Fluorocarbon synthesis via free-radical reactions

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FLUOROCARBON SYNTHESIS VIA FREE-RADICAL REACTIONS

Submitted by

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(Collingwood College)

A candidate for the degree of Doctor of Philosophy
1983

TO MY PARENTS AND CATHY

ACKNOWLEDGEMENTS

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

I would also like to thank the many technical and laboratory staff for their assistance and my fellow students for their helpful discussions.

Thanks are due also to the Science Research Council for providing a maintenance grant.

Finally, without the support of my parents and my fiancée Cathy, the writing of this thesis would have been more traumatic.

MEMORANDUM

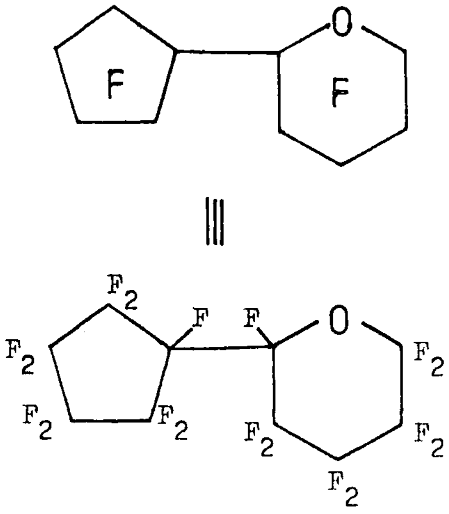
The work described in this thesis was carried out at the University of Durham between October 1979 and October 1982. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

Part of this work has formed the basis of a patent application.

NOMENCLATURE

1. The prefix perfluoro is used before a name to denote that the compound or the part of the compound following the prefix is fully fluorinated.
2. A capital F in a ring denotes that the ring and all unmarked substituents are fully fluorinated.

eg.



ABSTRACT

The effect of substituents on carbon-hydrogen bond reactivity in free radical addition to fluoroalkenes has been investigated. Ethers, esters, amines, amides, and borates all gave free radical adducts, and an order of reactivity has been compiled. This was explained by the inductive electron withdrawing effects of substituents. The reactivity of cyclic ethers and amides has been discussed in terms of the stereoelectronic effect.

The ease of hydrogen abstraction from the substrates was estimated using a method based on the thermal decomposition of di-t-butyl peroxide. A correlation between the ease of hydrogen abstraction and free-radical reactivity was demonstrated.

Further reactions of the adducts has given good synthetic routes to other functionally substituted fluorocarbons. Polyfluorinated acid chlorides were obtained in good yields from the oxidative chlorination of borate and alcohol adducts.

Remarkably high yields of perfluorinated ethers were produced from the high temperature cobalt trifluoride fluorination of ether adducts. The best yields were obtained with cyclic ether and ethyl and propyl dialkyl ether adducts using a reaction temperature of 440°C. Methoxy groups and,chlorine atoms in positions susceptible to elimination,were less stable under these conditions. The structure of polyfluorinated ethers isolated when using lower reaction temperatures indicate that the first steps of fluorination occur adjacent to oxygen and via unsaturated intermediates.

Chlorination of a methyl ether adduct gave attack at the most nucleophilic site,while bromination gave attack at the position which gave the most stable radical.

Attempts at the dehydrodimerization of adducts were unsuccessful.

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INTRODUCTION

CHAPTER 1

PREPARATION OF POLYFLUOROETHERS

A. INTRODUCTION.

Fluorine containing organic compounds have many desirable properties which makes them suitable for many diverse applications such as plastics, anaesthetics, refrigerants, pesticides, surfactants, and blood substitutes. A number of books have been published on the subject of organofluorine compounds and their unique chemistry.[1,2,3,4,5,6] Also, a wide range of methods have been developed for their synthesis. This thesis will discuss the application of a synthetic strategy in which a carbon hydrogen bond is used as a functional group in order to introduce functionality into a fully fluorinated compound. The reaction that has been investigated is the free radical addition of a carbon hydrogen bond to an alkene from both a synthetic and a mechanistic standpoint. Also the reactivity of the products from such reactions has been examined. Preliminary work in this field has been summarized.[7] Most of the products formed have been ethers so it has been valuable to review the methods that are available for the synthesis of highly fluorinated ethers. There are three general methods available:

(a) fluorination of the hydrocarbon equivalent,
(b) joining together of two already fluorinated species, and
(c) ring opening of fluorinated epoxides.

These methods will be discussed briefly.

B. FLUORINATION OF ETHERS AND RELATED COMPOUNDS.

1. ELECTROCHEMICAL FLUORINATION.

The technique of electrochemical fluorination, developed by Simons,[8] has been applied extensively to the exhaustive fluorination of ethers.

The process involves the electrolysis of the ether in a solution of anhydrous hydrogen fluoride using a direct voltage of 5 to 6V, which is not high enough to generate elemental fluorine, a current density of 0.1 to 2.0Adm^{-2}, and a temperature of 0 to 20°C. The fluorinated product is generated at the anode, which is usually nickel, while the cathode may be nickel or steel. Metal fluoride salts may have to be added to the electrolyte in order to make it conducting, however with ethers this is not usually necessary due to the formation of onium species, $R_2OH^+H_{n-1}F_n^-$. A recent review on the electrochemical fluorination of ethers is available.[9]

a. Acyclic Ethers.

The electrochemical fluorination of dialkyl ethers gives low yields of perfluorodialkyl ethers.[10] The results obtained to date are summarized in Table 1. There is extensive carbon oxygen bond fission resulting in the formation of acid fluorides and carbon carbon bond fission which increases with the size of the alkyl groups. This means that larger molecular weight ethers may not be made by this route. Polyethylene glycol ethers and acetates have been used but again low yields of perfluoroethers were obtained. A study into the effects of chlorine substituents showed that a chlorine on the alpha carbon of the ether was readily removed during electrochemical fluorination while a chlorine on the beta carbon was retained.

b. Cyclic Ethers.

Two approaches have been used to prepare perfluorocyclic ethers. The first is the electrochemical fluorination of the hydrocarbon counterpart of the desired perfluoroether, as shown in Table 2. In general cyclic ethers give a much higher yield of the perfluorinated ether than the equivalent acyclic ether. The electrochemical fluorination of alpha substituted oxolanes shows that the higher the molecular

Table 1.

Electrochemical Fluorination of Acyclic Ethers.

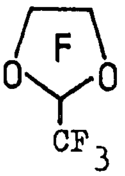
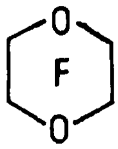
Ether	Product (% yield)	Reference
$(C_nH_{2n+1})_2O$	$(C_nF_{2n+1})_2O$ n=1,2,3,4,5,6	[10]
$(C_2H_5)_2O$	$(C_2F_5)_2O$ (32) + CF_3COF (36) $+C_2F_6$	[9]
$(C_4H_9)_2O$	$(C_4F_9)_2O$ (15) + C_3F_7COF (20) + C_2F_5COF (3) + CF_3COF	[9]
$C_nH_{2n+1}OC_4H_9$	$C_nF_{2n+1}OC_4F_9$ n=5(14),6(10)	[9]
$C_4H_9OCH_2CH_2OH$	$C_4F_9OCF_3$	[10]
$EtOCH_2CH_2O\underset{\overset{\mid}{EtOCH_2}}{CH_2}$	$C_2F_5OCF_2CF_2OCF_2CF_2CC_2F_5$ (4)	[10]
$CH_3OCCl{=}CCl_2$	$CF_3OCF_2CFCl_2$(I) + $CF_3OCF_2CF_2Cl$(II) (29) (15) $+CHF_2OCF_2CFCl_2$ (10)	[11]
$CCl_3OCF_2CFCl_2$	(I) (29) + (II) (15) + $CF_2ClOCF_2CFCl_2$ (39)	[11]
$(CH_3OCH_2)_2$ or $(CH_3OCH_2CH_2)_2O$	CF_3COF + CF_3OCF_2CCF + $CF_3OC_2F_5$ + $(C_2F_5)_2O$	[12]
$CH_3OCH_2CH_2\underset{\overset{\|}{O}}{C}CH_3$	CF_3OCF_3 + CF_3OCHF_2 + CF_2HOCHF_2 + $CF_3OCF_2CF_3$ + $(CF_3CF_2)_2O$ + $CF_3OCF_2CF_2OCF_3$ + $CF_3CCF_2CF_2CCF_2CF_3$ +  +  + 	[13]

Table 1 - cont.

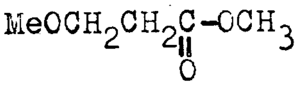
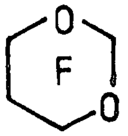
Ether	Product (% yield)	Reference
 $MeOCH_2CH_2\underset{\underset{O}{\|}}{C}-OCH_3$	FCH_2OCF_3 + $(CF_3)_2CHF$ + $CF_3OCHFCF_3$ + $CF_2HOCF_2CF_3$ + $CF_3OCF_2CHF_2$ + $(CF_3O)_2CF_2$ + $CF_3OCF_2CF_2CF_3$ + 	[14]

Table 2.

Electrochemical Fluorination of Cyclic Ethers.

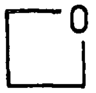
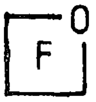
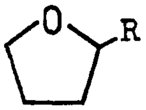
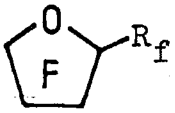
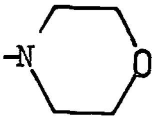
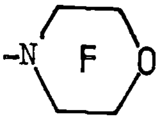
Ether	Product (% yield)	Reference
		[15]
		
R=H	R_f=F(42)	[15]
R=C_nH_{2n+1} n=2,3,4,5	R_f= C_nF_{2n+1} n=2,3,4,5 (41)	[16]
R=$CH_2OC_nH_{2n+1}$ n=2,3,4,5,6,7	R_f=$CF_2OC_nF_{2n+1}$ n=2 (42), 3 (39), 4 (42), 5 (19) i-5 (18), 6 (9), 7 (5)	[17]
R=CH_2NEt_2	R_f= $CF_2N(C_2F_5)_2$ (16)	[17]
R=CH_2-	R_f= CF_2- (35)	[17]

Table 2 - cont.

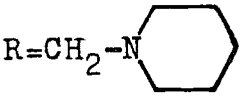
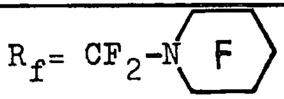
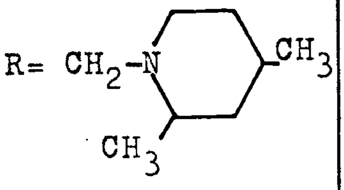
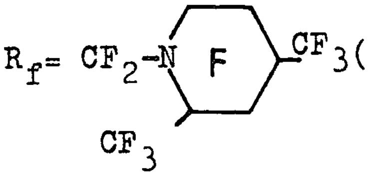
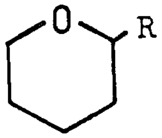
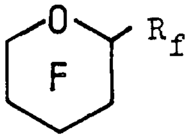
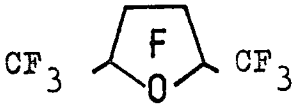
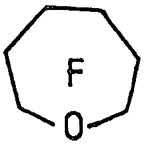
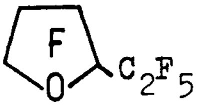
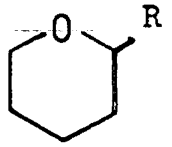
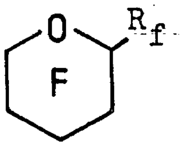
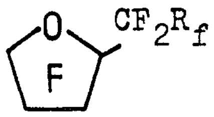
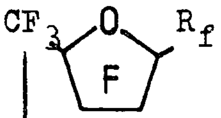
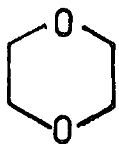
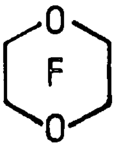
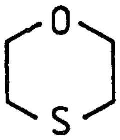
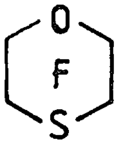
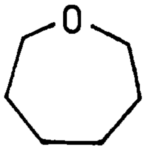
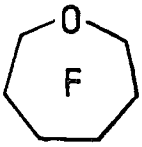
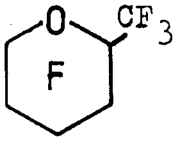
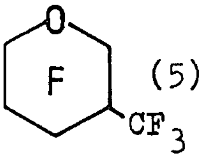
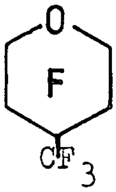
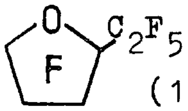
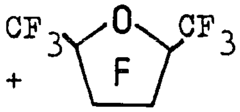
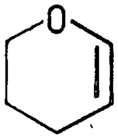
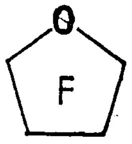
Ether	Product (% yield)	Reference
	 (18)	[17]
	 (3)	[17]
R= CH_2Cl	$R_f= CF_2Cl$ (5)	[18]
		
R= H	R =F (35)	[15]
R= C_nH_{2n+1} n=1,2,3,4,5	$R_f= C_nF_{2n+1}$ n=1 (28),2,3,4 (23),5 (18)	[19]
n=1	n=1 (28)+  (3)+  (3) + $nC_4F_9O\ C_2F_5$ (6) +  (10)	[18]
R= CH_2Cl	$R_f= CF_2Cl$ (1)	[18]
 R=Et,Pr,Me_2CH, Bu,Amyl	 +  + (23-30)  + $nC_4F_9OCF_2R'$ (2-11) (2-4)	[20]
	 + $CF_3OCF_2CF_2OCF_3$ (3) (14)	[21]

Table 2 - cont.

Ether	Product (% yield)	Reference
	 (21) +$C_2F_5CCF_2CF_2SF_5$ (5) +$(C_2F_5)_2O$ (10)	[22]
	 (11) +  (7) +  (5) +  (5) +  (11) +  (1) + $nC_4F_9OC_2F_5$ (2)	[18]
	Fluoropolymer	[23]

weight of the alkyl substituent the lower the yield of product. The presence of an oxygen atom in the side chain does not affect the yield of product, while a nitrogen atom greatly reduces the yield. The use of an unsaturated compound or the presence of hydroxy groups appear to be undesirable due to the deposition of polymeric films on the anode. The addition of a depolarizer compound to the electrolyte, for example ethyl acetate or methyl pentanoate, increases the yield of perfluorooxolane from oxolane by preventing polymerisation.[24]

The second approach is to use straight chain carboxylic acids, or their derivatives, which cyclize upon electrochemical fluorination to produce perfluoroethers. Much lower yields of perfluorocyclic ethers are obtained by this route than by using the hydrocarbon ether direct, particularly when using carboxylic acids, Table 3. Better yields are obtained by using acid halides, alcohols, or halohydrins. Aldehydes gave low yields of ethers and they were accompanied by the formation of tarry products. The advantage of using substances of this type is that they are usually much more readily available than the hydrocarbon ether. Better yields have been achieved by having a bromine atom on the gamma carbon atom of the acid derivative.[39]

electrochemical fluorination; $\longrightarrow$		+	$n\text{-}C_3F_7COF$
$CH_3CH_2CH_2COCl \longrightarrow$	24%		34%
$BrCH_2CH_2CH_2COCl \longrightarrow$	36%		17%

Also during the fluorination of octanoyl chloride the ratio of cyclic ethers to acid fluoride by-product is inversly proportional to the concentration of the solute.[29]

Recently the second approach has been extended to the synthesis of bicyclic perfluoroethers. This is achieved by using substrates

Table 3.

