22**, 3895.

131. G. A. Olah, A. P. Fung and D. Meidar, *Synthesis*, 1981, 280.

132. H. A. Silverwood and M. Orchin, *J. Org. Chem.*, 1962, **27**, 1962.

133. P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, 1960, 144.

134. M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, 1939, **61**, 3432.

135. L. Spielgler and J. M. Tinker, *J. Am. Chem. Soc.*, 1939, **61**, 940.

136. M. Hauptschein and R. E. Oesterling, *J. Am. Chem. Soc.*, 1960, **82**, 2868.

137. R. D. Chambers and B. Grievson, *J. Fluorine Chem.*, 1985, **30**, 227.

138. J. March, *Advanced Organic Chemistry,* John Wiley & Sons, New York, 1985.

139. F. Fringuelli, R. Germani, F. Pizzo and G. Savelli, *Tetrahedron Lett.*, 1989, **30**, 1427.

140. R. E. Banks, F. Cuthbertson and W. K. R. Musgrave, *Anal. Chim. Acta,* 1955, **13**, 442.

141. S. Marmor, *J. Org. Chem.*, 1963, **28**, 250.

142. J. Read and M. M. Williams, *J. Chem. Soc.*, 1917, **111**, 240.

143. J. Read and M. M. Williams, *J. Chem. Soc.*, 1920, **117**, 359.

144. J. Read and A. C. P. Andrews, *J. Chem. Soc.*, 1921, **119**, 1774.

145. N. Ono, H. Miyake, T. Saito and A. Kaji, *Synthesis*, 1980, 952.