Electrochemical Fluorination of Straight Chain Carboxylic Acid Derivatives

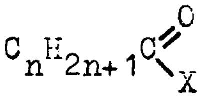
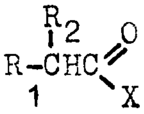
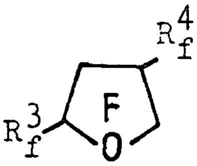
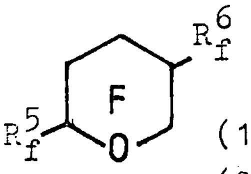
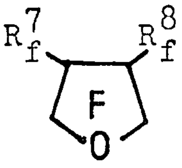
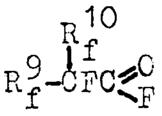
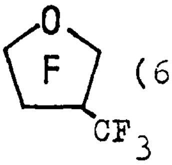
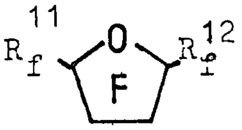
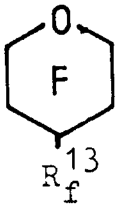
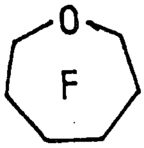
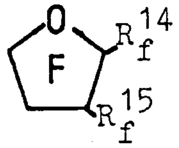
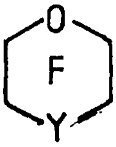
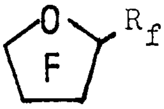
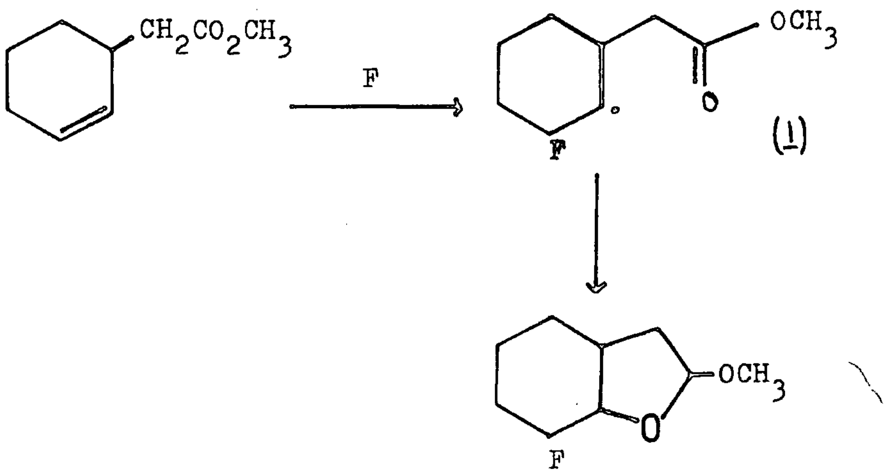
Substrate	Product (% yield)	Reference
$CH_3(CH_2)_nCO_2H$ n=4,5,6,7,8	$C_{n+2}F_{2(n+2)}O$ mixture 5-and 6-membered rings	[25]
n=3	 (7)	[26]
n=4	cyclic ethers (13)	[26]
 $C_nH_{2n+1}C\begin{smallmatrix}\nearrow O\\ \searrow X\end{smallmatrix}$ X=halogen n=3,4, 7	mixture of perfluoro oxalanes and oxanes (19-32)	[27] [29]
 $R_1\text{-}\overset{R_2}{\overset{\mid}{C}}HC\begin{smallmatrix}\nearrow O\\ \searrow X\end{smallmatrix}$ X=Cl or OMe R_1=n-Pr,n-Bu, n-Pentyl, i-Pr R_2=Me,Et n-Pr, n-Bu	 (111) +  (1V)+ (5-21) (2-7)  (V) +  $R_f^9\text{-}\overset{R_f^{10}}{\overset{\mid}{C}}FC\begin{smallmatrix}\nearrow O\\ \searrow F\end{smallmatrix}$ (V1) (2) (3-13)	[28,31]
Me_3CCOCl or $Me_2CHCOCl$	 (6) + $(CF_3)_2CFCOF$	[30]

Table 3 cont.

Substrate	Product (% yield)	Reference
R- OH R=n-Bu,n-Pentyl, n-Hexyl, n-Octyl n-Heptyl $R=CH_2=CHCH_2CH_2-$ $R=CH\equiv CCH_2CH_2-$ $R=CH_3-\underset{CH_3}{CH}CH_2CH_2-$ $R=CH_3CH_2\underset{CH_3}{CH}CH_2CH_2-$ $R={}^tBuCH_2CH_2-$ $R=CH_3CH_2\underset{CH_3CH_2}{CH}CH_2-$	(111) (9-18) + (1V) (1-4) +  +  + (V11) (0-3) (V111) (0-1)   (1X) (trace) (X) (0-8)	[32,33]
$R=HO(CH_2)_4-$		[34]
$R=HO(CH_2)_5-$		[35]
$(HOCH_2CH_2)_2X$ X=S,O,NH,NMe,NEt	 $Y=S,O,NF,NCF_3,NCF_2CF_3$	[36]
RCHO R=n-Pr,n-Bu, n-Pentyl n-Hexyl n-Heptyl	(111) (trace-6) + (1V) (0-1) + (V11) (0-1) + (V111) (0-0.6)	[32,37]
$CH_3(CH_2)_nCHOHCH_2Cl$ n=1,2,3,4,5	 R_f= F,C_{1-4}n-perfluoroalkyl (12-19)	[38]

containing a ring system in such a position that cyclization will occur onto the ring. Examples that have been reported are listed in Table 4. Increased yields of cyclized products are obtained by using methyl ester rather than acid chloride derivatives, also by using unsaturated ring substrates. It has been proposed that the formation of resonance stabilized intermediate radicals (1) provides a driving force for ring closure in these reactions.[9]



c. Fluorine Substituted Substrates.

Electrochemical fluorination has been applied to the fluorination of substrates which are already partially fluorinated. A nucleophilic reaction between alcohols or polyols and tetrafluoroethene or hexafluoropropene result in the formation of polyfluoroalkylethers which were then fluorinated to produce the perfluoroalkyl ether.[45]

$$(HOCH_2)_2CHOH \quad + \quad CF_3CF{=}CF_2 \xrightarrow[Et_3N]{MeCN} (CF_3CFHCF_2OCH_2)_2CH(OCF_2CFHCF_3)$$

$$\Big\downarrow \text{ electrochemical fluorination}$$

$$(C_3F_7OCF_2)_2CFOC_3F_7$$

Table 4.

Electrochemical Fluorination of Cyclic Carboxylic Acid Derivatives

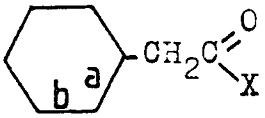
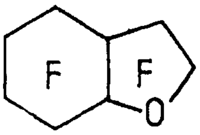
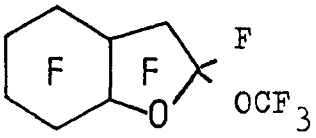
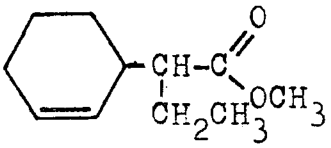
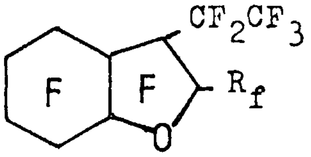
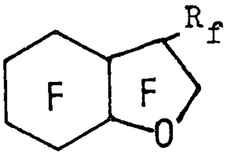
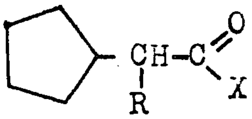
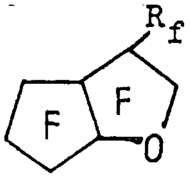
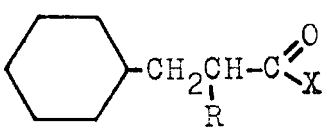
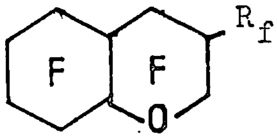
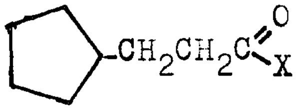
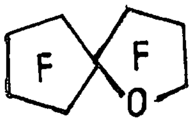
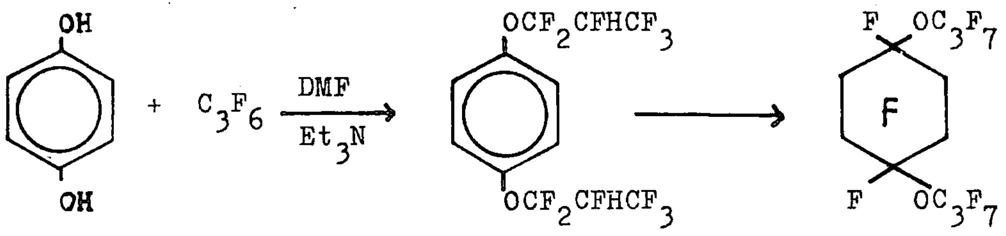
Substrate	Product (% yield)	Reference
 X=Cl,OMe a= C=C,X= OMe b= C=C,X= OMe	 +  (7-19) (0-9)	[40]
	 R_f=F(30) OCF$_3$(10)	[40]
RR^{1}CHCOR^2 R^1=H,C$_{1-4}$n-alkyl R=cyclohexyl Δ^2-cyclohexenyl R^2=OH,halogen,OMe	 R_f=F,C$_{1-4}$perfluoroalkyl	[41]
 X=OH,halogen,OMe R=H,C$_{1-4}$n-alkyl	 R_f=F,C$_{1-4}$perfluoroalkyl	[42]

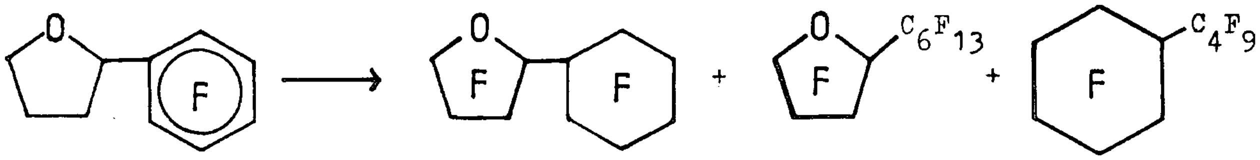
Table 4 cont.

Substrate	Product (% yield)	Reference
 X=OH,halogen,OMe R=H, CH_3	 R_f=F (22) R_f=CF_3 (13)	[43]
 X=OH,halogen,OMe	 (12)	[44]

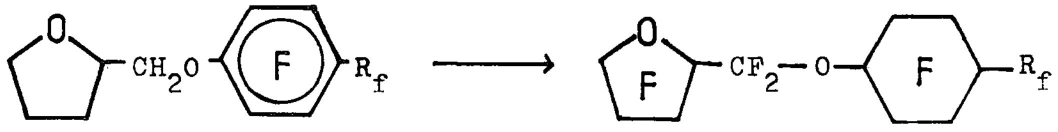
A similar strategy has been used with phenols.[46]



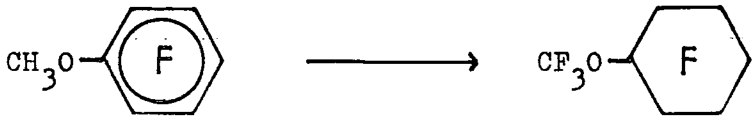
Remarkably very high yields of perfluoroethers have been claimed from the electrochemical fluorination of alpha substituted polyfluorophenyl deriv. of oxolane which were prepared via Grignard reactions.[47]



54%



R_f = F (98%)
R_f = CF_3 (97%)



(93%)

Also electrochemical fluorination has been used to provide the final step in the preparation of a number of perfluoropolyethers.[48]

$$F(CF(CF_3)CF_2O)_nCHFCF_3 \xrightarrow{\text{electrochemical fluorination}} F(CF(CF_3)CF_2O)_nCF_2CF_3$$

n = 1 , 2 , 4 (77%, n = 1)

2. DIRECT FLUORINATION.

The reaction of elemental fluorine with hydrocarbon substrates is a very exothermic process, as illustrated in Scheme 1.[49]

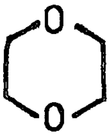
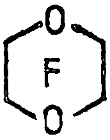
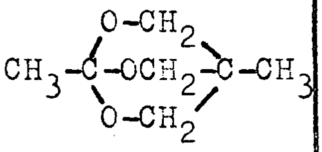
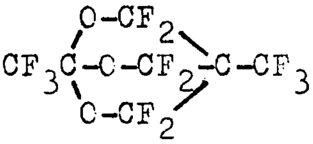
Scheme 1

Step	Reaction	ΔH°_{298K}(kcal/mol)
Initiation	$F_2 \longrightarrow 2F\cdot$	+37.7
	$F_2 + R\text{-}H \longrightarrow R\cdot + HF + F\cdot$	+3.9
Propagation	$R\text{-}H + F\cdot \longrightarrow R\cdot + HF$	-33.8
	$R\cdot + F_2 \longrightarrow RF + F\cdot$	-69.1
Termination	$R\cdot + F\cdot \longrightarrow RF$	-106.8
	$R\cdot + R\cdot \longrightarrow R\text{-}R$	-83.8
	$F\cdot + F\cdot + M \longrightarrow F_2 + M$	-37.7
Overall Reaction	$R\text{-}H + F_2 \longrightarrow RF + HF$	-102.9

Therefore direct fluorination reactions have been very difficult to control and usually result in extensive chain fragmentation. This was partially overcome by early workers by diluting the fluorine with nitrogen and using heat sinks of gold or silver pellets.[50] A recent approach to this problem has been the development of a cryogenic reactor by Lagow and co-workers.[49] This method increases the proportion of fluorine in the carrier gas gradually as the reaction proceeds . The apparatus contains several reaction zones which are controlled at temperatures from -190°C to +20°C, such that the temperature is sufficiently low in each zone to condense the partially fluorinated compounds to allow further fluorination.[51] A number of ether compounds have been fluorinated by this technique to give perfluoroethers in yields comparable to those obtained by electrochemical fluorination, Table 5. Solid polyethers have been subjected to this technique, first

Table 5.

Direct Fluorination of Ethers.

Substrate	Products (% yield)	Reference
$MeO(CH_2)_2OMe$	$CF_3O(CF_2)_2OCRF_2$ R= H (25) F (21)	[52]
$EtO(CH_2)_2OEt$	$CF_3CF_2O(CF_2)_2OCF_2CF_3$ (18)	[52]
$[MeO(CH_2)_2]_2O$	$CF_3O(CF_2)_2O(CF_2)_2OCF_3$ (16)	[52]
	 (39) + $(CF_3)_2O$ (58) + $CF_3OCH_2CH_2OCF_3$ (4)	[53]
	 (10)	[54]

at ambient temperatures to produce a perfluorinated polymer, then at 110°C using pure fluorine to promote fragmentation. Thus a large range of perfluorinated ethers were obtained from poly(ethylene oxide),[55]

$$-(CH_2CH_2O)_n- \xrightarrow[\text{(i) ambient. (ii) } 110^{\circ}C]{F_2\ /\ He} R_f'-(OCF_2CF_2)_n-OR_f''$$

$R_f' = R_f'' = CF_3$, $n = 1$ to 6

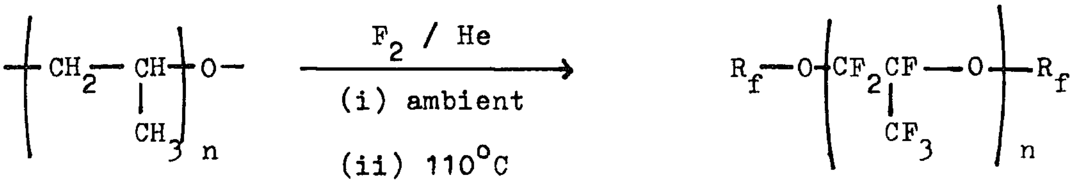
$R_f' = CF_3$, $R_f'' = C_2F_5$, $n=1$ to 6

$R_f' = R_f'' = C_2F_5$, $n = 1$ to 3

from polymethylene oxide,[56]

$$-(CH_2O)_n- \xrightarrow{F_2\ /\ He} COF_2 + \text{fluoroethers}$$

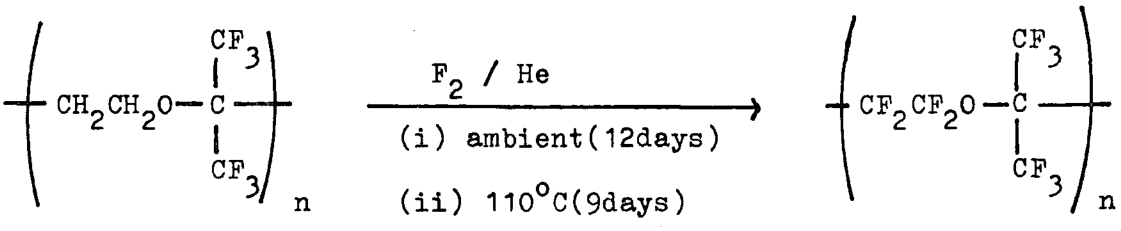
and from polypropylene oxide.[56]



$$\left[-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O-\right]_n \xrightarrow[\text{(i) ambient (ii) } 110^{\circ}C]{F_2\ /\ He} R_f-O-\left[CF_2\underset{\displaystyle CF_3}{\underset{|}{CF}}-O-\right]_n-R_f$$

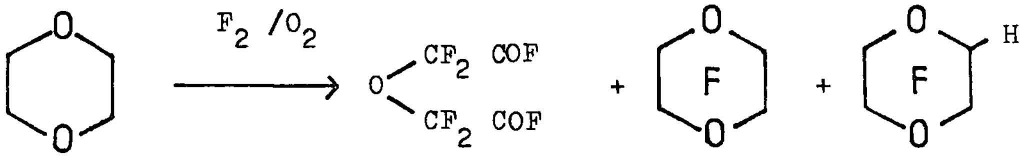
$R_f = CF_3$, C_2F_5 , $n-C_3F_7$

Similarly an ethylene hexafluoroacetone copolymer was fluorinated to give a series of branched perfluoropolyethers.[57]



$$\left[-CH_2CH_2O-\overset{\displaystyle CF_3}{\underset{\displaystyle CF_3}{C}}-\right]_n \xrightarrow[\text{(i) ambient(12days) (ii) } 110^{\circ}C\text{(9days)}]{F_2\ /\ He} \left[-CF_2CF_2O-\overset{\displaystyle CF_3}{\underset{\displaystyle CF_3}{C}}-\right]_n$$

Mixtures of fluorine and oxygen have been used to simultaneously fluorinate and introduce oxygen functionality into compounds, including p-dioxan.[58]



3. HIGH VALENCY METAL FLUORIDES.

The advantage of using metal fluorides rather than elemental fluorine to fluorinate a hydrocarbon substrate may be seen by the much lower heat of reaction for fluorination which results from the endothermic nature of the reaction below.

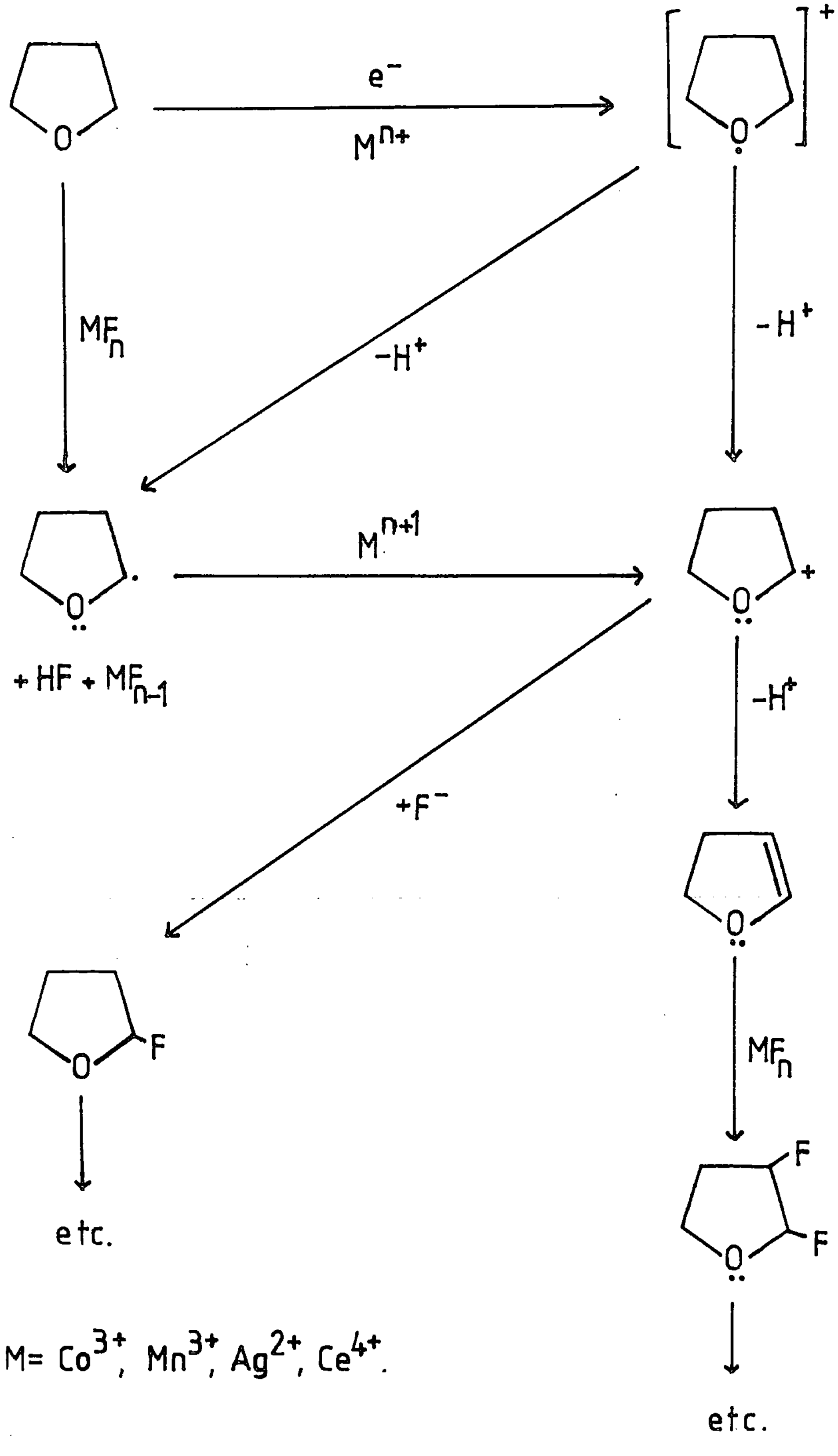
$$2\ CoF_3 \longrightarrow 2\ CoF_2 + F_2 \quad \Delta H^{\circ}_{473} = +52\ \text{kcal/mol}$$

A current explanation of the mechanism of this type of fluorination involves an initial oxidation of the substrate by the metal ion to a radical cation,[59] Scheme 2. A less favoured alternative is the abstraction of a hydrogen atom. These steps are followed either by the formation of unsaturated systems which are then fluorinated,[59] or by the addition of a fluoride ion.[60]

The exhaustive fluorination of ether materials by high valency metal fluorides, and by cobalt trifluoride in particular, has frequently been reported, Table 6. In all cases a complex mixture of polyfluorinated products were obtained. The presence of fluorine substituents on the ether enables better yields of products to be formed and with less fragmentation, although this has not been developed into a route to fully fluorinated ethers.

Scheme 2.

Mechanism of Fluorination of Oxolane by Metal Fluorides.[59,60]



M= Co^{3+}, Mn^{3+}, Ag^{2+}, Ce^{4+}.

Table 6.

Metal Fluoride Fluorination of Ethers and Derivatives.

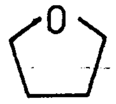
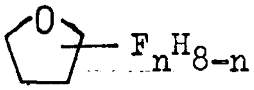
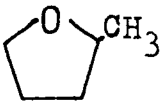
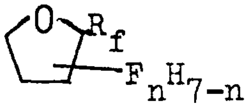
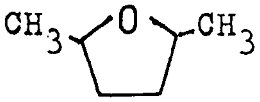
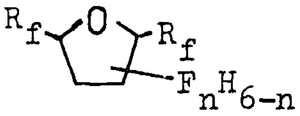
Substrate	Metal Fluoride (Temperature)	Product (% yield)	Ref.
Et_2O	CoF_3(60-80°C)	$CFH_2CFHOCFHCF_2H$ + $(CF_2HCFH)_2O$ + $CF_2HCF_2OCFHCF_2H$	[61]
	$KCoF_4$(200°C)	$CH_3CH_2OCFHCF_2H$	[61]
EtOMe	CoF_3(60-80°C)	$CF_2HCFHOCH_3$ + $CF_2HCFHOCH_2F$ + $CF_2HCF\ HOCF_2H$ + $CF_2HCF_2OCH_3$	[61]
	$KCoF_4$(200°C)	$CF_2HCFHOCH_3$	[61]
$CF_2HCFHOCH_3$	CoF_3(114°C)	$CF_2HCF_2OCH_2F$ + $CF_2HCFHOCF_2H$	[61]
	CoF_3(110°C)	 n=7 (4.2%),6 (17.1%) 5 (57.7%),4 (6.9%)	[62]
	$KCoF_4$(110°C)		[63]
	$KCoF_4$(110°C)		[63]

Table 6(Cont.)

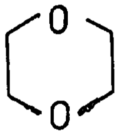
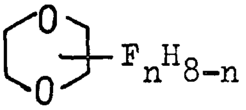
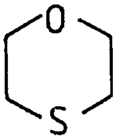
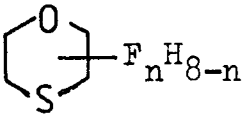
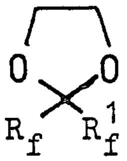
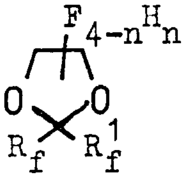
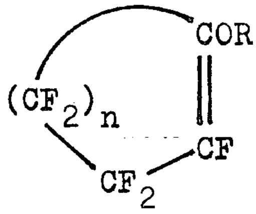
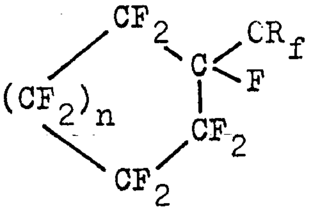
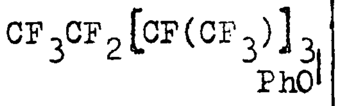
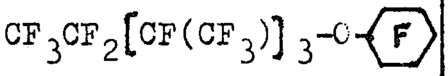
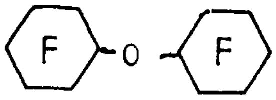
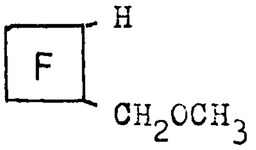
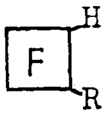
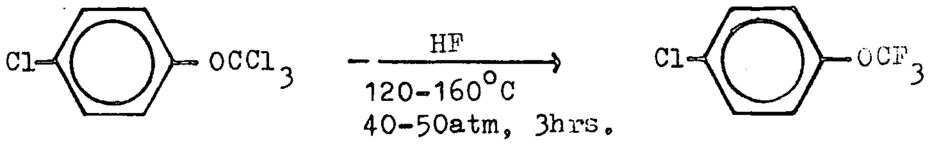
Substrate	Metal Fluoride (Temperature)	Product (% yield)	Ref.
	CoF_3(100°C) and $KCoF_4$(230°C)	 n=7 (22%),6 (33.5%) 5 (27.5%),4 (2.6%)	[64] [64]
	$KCoF_4$(220°C)	 n=7,6,5,4	[64]
 $R=R^1=CF_3, CHF_2$ $R=CF_3, R^1=CF_2Cl$	CoF_3(140°C)	 n=0,1,2	[65]
 n=1,2, R=Me n=3, R=Me,Et, CH_2CF_3, $CH_2CF_2CF_2H$	CoF_3(110°C)	 R_f=polyfluoroalkyl	[66]
$CHF_2CF_2CHClOCHF_2$	CoF_3(155°C)	$CHF_2CF_2CHFOCHF_2$	[67]
$CHFClCF_2CH_2OCH_3$	CoF_3 (110-140°C)	$CF_2ClCF_2CF_2OCH_2F$ + $CF_2ClCF_2CH_2OCHF_2$ + $CF_2ClCF_2CHFOCHF_2$ + $CHFClCF_2CFHOCHF_2$	[67]

Table 6(Cont.)

Substrate	Metal Fluoride (Temperature)	Product (% yield)	Ref.
 $\underset{PhO}{CF_3CF_2[CF(CF_3)]_3}$	CoF_3 (170°C)		[68]
Ph-O-Ph	CoF_3	 (32)	[69]
$CF_3CFHCF_2CH_2OCH_3$	CoF_3 (120°C)	$CF_3CFHCF_2CH_2OCF_2H$ + $CF_3CFHCF_2CFHOCF_2H$ + $CF_3CFHCF_2CFHOCFH_2$	[7]
	CoF_3 (120°C)	 R=$CFHOCF_2H$, CF_2OCF_2H	[7]

4. HALOGEN EXCHANGE.

Halogen exchange may be used to prepare alpha-fluoroethers, with the exception of those containing a methyl or monohalogenomethyl group adjacent to the halogenated alpha-carbon atom. A variety of reagents may be employed to effect this transformation.[70] Anhydrous hydrogen fluoride normally requires vigorous conditions and a catalyst of antimony(V) chloride.

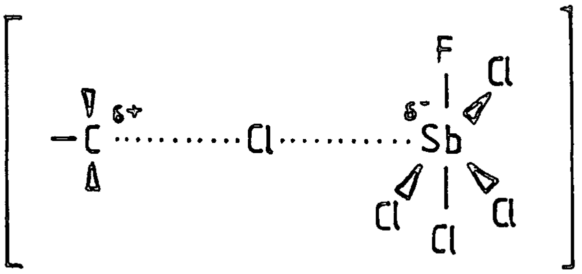


82% [71]

Much milder conditions are needed for antimony fluorides. Antimony(III) fluoride is similar in reactivity to hydrogen fluoride for halogen exchange. The best activities are obtained by converting some or all of the antimony to the pentavalent state by the addition of chlorine, bromine, or antimony pentachloride. The relative reactivities of antimony fluorides for halogen exchange have been arranged into a series.[72]

$$SbF_3 < (SbF_3 + SbCl_3) < (SbF_3 + SbCl_5) < SbF_3Cl_2 < SbF_5$$

The high activity of the pentavalent antimony compounds may be explained by the ability of antimony to use d-orbitals to form highly stable hexacoordinate halide complex intermediates.

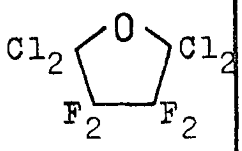
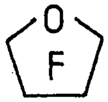


A few representative reactions of this type are given in Table 7.

Groups I and II metal fluorides are used to exchange one or two halogen atoms with fluorine. Potassium fluoride has been used most extensively, being a compromise between activity and availability.

Table 7.

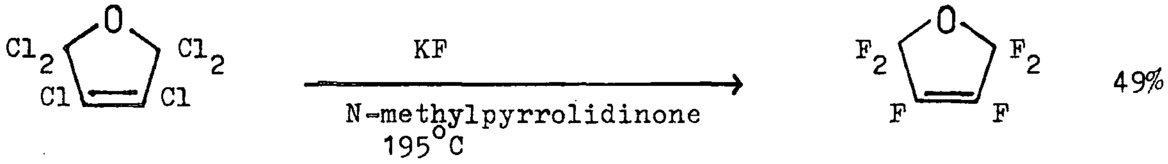
Fluorination by Antimony Fluorides.

Substrate	Reaction Conditions	Products (% yield)	Ref.
CCl_3OCH_3	SbF_3,reflux	CF_3OCH_3+ $CClF_2OCH_3$	[73]
$CCl_3CCl_2OCH_3$	SbF_3,reflux	$CCl_3CF_2OCH_3$ (84)	[74]
$(CCl_2{=}CCl)_2O$	SbF_3/Cl_2 70-80°C	$(CCl_3CF_2)_2O$	[75]
	SbF_3Cl_2 155°C 15atm. 24hours	 (67)	[76]

Within group I, the fluoride activity increases with the size of the cation. The fluorinating efficiency of a number of fluorides was determined during the preparation of ethers CCl_3CHFOR and CH_2FOR, (R= alkyl) from the corresponding alpha-chloroethers.[77] The descending order of efficiency was $HgF_2 > TlF > AgF > KF,AlF_3 > CrF_3$. Although in general potassium fluoride will only replace single halogen atoms[78] in an S_N2 type process,

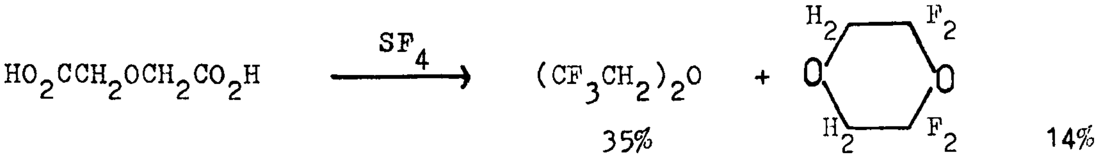
$$(ClCH_2CH_2)_2O \xrightarrow[\underset{125^{\circ}C\ ,\ 10hrs.}{O(CH_2CH_2OH)_2}]{KF} (FCH_2CH_2)_2O \qquad 39\%$$

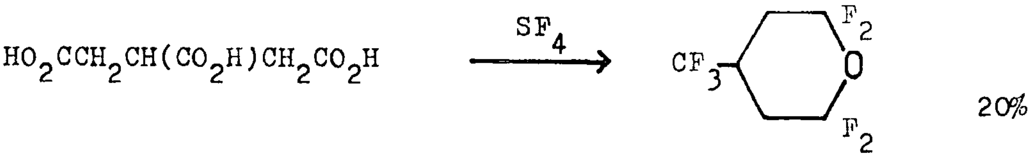
a double bond in a perhalogenocyclic ether results in vinylic displacement to produce a perfluoroether.[79]



5. SULPHUR TETRAFLUORIDE FLUORINATION.

Sulphur tetrafluoride may be used to transform a carboxylic acid group to trifluoromethyl, a carbonyl group to difluoromethylene, and an hydroxy group to fluoride.[80] Certain polycarboxylic acids cyclise to give tetrafluoroethers.[81]





A similar reaction occurs with aromatic polycarboxylic acids.[82] Fluorination of polychloroacetic acids gave fluoroethers as by-products in yields of 14 to 24%.[83]

$$\mathrm{RCOOH} \xrightarrow[60^{\circ}\mathrm{C}]{SF_4} \mathrm{RCF_3} + \mathrm{(RCF_2)_2O}$$

$R = CH_3$, CH_2Cl,
$CHCl_2$, CCl_3

Aliphatic esters gave very low yields of 1,1-difluoroethers[81] however polyfluoroesters may be converted to ethers in excellent yield with sulphur tetrafluoride catalysed by hydrogen fluoride.[84] Monoesters, diesters, polyesters, and carbonates can be used in this general reaction.

$$R_f^1COOR_f^2 \xrightarrow[150\ -\ 185^{\circ}\mathrm{C}]{SF_4/HF} R_f^1CF_2OR_f^2 + SOF_2$$

R_f^1=perfluoroalkyl
R_f^2=polyfluoroalkyl

81 - 92%

Treatment of alcohols or phenols with carbonyl fluoride will give fluoroformates which can be fluorinated to trifluoromethyl ethers.[85]

$$C_6H_5OH \xrightarrow{COF_2} C_6H_5OCOF \xrightarrow[150-175^{\circ}\mathrm{C}]{SF_4/HF} C_6H_5OCF_3 \quad 62\%$$

With alcohols, one or more electron withdrawing substituents on the beta-carbon atom are necessary to give a good yield of the trifluoromethyl ether.[86]

$$RCH_2OH \xrightarrow[(ii)\ SF_4/HF]{(i)\ COF_2} RCH_2OCF_3$$

R= CH_2Cl 15-42%
R= CCl_3 72%

C. FORMATION OF ETHERS FROM PREFORMED FLUORINATED UNITS.

In this section the methods that are available for the synthesis of polyfluoroethers by the addition of two preformed polyfluorinated units are discussed. This is a very large area and most of the reactions are not discussed comprehensively although review articles are noted from which further details may be obtained.

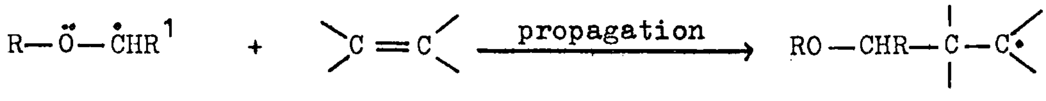
1. FREE RADICAL ADDITION OF ETHERS TO FLUOROALKENES.

The free radical addition of an ether to a double bond proceeds via a chain mechanism to form an ether product. The reaction may be initiated thermally by the use of chemical initiators, photochemically, or by high energy radiation such as gamma rays. The initiation step consists of the abstraction of a hydrogen atom from the ether substrate to produce a radical (2) which will be stabalized due to the lone pair of electrons on the oxygen.

$$R\text{-}OCH_2R^1 \xrightarrow{\text{initiation}} R-\ddot{O}-\dot{C}HR^1 \longleftrightarrow R-\overset{+}{\dot{O}}-\bar{\ddot{C}}HR^1$$

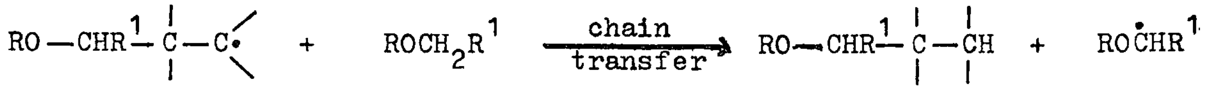
(2)

Addition of (2) to the double bond in the propagation step will form an intermediate radical (3) which will abstract a hydrogen atom from the ether substrate to form the product (4) in the chain transfer step.



$$R-\ddot{O}-\dot{C}HR^1 + >C=C< \xrightarrow{\text{propagation}} RO-CHR-\overset{|}{\underset{|}{C}}-\dot{C}<$$

(3)

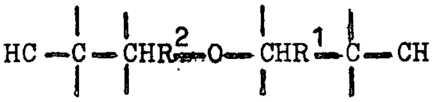


$$RO-CHR^1-\overset{|}{\underset{|}{C}}-\dot{C}< + ROCH_2R^1 \xrightarrow[\text{transfer}]{\text{chain}} RO-CHR^1-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}H} + RO\dot{C}HR^1$$

(4)

The orientation of addition of (2) to an unsymmetrically substituted alkene depends on a complex interplay of polar effects, steric effects, strength of the forming bond, and stability of the produced radical.[87]

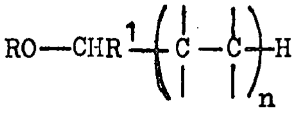
Product (4) is termed a mono-adduct and further reaction of this with another alkene molecule will produce di-adducts (5).



$$\mathrm{HC{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}HR^{2}{-}O{-}\overset{|}{\underset{|}{C}}HR^{1}{-}\overset{|}{\underset{|}{C}}{-}CH}$$

(5)

Telomerization is a frequent side reaction where the intermediate radical (3) adds to another alkene molecule to produce telomers (6) rather than abstract a hydrogen atom from the substrate.



$$\mathrm{RO{-}CHR^{1}{-}\left(\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\right)_{n}{-}H}$$

(6)

This is particularly common with polyfluoroethenes. Termination of the chain reaction will occur by many reactions including radical dimerisations and loss of energy by wall collisions.

A variety of ethers and polyfluoroalkenes have been reacted and the results are summarized in Table 8. The yields of polyfluoroethers are usually very high when hydrocarbon ether substrates are used. However, the introduction of electronegative groups into the ether results in lower yields, as seen from the relative reactivities of a series of substituted diethyl ethers towards hexafluoropropene shown in Table 9. Relative reactivities have been determined by competition experiments for a number of ethers and they are in the order, oxolane 2.4, diethyl ether 1.0, and p-dioxan 0.36.[94] The addition of these ethers to 1,2-dichloroperfluorocycloalkenes produces both mono-adducts and dehydrochlorinated adducts in different proportions. This difference was attributed to the ease of abstraction of the hydrogen atom from the ether; the easier the abstraction the less the amount of dehydrochlorination, giving a similar order of reactivity as above.[102]

Table 8.

Free Radical Addition of Ethers to Polyfluoroalkenes.

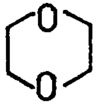
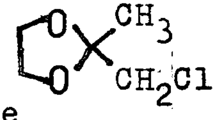
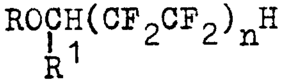
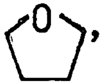
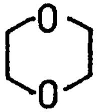
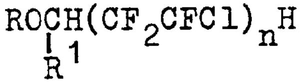
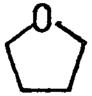
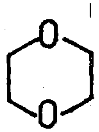
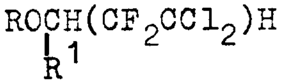
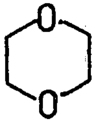
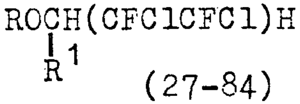
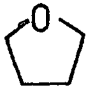
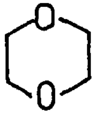
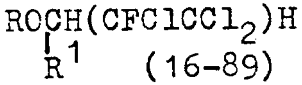
Alkene	Ether	Method of Initiation	Products (%yield)	Reference
$CF_2=CF_2$	Et_2O, , , $CH_2(OMe)_2$, $(CH_2OMe)_2$, , , tetraglyme	$(PhCOO)_2 110^oC$	 $\underset{R^1}{ROCH}(CF_2CF_2)_nH$ n=1,2,3,4	[88,89]
$CF_2=CFCl$	Et_2O, , , $CH_2(OMe)_2$	gamma	 $\underset{R^1}{ROCH}(CF_2CFCl)_nH$ n=1,2,3	[90,91,92]
$CF_2=CCl_2$	Et_2O, , 	gamma	 $\underset{R^1}{ROCH}(CF_2CCl_2)H$	[93]
$CFCl=CFCl$	Et_2O, , 	gamma	 $\underset{R^1}{ROCH}(CFClCFCl)H$ (27-84)	[93]
$CCl_2=CFCl$	Et_2O, , 	gamma	 $\underset{R^1}{ROCH}(CFClCCl_2)H$ (16-89)	[93]

Table 8-cont.

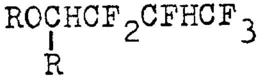
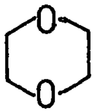
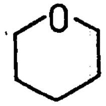
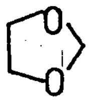
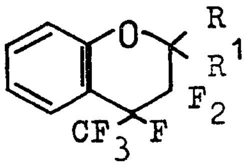
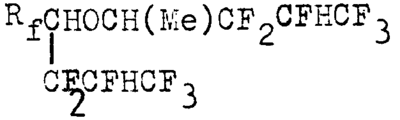
Alkene	Ether	Method of Initiation	Products (% yield)	Reference
$CF_2=CFCF_3$	Me_2O	gamma	 $RO\underset{R}{C}HCF_2CFHCF_3$ (70)	[7]
	Et_2O,  , 	gamma	(43) (90) (81)	[94]
		thermal(280°C)	(10)	[95]
		gamma		[96]
	$PhOCHRR^1$	$(^tBuO)_2$	 R,R^1=Hor CH_3 (36-56)	[97]
	R_fCF_2OEt	gamma	$R_fCF_2OCH(CH_3)CF_2CFHCF_3$ $R_f=CHF_2$ (8),CHFCl (10) $CHCl_2$ (22)	[98]
	R_fCH_2OEt $R_f=CF_3,CHF_2,CH_2F,CH_3,CH_2Cl,$ CHF_2CF_3	gamma	$R_fCH_2OCH(Me)CF_2CFHCF_3$+  $R_f\underset{CF_2CFHCF_3}{C}HOCH(Me)CF_2CFHCF_3$	[98]

Table 8-cont.

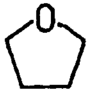
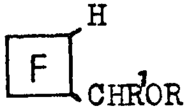
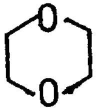
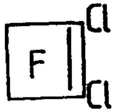
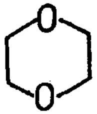
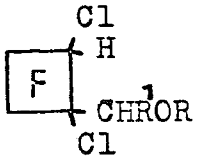
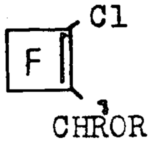
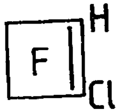
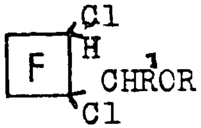
Alkene	Ether	Method of Initiation	Products (% yield)	Reference
$CF_2=C(CF_3)_2$		gamma, UV, PhCOOOH	1:1 + 2:1 adducts	[99]
$CF_2=CFOCF_3$		gamma, UV, PhCOOOH	1:1 + 2:1 adducts	[99]
	Me_2O	gamma, $(PhCOO)_2$ 80°C	 (51-74)	[100]
	Et_2O,  , 	gamma	(58-80) + 2:1 adducts	[101]
	Et_2O,  , 	gamma	 (4-81) +  (14-30)	[102]
	Et_2O, THF, dioxon	gamma		[103]

Table 8-cont.

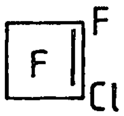
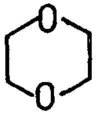
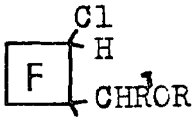
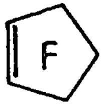
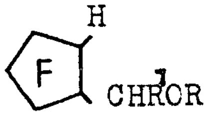
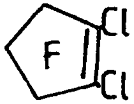
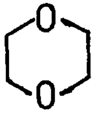
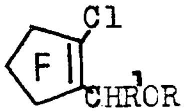
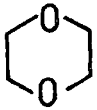
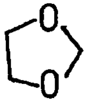
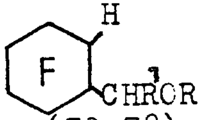
Alkene	Ether	Method of Initiation	Products (%yield)	Reference
	Et_2O, , 	gamma		[103]
	Me_2O	gamma $(PhCOO)_2 85^{\circ}C$	 (51-58)	[100]
	Et_2O, , 	gamma	 (28-65)	[102]
	Me_2O , , 	gamma $(PhCOO)_2 85^{\circ}C$	 (73-78)	[100] [96]

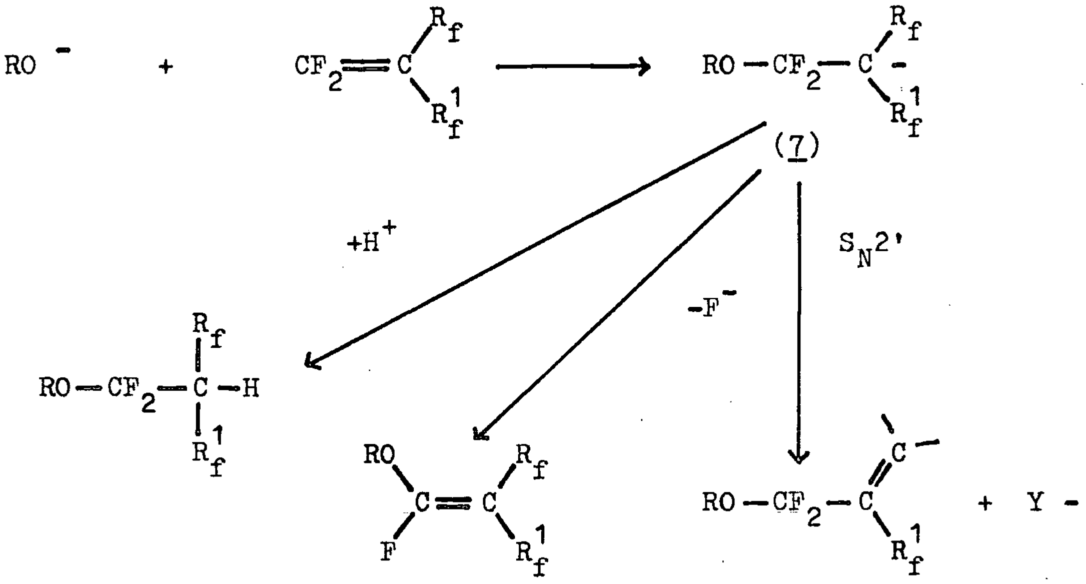
Table 9.

Relative Reactivities of Substituted Diethyl Ethers Towards Hexafluoropropene [98]

Ether	Relative Reactivity
$RCH_2OCH_2CH_3$	
R= CH_3-	1000
CH_2F-	260
CHF_2-	110
CF_3-	56
CH_2Cl-	320
CHF_2CF_2-	46
$R^1CF_2OCH_2CH_3$	
R^1=CHF_2-	0.8
CHFCl-	1.0
$CHCl_2$-	<0.1

2. NUCLEOPHILIC ADDITION TO POLYFLUOROALKENES.

The base catalysed nucleophilic addition of alcohols to polyfluoroalkenes produces polyfluoroethers usually in very good yield. The electrophilic nature of polyfluoroalkenes renders them very susceptible to nucleophilic attack and the intermediate carbanion (7) may follow one of three routes depending on the nature of the alkene.[104]



Y = F, Cl, Br, I

Polyfluoroethylenes react with alcohols using a base catalyst to give usually the saturated ether,

$$CH_3OH \quad + \quad CF_2{=}CFCl \xrightarrow{\text{base}} CH_3OCF_2CClFH$$

$$n\text{-}C_4H_9OH \quad + \quad CF_2{=}CF_2 \xrightarrow[\text{pressure}\ 0\text{-}38^\circ C]{10\%\ n\text{-}BuONa} n\text{-}C_4F_9OCF_2CF_2H \quad (81\%)$$

whereas using neat alkali metal alkoxides appreciable amounts of the unsaturated ether may be obtained.[104]

$$CF_3CH_2OK \quad + \quad CF_2{=}CHCl \xrightarrow[110^\circ C]{\text{toluene/ether}} CF_3CH_2OCF{=}CHCl \quad (50\%)$$

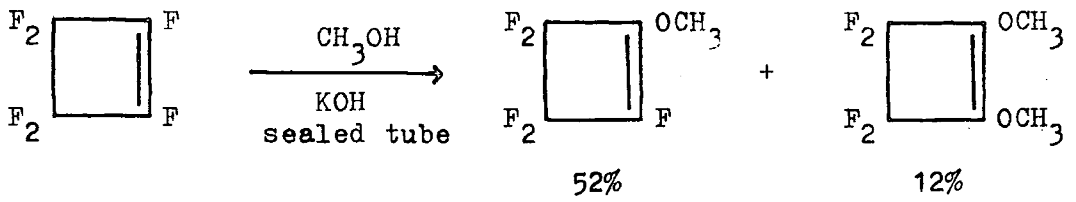
Base catalysed addition to polyfluoropropenes give mainly the saturated ethers.[104]

$$CH_3OH \quad + \quad CF_2{=}CFCF_3 \xrightarrow[60^{\circ}C,\ 13hr,\ autoclave]{KOH} CH_3OCF_2CFHCF_3 \quad 83\%$$

Perfluoroisobutene reacts with alcohols, in the absence of base, to form ethers due to the stability of the intermediate carbanion.[104]

$$CH_3OH \quad + \quad CF_2{=}C(CF_3)_2 \longrightarrow \begin{array}{ll} CH_3OCF_2CH(CF_3)_2 & 65\% \\ + & \\ CH_3OCF{=}C(CF_3)_2 & 8\% \end{array}$$

With cyclic fluoroalkenes, substitution usually predominates over addition.[104]



Fluorinated alcohols have been used to add to fluoroalkenes.[105]

$$CHF_2CHOH \quad + \quad CF_2{=}CXF \xrightarrow[DMSO,60^{\circ}C]{KOH} CHF_2CH_2OCF_2CHXF$$

X= F , Cl

Comprehensive lists of these reactions have been published in various review articles[1 , 104]

3. ADDITION OF PERFLUOROALKYL HYPOHALITES TO ALKENES.

Perfluoroalkyl hypofluorites react very violently with alkenes. For example trifluoromethyl hypofluorite reacts explosively with tetrafluoroethene to form polytetrafluoroethene and degradation products, rather than perfluoroethyl methyl ether. Also the addition to ethene was possible only at high dilution with an inert gas.[106] On the other hand, perfluoroalkyl hypochlorites add readily to both unsubstituted and halosubstituted alkenes to form ethers almost quantatively.[107]

$$R_fOCl \quad + \quad CF_2{=}CF_2 \longrightarrow R_fOCF_2CF_2Cl$$

$R_f = CF_3,\ iC_3F_7,\ (CF_3)_3C$

$$CF_3OCl \quad + \quad CF_2{=}CH_2 \longrightarrow CF_3OCF_2CH_2Cl$$

The direction of addition of both alkyl and perfluoroalkyl hypochlorites to polyfluoroalkenes is such that the chlorine atom ends up on the most electron rich carbon of the alkene. Whether the mechanism for this reaction is electrophilic or radical in nature is uncertain.

4. REACTION OF METAL ALKOXIDES WITH HALOALKANES.

A major route historically to polyfluoroethers is the action of alcohols or alkoxides on fluorocarbon halides first reported by Swarts in 1899.[108] This method resembles the Williamson synthesis of ethers.

$$CHF_2CF_2Cl \quad + \quad C_2H_5OH \xrightarrow{KOH} CHF_2CF_2OC_2H_5 \quad 70\%$$

However a different mechanism is usually involved with initial elimination to form an alkene followed by nucleophilic attack by the alcohol.[109] This explains why the alkoxy moeity becomes attached to the carbon with the most fluorine atom substituents.

$$CHClFCHF_2 \xrightarrow[120^{\circ}C]{NaOC_2H_5} CH_2ClCF_2OC_2H_5 \quad 53\%$$

Difluoromethyl fluoroalkyl ethers may be prepared by the reaction of fluoroalkanols with chlorodifluoromethane in the presence of a base.

$$R_fOH \xrightarrow[NaOH]{CHF_2Cl} R_fOCHF_2$$

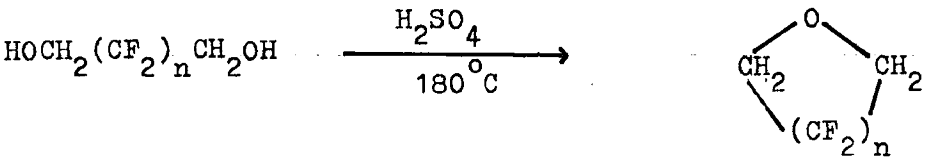
$$R_f = CHF_2CH_2\ ,\quad CHFCF_2CH_2$$
$$CF_3CF_2CF_2CH_2\ ,\quad (CF_3)_2(CH_3)C$$

It has been postulated that difluorocarbene is an intermediate in this reaction.[110]

5. MISCELLANEOUS METHODS.

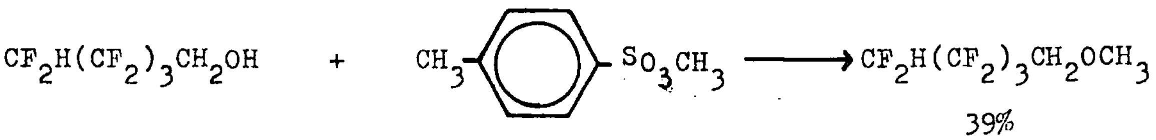
A number of methods for the preparation of polyfluoroethers have been reported that, although they do not have wide application, may be particularly useful for the production of specific ethers.

The dehydration of polyfluoroglycols produces ethers in high yield.[76]



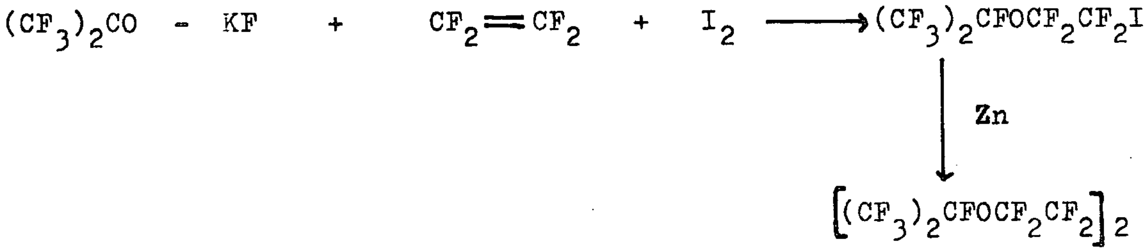
$n = 2$ or 3 86 - 97%

Polyfluoroethers are formed during the decomposition of tosylates of alcohols or glycols.[111]



39%

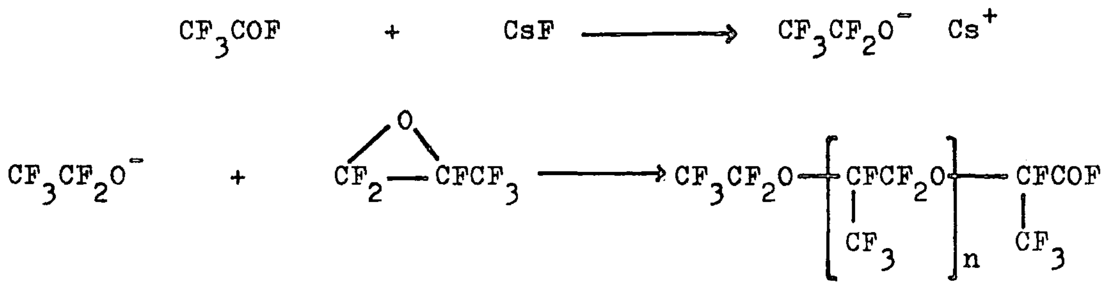
The fluoride ion catalysed addition of hexafluoroacetone and tetrafluoroethene may be used to prepare ethers.[112][113]



$$(CF_3)_2CO - KF + CF_2{=}CF_2 + I_2 \longrightarrow (CF_3)_2CFOCF_2CF_2I \xrightarrow{Zn} \left[(CF_3)_2CFOCF_2CF_2\right]_2$$

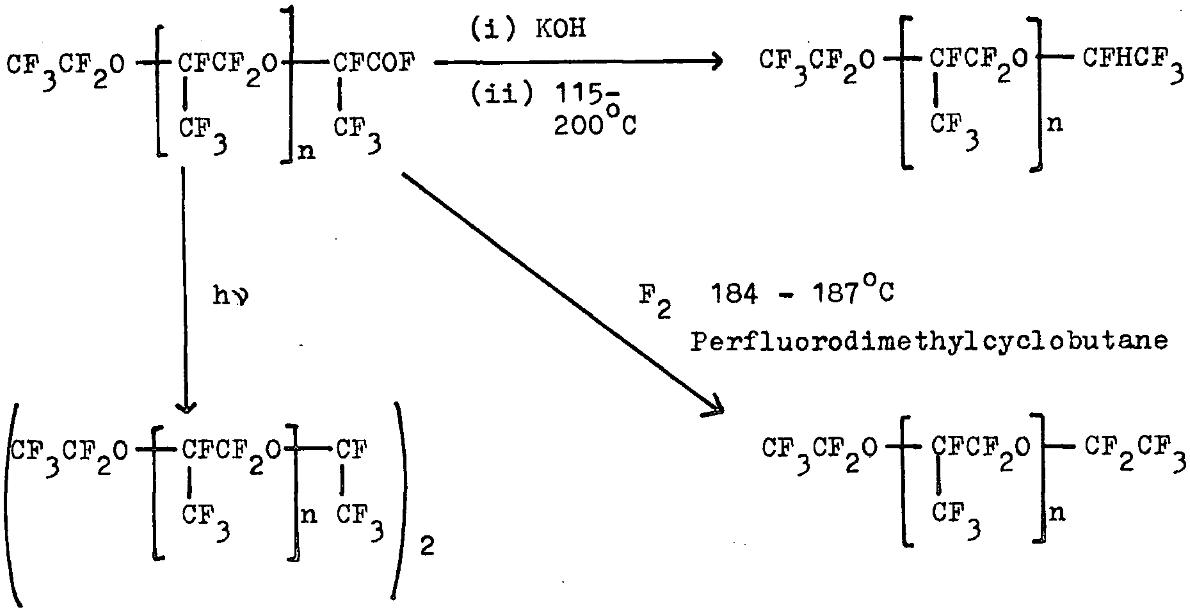
D. SYNTHESIS OF POLYFLUOROETHERS USING POLYFLUOROEPOXIDES AND RELATED REACTIONS.

The polymerization of epoxides has been applied to the synthesis of polyfluoropolyethers which have industrially important properties. Several partially fluorinated epoxides have been polymerized using Lewis acid catalysts. Aluminium chloride and ferric chloride were the most effective for achieving maximum conversions of 3,3,3-trifluoro-1,2-epoxypropane and 2-methyl-3,3,3-trifluoro-1,2-epoxypropane to polymers.[114] Hexafluoropropylene oxide has been polymerized using a catalyst of an alkali metal fluoride such as caesium fluoride in the presence of an acid fluoride such as trifluoroacetyl fluoride in diglyme.[115]

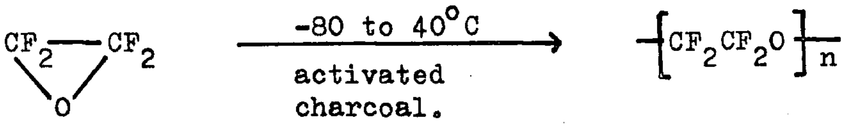


n= 1 to 6 (8)

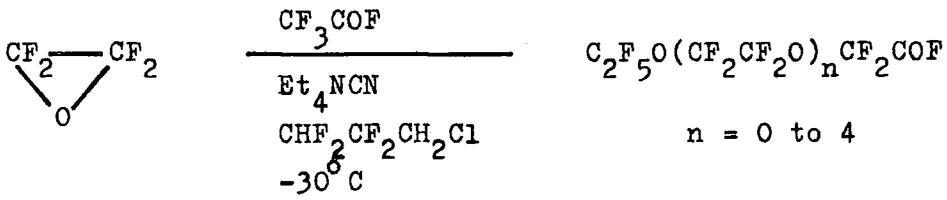
Other catalysts that have been used include alkali metal fluorides, quarternary ammonium halides, and quarternary phosphorus or arsenic salts. The perfluoropolyethers (8) contain acid fluoride end groups which may be removed by a number of methods. The acid fluoride group may be replaced by hydrogen by hydrolysis of (8) followed by pyrolysis of the potassium salt.[116] Similarly the hydrolysis of (8) followed by fluorination at a high temperature in an inert solvent will replace the acid fluoride group by fluorine.[117] The photolysis of (8) eliminates carbon monoxide and forms dimers of (8) to double the molecular weight of the perfluoropolyether.



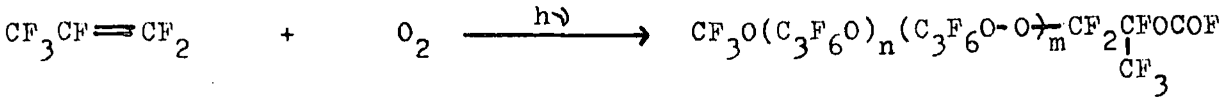
High molecular weight polyethers can be prepared by the free radical polymerization of perfluoroethylene oxide using either fluorine gas or high energy radiation initiation.[118] Activated charcoal may be used as a catalyst.[119]



Lower molecular weight perfluoropolyethers are obtained by using a perfluoroalkanoyl fluoride catalyst.[120]

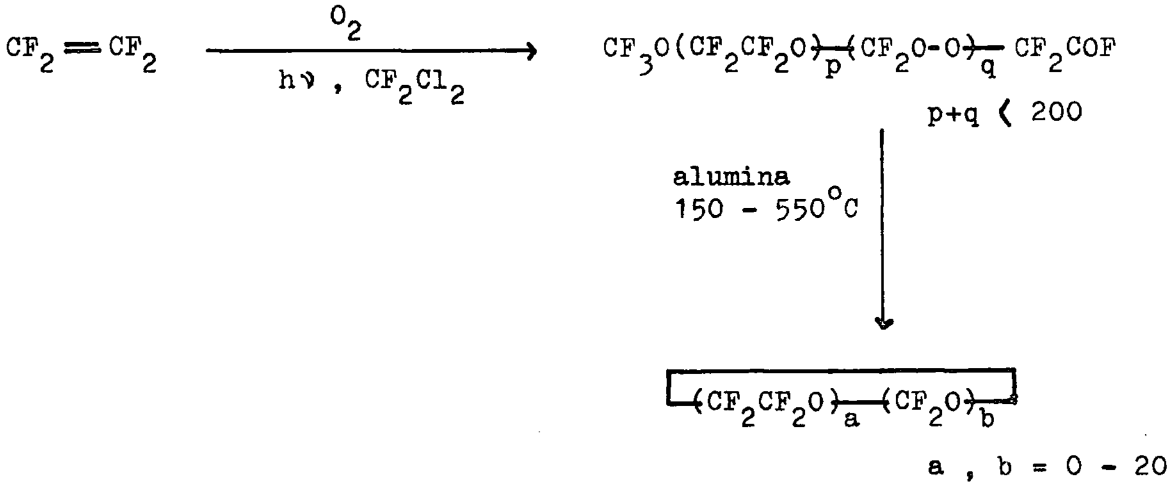


In place of epoxides the direct photo-oxidation of perfluoroalkenes has been used to obtain polyfluoropolyethers. The photo-oxidation of hexafluoropropene at low temperatures yields peroxides which can be thermally decomposed and fluorinated to give perfluoropolyethers.



$$CF_3CF{=}CF_2 + O_2 \xrightarrow{h\nu} CF_3O(C_3F_6O)_n(C_3F_6O{-}O)_m CF_2\underset{CF_3}{C}FOCOF$$

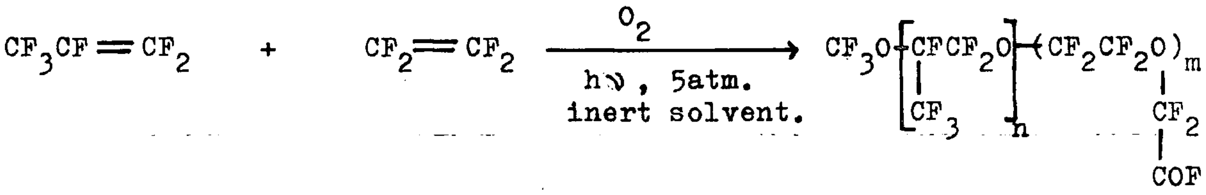
A similar photo-oxidation occurs with tetrafluoroethene and cyclic perfluoropolyethers may be prepared in low yield by the decomposition of the produced perfluoropolyether peroxide[121]



$$CF_2{=}CF_2 \xrightarrow[h\nu\ ,\ CF_2Cl_2]{O_2} CF_3O(CF_2CF_2O)_p(CF_2O\text{-}O)_q\,CF_2COF \quad p+q < 200$$

$$\xrightarrow{\text{alumina},\ 150-550^{\circ}C} \boxed{(CF_2CF_2O)_a(CF_2O)_b} \quad a\ ,\ b = 0 - 20$$

A mixture of perfluoroalkenes can be used in this reaction to obtain perfluorocopolyethers, for example tetrafluoroethene and hexafluoropropene and the acid fluoride end groups removed either photochemically or thermally followed by direct fluorination.[122]



$$CF_3CF{=}CF_2 \quad + \quad CF_2{=}CF_2 \xrightarrow[h\nu\ ,\ 5atm.\ \text{inert solvent.}]{O_2} CF_3O\Big[\underset{\displaystyle CF_3}{CF}CF_2O\Big]_n(\underset{\displaystyle \overset{|}{CF_2}\atop{\displaystyle \overset{|}{COF}}}{CF_2CF_2O})_m$$

In general these methods are useful for the preparation of perfluoropolyether mixtures but they are not suitable for specific compounds, especially of low molecular weight.

DISCUSSION

CHAPTER 2

FREE RADICAL ADDITION OF OXYGEN FUNCTION SUBSTRATES TO FLUOROALKENES.

A. INTRODUCTION.

The carbon hydrogen bond can be used as a functional group for free radical additions to fluoroalkenes. A variety of oxygen containing systems have been added and the subject has been reviewed by a previous worker in the laboratory.[7] It is apparent from published work that, although many systems have been investigated, there has been little system atic study of the relationship between structure and reactivity. Consequently part of these investigations has been a study of the effect of various substituents on the reactivity of ethers in additions to fluoroalkenes. An oxygen atom interacts with an adjacent radical centre as illustrated in Figure 1 to lower the energy of the system.

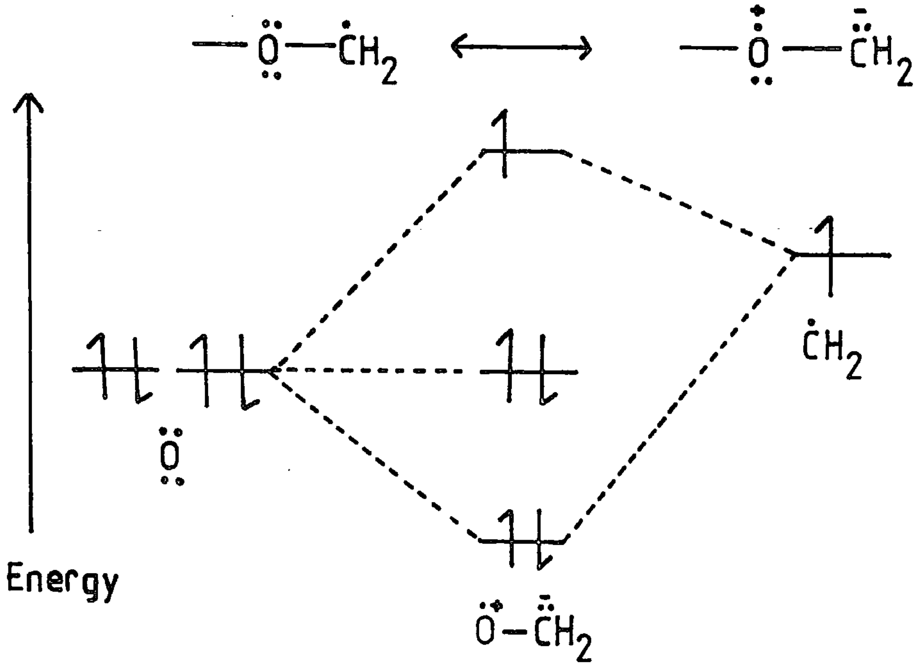


Figure 1

We have studied the following structural changes:

(a) The effect of electron withdrawing substituents on the reactivity of the ether, eg. $XOCH_3$ and XCH_2OCH_2Y.

(b) The substituent and stereoelectronic effects in various cyclic ethers.

(c) The effect of structural changes on the alkene itself, eg. the series $CF_2{=\!=}CF_2$, $CF_2{=\!=}CFR_f$, $R_fCF{=\!=}CFR_f$, $(R_f)_2C{=\!=}CFR_f$, $(R_f)_2C{=\!=}C(R_f)_2$, where R_f= perfluoro-alkyl or -cycloalkyl, etc.

This chapter contains results, structural and synthetic aspects, while the mechanistic aspects are discussed and drawn together in Chapter 4. The yield of product has been used as an indication of the reactivity of the substrate. Of course this method is valid only for reactions carried out under standard, ie comparable, conditions. This was achieved by sealing the two reactants into similar volume glass Carius tubes, after degassing to remove dissolved air. An excess of the substrate was used, usually in a 2.5:1 molar ratio with the fluoroalkene. A cobalt-60 gamma ray source was used as the initiator and the reactants were irradiated to a constant dose of 10 Mrad. It is felt that comparison of such reactions is adequate for the qualitative approach that we are adopting. Two sets of variables have been used during this study;

(a) the substrate was varied with a particular fluoroalkene ie hexafluoropropene, and

(b) the fluoroalkene was varied with a particular substrate.

B. ADDITION OF ETHERS TO FLUOROALKENES.

Previous work on the addition of ethers to fluoroalkenes has been listed in Table 8. It was necessary to repeat a few of these reactions in order to check their reactivity under the conditions used in this study.

1. ADDITIONS TO HEXAFLUOROPROPENE.

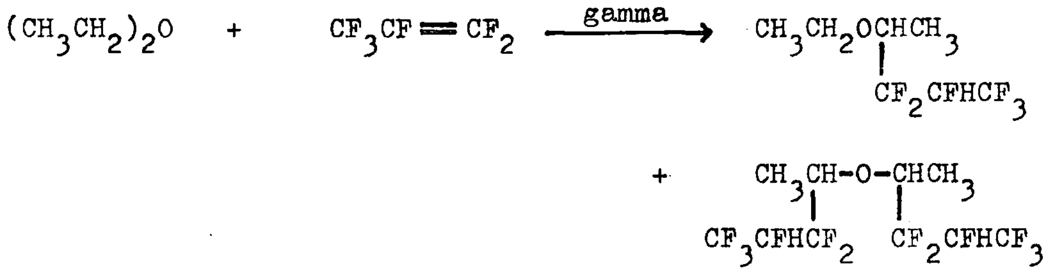
a. Acyclic Ethers.

The series of dialkyl ethers RCH_2OCH_2R react with hexafluoropropene to form adducts usually in good yield. With dimethyl ether (R=H) a monoadduct (9) was formed as the sole product.

$$CH_3OCH_3 \quad + \quad CF_3CF{=}CF_2 \xrightarrow{\text{gamma}} CH_3OCH_2CF_2CFHCF_3$$

(9) 68%

Diethyl ether ($R=CH_3$) gave a mixture of monoadduct (10) and diadduct (11) in roughly equal proportions.



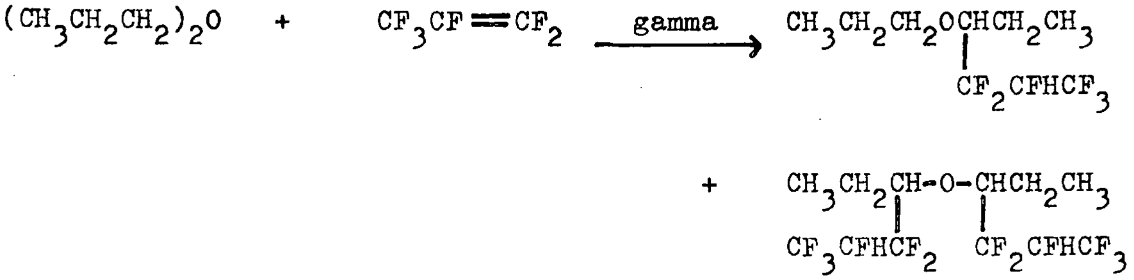
$$(CH_3CH_2)_2O \quad + \quad CF_3CF{=}CF_2 \xrightarrow{\text{gamma}} CH_3CH_2O\underset{\substack{|\\ CF_2CFHCF_3}}{C}HCH_3$$

(10) 38%

$$+ \quad CH_3\underset{\substack{|\\ CF_3CFHCF_2}}{C}H\text{-}O\text{-}\underset{\substack{|\\ CF_2CFHCF_3}}{C}HCH_3$$

(11) 43%

Similarly di-n-propyl ether ($R=C_2H_5$) gave both a monoadduct (12) and a diadduct (13) although the diadduct was the predominant product.



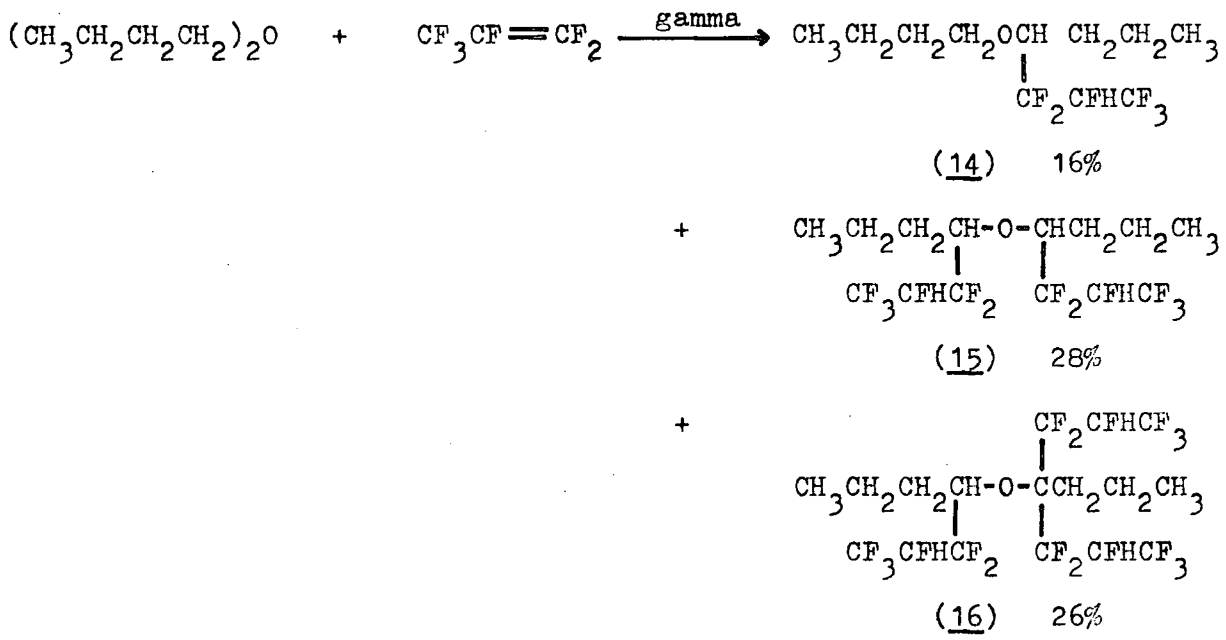
$$(CH_3CH_2CH_2)_2O \quad + \quad CF_3CF{=}CF_2 \xrightarrow{\text{gamma}} CH_3CH_2CH_2O\underset{\substack{|\\ CF_2CFHCF_3}}{C}HCH_2CH_3$$

(12) 12%

$$+ \quad CH_3CH_2\underset{\substack{|\\ CF_3CFHCF_2}}{C}H\text{-}O\text{-}\underset{\substack{|\\ CF_2CFHCF_3}}{C}HCH_2CH_3$$

(13) 28%

Dibutyl ether ($R=C_3H_7$) gave a mixture of products from which mono- (14), di- (15), and tri-adducts (16) were isolated.



$$(CH_3CH_2CH_2CH_2)_2O + CF_3CF{=}CF_2 \xrightarrow{\text{gamma}} CH_3CH_2CH_2CH_2O\underset{\displaystyle CF_2CFHCF_3}{\underset{|}{CH}}CH_2CH_2CH_3$$

(14) 16%

$$+\ CH_3CH_2CH_2\underset{\displaystyle CF_3CFHCF_2}{\underset{|}{CH}}\text{-}O\text{-}\underset{\displaystyle CF_2CFHCF_3}{\underset{|}{CH}}CH_2CH_2CH_3$$

(15) 28%

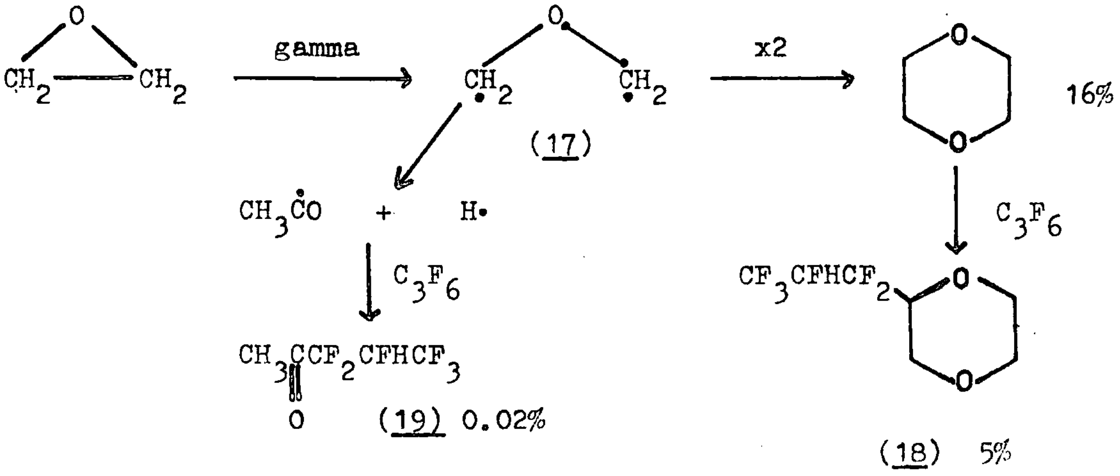
$$+\ CH_3CH_2CH_2\underset{\displaystyle CF_3CFHCF_2}{\underset{|}{CH}}\text{-}O\text{-}\overset{\displaystyle CF_2CFHCF_3}{\overset{|}{\underset{\displaystyle CF_2CFHCF_3}{\underset{|}{C}}}}CH_2CH_2CH_3$$

(16) 26%

However di-iso-propyl ether did not react at room temperature. Therefore increasing the size of R gave a higher proportion of polyadducts.

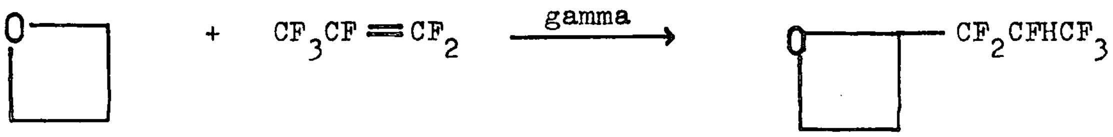
b. <u>Cyclic Ethers</u>.

The effect of ring size on cyclic ether addition to hexafluoropropene was systematically investigated. Ethylene oxide did not form any addition products, although there were some ring opened products, (18) and (19), which can be rationalized by the radiolytic cleavage of the oxirane ring. The resulting diradical (17) may dimerize to p-dioxan and form the p-dioxan adduct (18). Alternatively the radical (17) may rearrange to an acetoxy radical which will form the acetaldehyde adduct (19).



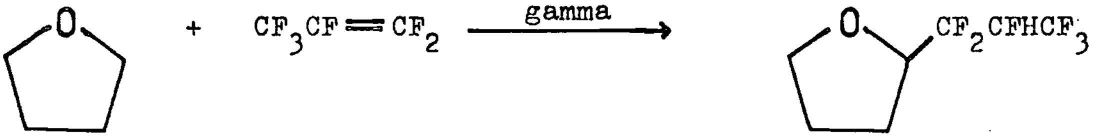
Evidence in favour of this mechanism is that the radiolysis of ethylene oxide produces, amongst other products, p-dioxan.

Oxetane gave a good yield of the mono-adduct (20) but a quantity of viscous non-fluorocarbon liquid remained, after the distillation of the product, that was probably polyether material derived from ring opening.



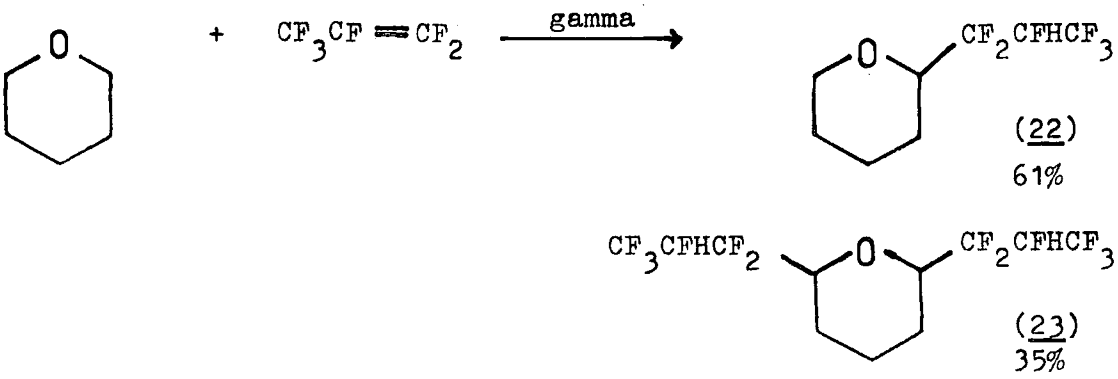
(20) 65%

In agreement with literature reports we found that oxolane reacted to give an almost quantitative yield of the mono-adduct (21).



(21) 95%

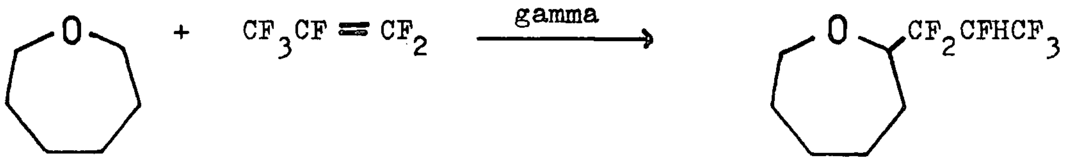
Oxane gave a small amount of the di-adduct (23) in addition to the mono-adduct (22).



(22) 61%

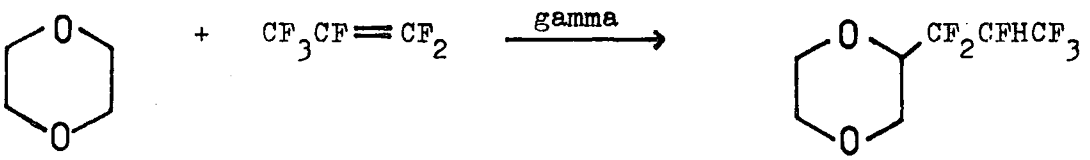
(23) 35%

Oxepane gave a good yield of the mono-adduct (24) however a small quantity of polyether material was formed.



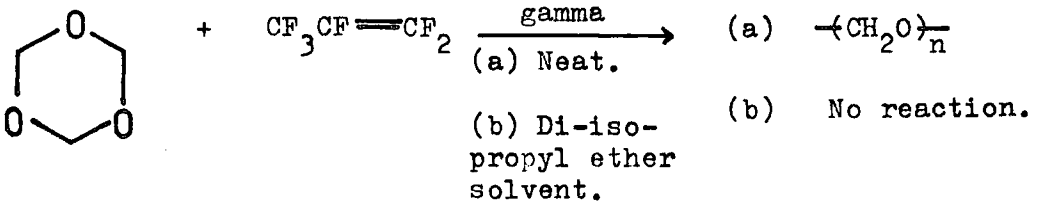
(24) 70%

The introduction of a second oxygen atom into the six membered ring does not effect reactivity as p-dioxan gave the mono-adduct (25) in high yield.

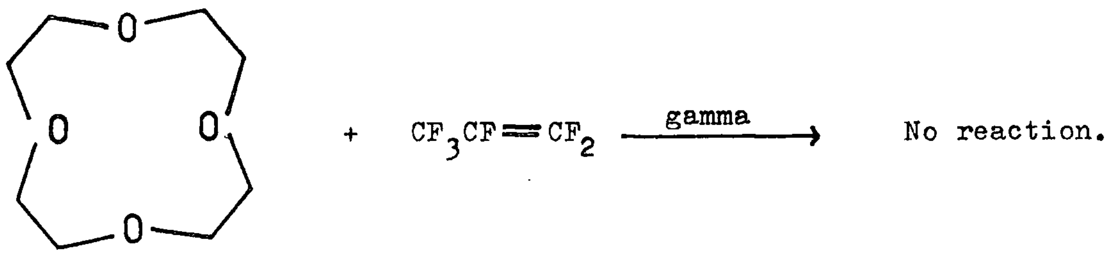


(25) 79%

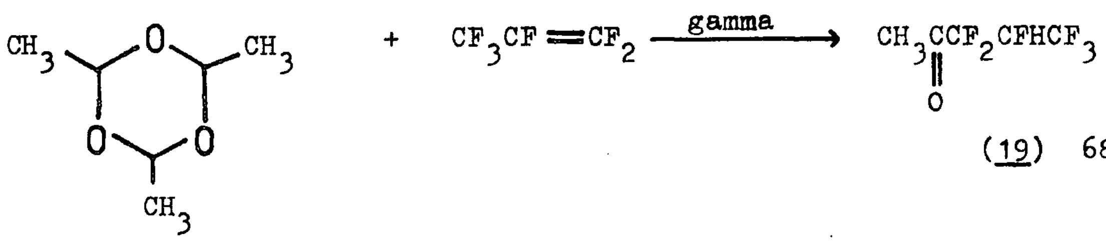
However with s-trioxan no addition products were formed with hexafluoropropene. This may have been a phase problem because s-trioxan is a crystalline solid. Therefore this reaction was repeated using a solvent of di-iso-propyl ether but there was still no detectable reaction.



Immiscibility was advanced as a reason why 18-crown-6 polyether did not react with hexafluoropropene.[7] For further clarification liquid 12-crown-4 polyether was reacted;however there was still no reaction.

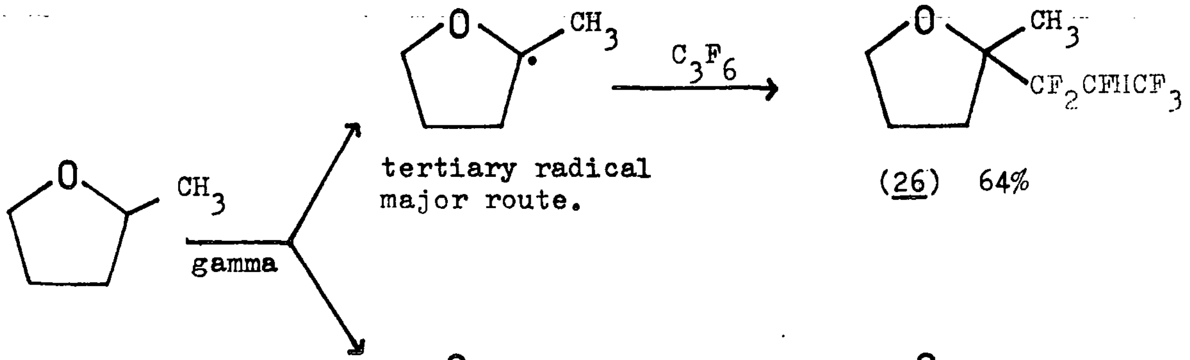


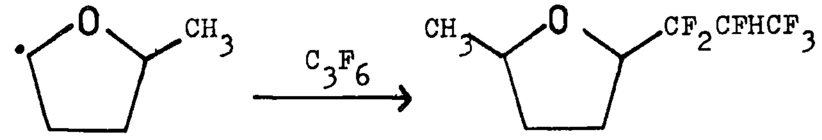
The attempted addition of 2,4,6-trimethyltrioxan gave only the acetaldehyde adduct (19) in good yield



(19) 68%

2-Methyloxolane has two possible hydrogen abstraction sites in a position alpha to the oxygen atom. Both types of adducts were formed, the main one (26) from the tertiary radical intermediate rather than from the secondary radical intermediate (27).





secondary radical minor route.

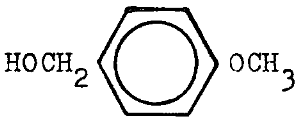
(27) 32%

Temp(°C).	Ratio (26)/(27)
18	2.01
75	1.90

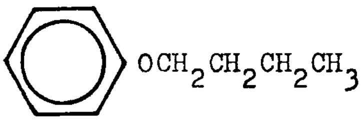
This result is in agreement with the relative stabilities of the two radicals, a tertiary radical being the most stable. An increase in temperature should make the reaction less specific and this was found to be the case when the reaction was carried out at 75°C.

c. Miscellaneous Attempted Additions.

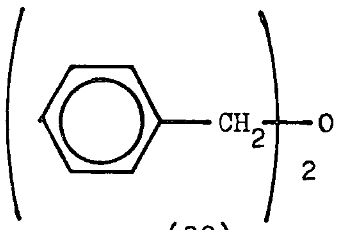
A phenyl substituent on an ether causes deactivation in the addition to hexafluoropropene.[7] Anisole was unreactive at 18°C but other workers obtained cyclized products using an elevated temperature.[97] During this study neither p-hydroxymethylanisole (28), n-butyl phenyl ether (29), nor dibenzyl ether (30) reacted at 18°C.



(28)



(29)

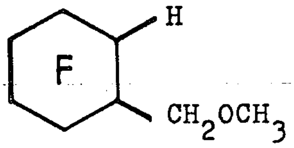


(30)

Similarly, both a chlorine atom eg (31) or a polyfluoroalkyl group eg (32), in a position beta to the free radical centre, deactivated the ether towards addition.

$(ClCH_2CH_2)_2O$

(31)

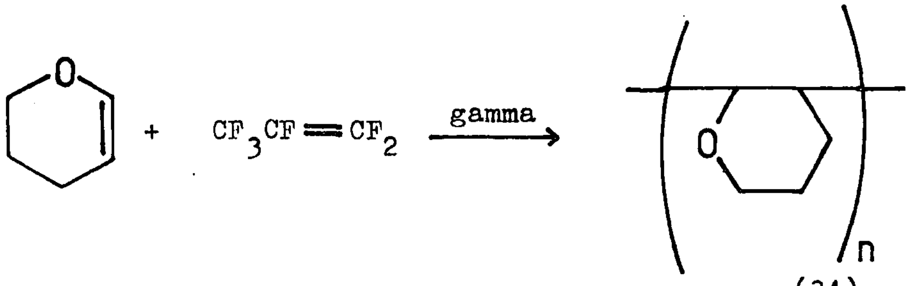


(32)

Vinyl ethers did not form any adducts and either co-polymers with the alkene (33) or homopolymers (34) were obtained. The polymer (34) was formed only in the presence of fluoroalkene.

$$CH_3CH_2CH_2CH_2OCH{=}CH_2 \quad + \quad CF_3CF{=}CF_2 \xrightarrow{\text{gamma}} \text{Co-polymer. (elastomer)}$$

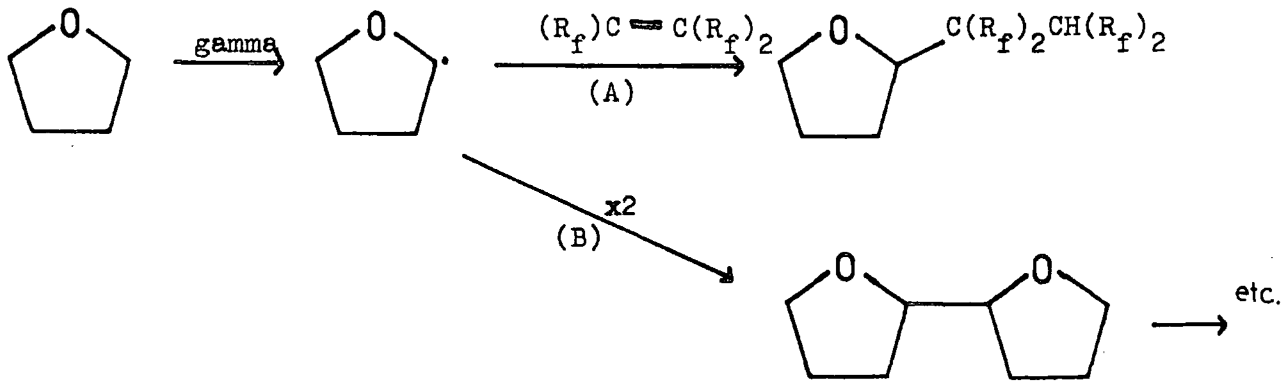
(33)



(34)

2. ADDITIONS WITH OXOLANE.

A number of fluoroalkenes were reacted with oxolane to give products as shown in Table 10. The fluoroalkenes were chosen in order to have increasing perfluoroalkyl substitution on the double bond. There is no discernible electronic effect on the high yield of adducts with the introduction of perfluoroalkyl substituents. With 2,3-dichlorohexafluorobut-2-ene a certain amount of dehydrochlorination took place to give (42a). Perfluoro-3-methylpent-2-ene gave a good yield of adducts which included a di-adduct (44). However perfluoro-3,4-dimethyl-4-ethylhex-2-ene gave very little product, presumably due to the steric effect of the one very bulky substituent. Perfluoro-3,4-dimethylhex-3-ene did not react, however in this reaction , and also in the previous two, a white polyether type material was isolated. This shows that radicals are formed but the addition reaction (A) is too slow to compete with the dimerization reaction (B).



Perfluorocyclohexa-1,3-diene gave a polymeric material which was not investigated further.

Table 10

Addition of Fluoroalkenes to Oxolane Using Gamma Ray Initiation at 18°C

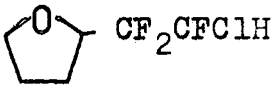
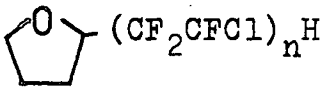
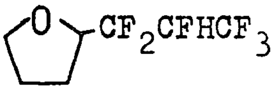
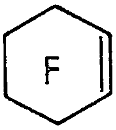
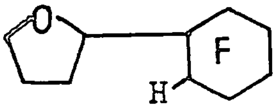
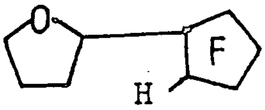
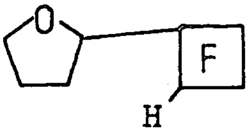
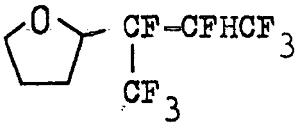
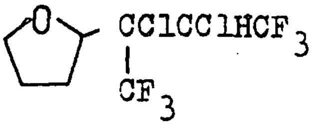
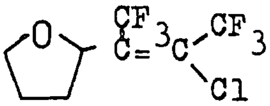
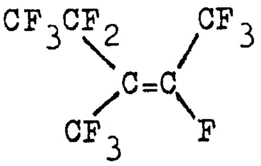
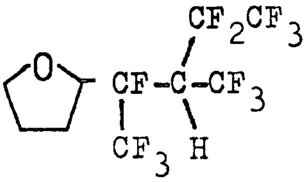
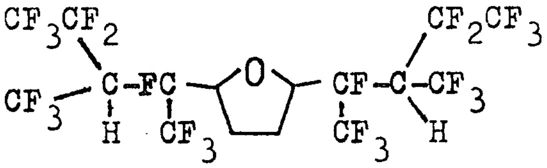
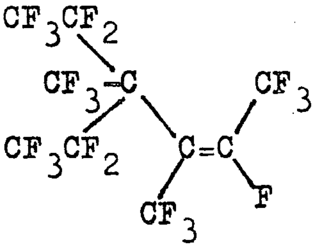
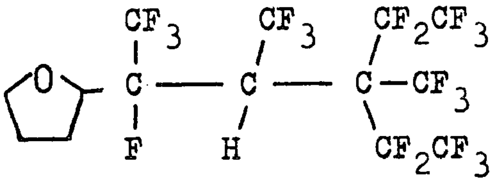
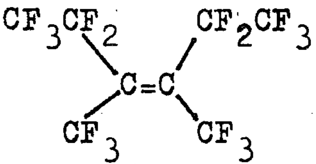
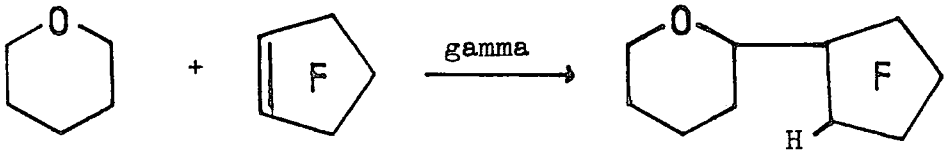
Fluoroalkene	Products	%Yield
$CF_2=CFCl$	 + (35)	78
	 (36)	20
$CF_3CF=CF_2$	 (37)	95
	 (38)	91
	 (39)	83
	 (40)	91
$CF_3CF=CFCF_3$	 (41)	89
$CF_3CCl=CClCF_3$	 (42)	89
	 (42a)	9

Table10cont.

Fluoroalkene	Products	%Yield
 cis/trans.	 (43)	70
	 (44)	22
 cis/trans.	 (45)	4
 cis/trans.	No reaction	-
	Polymer	-

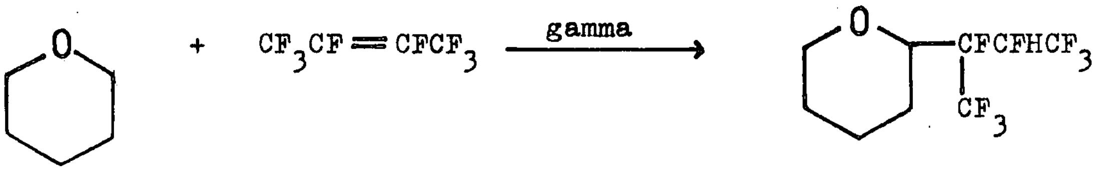
3. ADDITIONS WITH OXANE.

Oxane reacts with perfluorocyclopentene to give a good yield of mono-adduct (46).



(46)
76%

However perfluorobut-2-ene gave a low yield of mono-adduct (47) and some of the alkene was recovered.

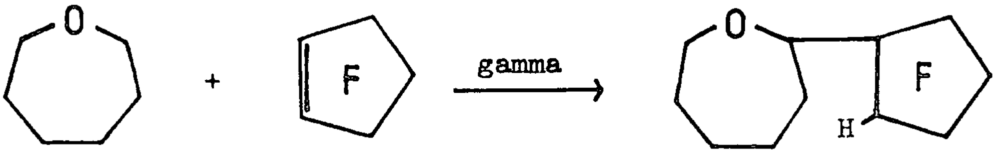


(47) 21%

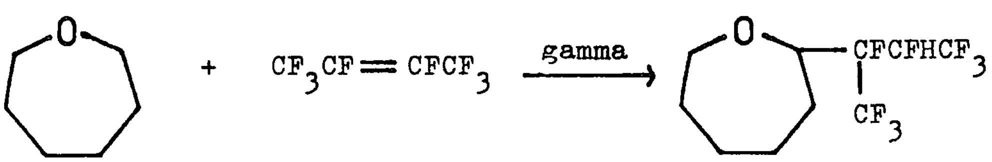
This behaviour is in contrast to that shown by oxolane.

4. ADDITIONS WITH OXEPANE.

The addition of oxepane to a series of fluoroalkenes gave results similar to those for oxolane. High yields of mono-adducts were formed from both perfluorocyclopentene (48) and perfluorobut-2-ene (49), in addition to hexafluoropropene discussed above.



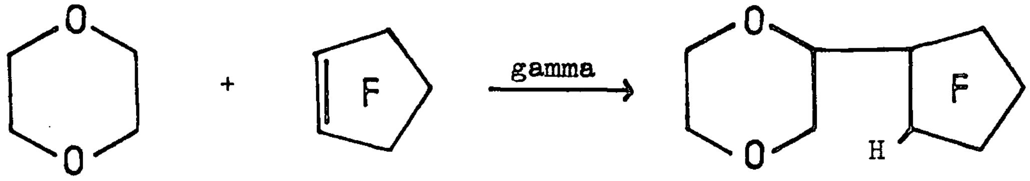
(48) 71%



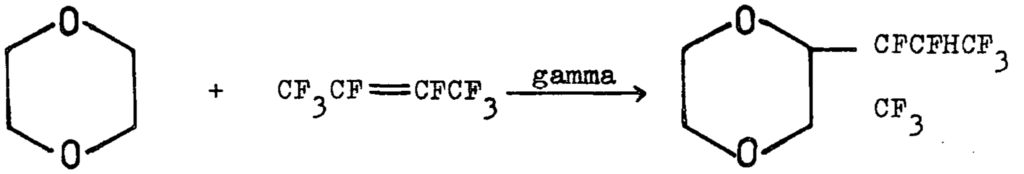
(49) 60%

5. ADDITIONS WITH 1,4-DIOXAN.

Although 1,4-dioxan gave a very high yield of mono-adduct with hexafluoropropene, this was not the case with more substituted alkenes. A much lower yield of mono-adduct (50) was isolated with perfluorocyclopentene. Perfluorobut-2-ene gave a very low yield of mono-adduct (51) and a comparable amount of a mixture of di-adducts.



(50) 49%

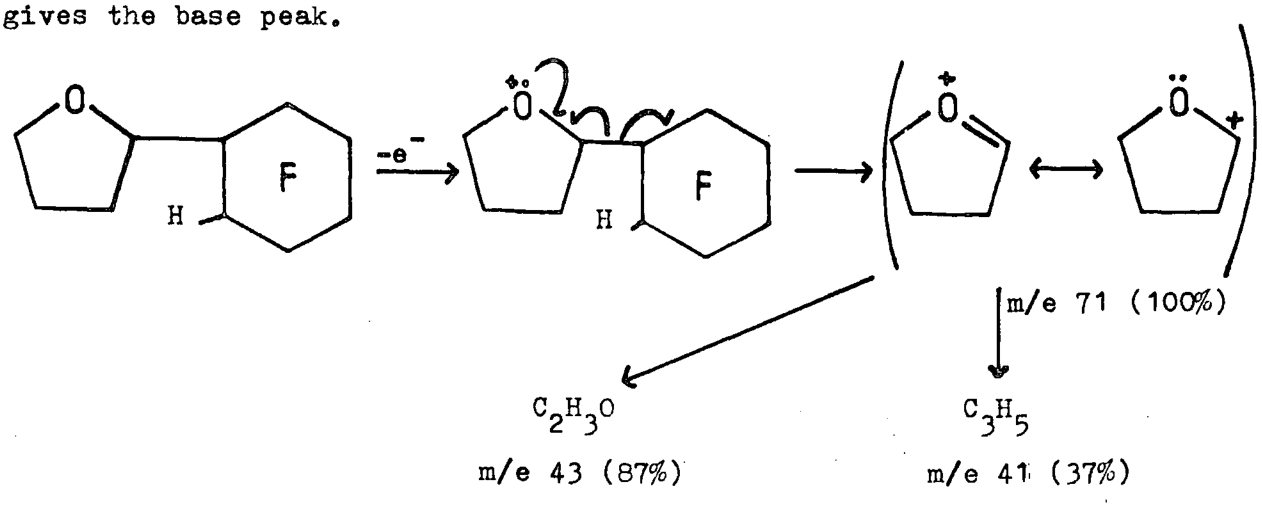


(51) 19%

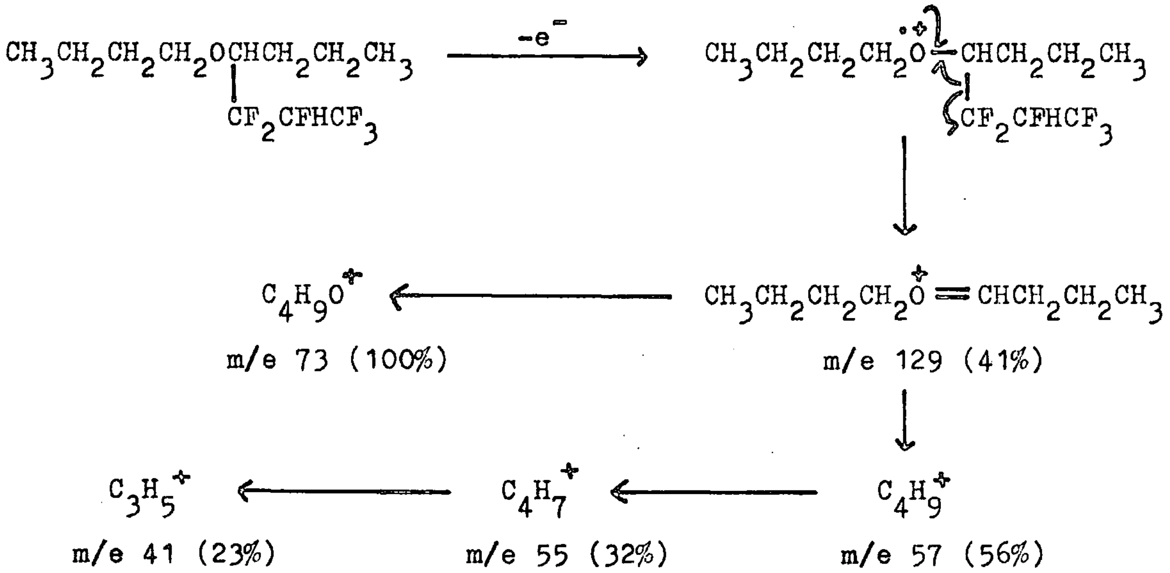
+ Diadducts 15%

6. IDENTIFICATION OF PRODUCTS.

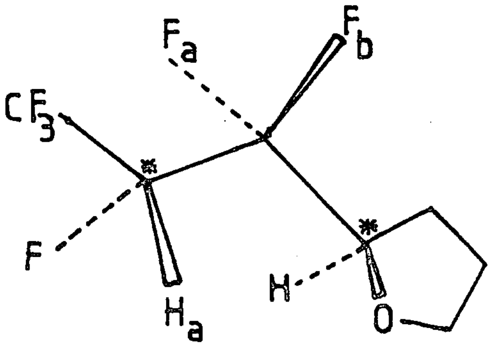
The most useful techniques for the characterisation of the ether adducts were mass spectroscopy and NMR spectroscopy. The mass spectra consisted of very small molecular ion peaks and with di-adducts the molecular ion peak was often missing. The principal fragmentation was the cleavage of the carbon-carbon bond adjacent to the oxygen atom on the most substituted side. With cyclic ether adducts this cleavage gives the base peak.



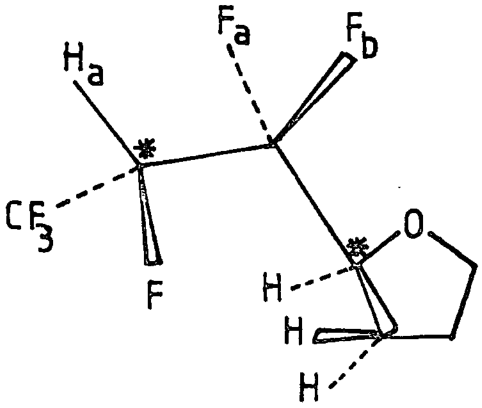
With acyclic ether adducts the resulting fragment is very susceptible to cleavage at the carbon-oxygen bond and this process gives the base peak.



The NMR spectra are very complex. The proton resonances are usually broad but the appearance of a doublet of multiplets at about 4.9 ppm (TMS reference) with a coupling constant of about 44Hz is very characteristic of the CFH proton. The 1,1,2,3,3,3-hexafluoropropyl grouping from hexafluoropropene adducts give a similar fluorine-19 spectrum irrespective of the rest of the adduct structure. The trifluoromethyl resonances occur as a multiplet at 74 to 77 ppm ($CFCl_3$ reference), the difluoromethylene resonances occur usually as an AB pattern at 119 to 131 ppm, and the tertiary fluorine resonances occur as a doublet of multiplets at 211 to 220 ppm. Most of the ether adducts contain two asymmetric centres which results in two sets of signals for each fluorine environment from (RS + SR) (52) and (RR + SS) (53) diasteriomers. In some cases the pairs of diasteriomers were separated by preparative GLC and the fluorine-19 spectra of each pair obtained, although they could not be assigned. French workers have carried out a NMR study into this type of compound using a spectrometer operating at 240MHz and applying decoupling and INDOR techniques.[96] They claimed to be able



(52) (RS + SR)



(53) (RR + SS)

to deduce coupling constants and consequently assign the steriochemistry of the two pairs. Our spectra were similar to a first approximation to that reported, therefore their assignments have been taken as correct for our purposes.

The polyfluorocycloalkene adducts were present as cis and trans isomers. The fluorine-19 chemical shift of the tertiary fluorine atoms in such adducts may be used to assign their stereochemistry.[100] The chemical shifts of the CFR and CFH fluorine atoms were found to be consistently at higher field in the cis isomer than in the trans isomer. The cycloalkene adducts reported here have been assigned similarly.

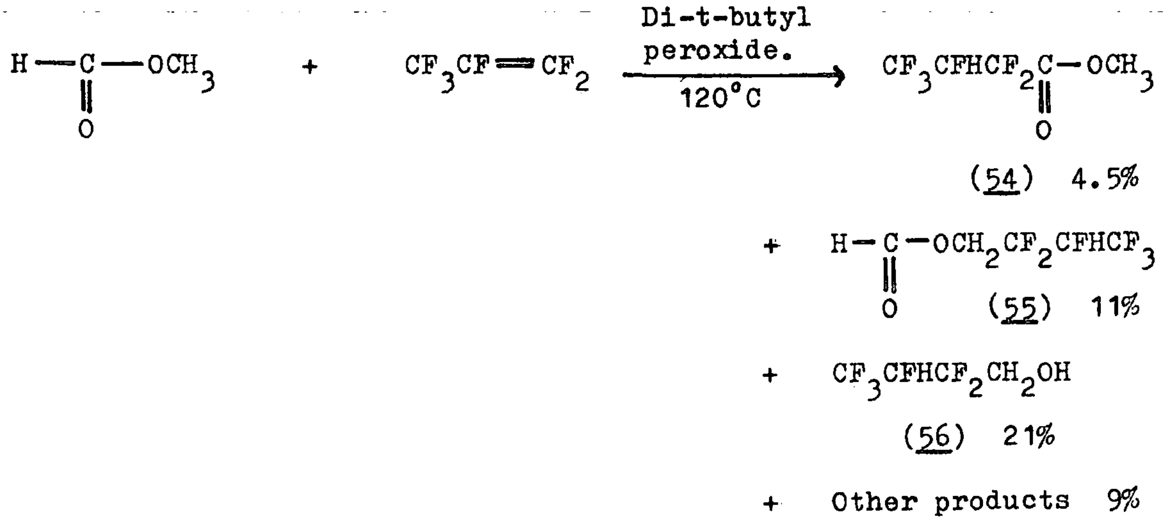
C. ADDITION OF ESTERS TO FLUOROALKENES.

An ester may be considered as a carbonyl substituted ether so a series of reactions were carried out to investigate their reactivity towards addition to fluoroalkenes. Methyl esters were used whenever possible in order to standardize the results and to make isolation and identification of the products easier. A few examples are reported in the literature, Table 11, and it is clear that the alkoxy group is more reactive than the carboxy group. Electronegative substituents result in much lower yields of mono-adducts.[124]

1. ADDITIONS TO HEXAFLUOROPROPENE.

All attempted reactions between esters and hexafluoropropene using gamma ray initiation at 18°C gave recovered starting materials. This shows that esters are much less reactive than ethers. It was possible to obtain products by using a much higher reaction temperature of 120°C and di-t-butyl peroxide as initiator.

Methyl formate reacted with hexafluoropropene to form products by hydrogen abstraction from both the methoxy group (55) and the aldehydic group (54).



$$H-\underset{\underset{O}{\|}}{C}-OCH_3 \quad + \quad CF_3CF{=}CF_2 \xrightarrow[120^\circ C]{\text{Di-t-butyl peroxide.}} CF_3CFHCF_2\underset{\underset{O}{\|}}{C}-OCH_3$$

(54) 4.5%

$$+ \quad H-\underset{\underset{O}{\|}}{C}-OCH_2CF_2CFHCF_3$$

(55) 11%

$+ \quad CF_3CFHCF_2CH_2OH$

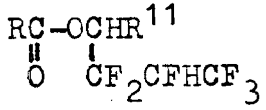
(56) 21%

\+ Other products 9%

The large amount of alcohol (56) formed may be due to hydrolysis of the ester (55) during isolation. Therefore the methoxy group is more

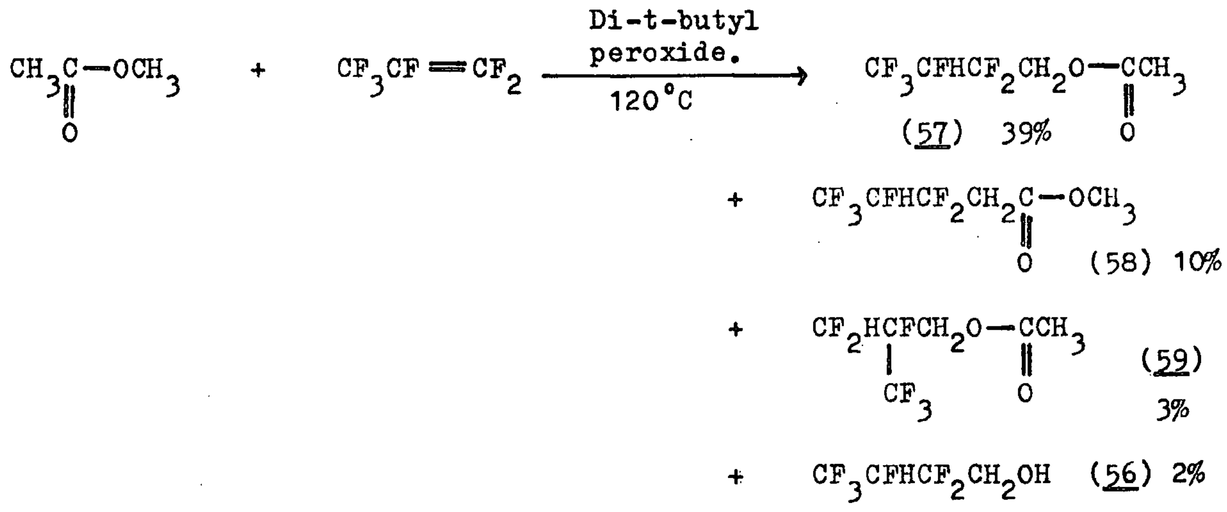
Table 11

Addition of Esters to Fluoroalkenes

Fluoroalkene	Ester	Conditions	Products (%Yield)	Reference
$CF_2=CF_2$	$EtCO_2Et$	Peroxide	Telomers	88
$CF_2=CFCF_3$	$MeCO_2Et$	$(^tBuO)_2$ 125°C	$CF_3CFHCF_2CHMeOCOMe$ (87%)	123
	RCO_2R^1 $R,R^1=Me,Et,Pr,CHMe_2,$ Bu,CH_2CHMe_2	gamma	 $\underset{\underset{O}{\Vert}}{RC}-O\underset{\underset{CF_2CFHCF_3}{\vert}}{C}HR^{11}$	124
	RCO_2Et $R=CHF,CHClF,CH_2Cl,$ $CHCl_2,CCl_3,CH_2CN$	gamma	--	124

reactive than the aldehyde group.

Methyl acetate gave products arising from hydrogen abstraction from the methoxy group (57) and (59) and from the carboxy group (58). In agreement with other work[114] the methoxy group was the preferred position of attack. Product (59) was derived from the addition of the ester radical to the substituted site of the alkene double bond. This may be due to the high reaction temperature causing the orientation of addition to be less specific.



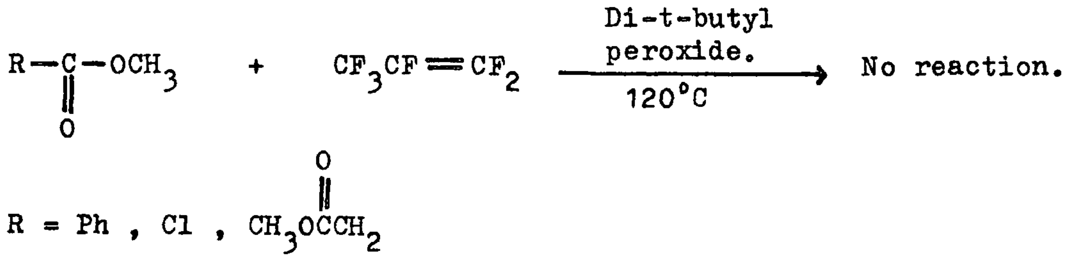
$$CH_3\underset{\underset{O}{\|}}{C}-OCH_3 + CF_3CF{=}CF_2 \xrightarrow[120^\circ C]{\text{Di-t-butyl peroxide.}} \underset{(\underline{57})\ 39\%}{CF_3CFHCF_2CH_2O}-\underset{\underset{O}{\|}}{C}CH_3$$

$$+\ CF_3CFHCF_2CH_2\underset{\underset{O}{\|}}{C}-OCH_3 \quad (58)\ 10\%$$

$$+\ CF_2H\underset{\underset{CF_3}{|}}{C}FCH_2O-\underset{\underset{O}{\|}}{C}CH_3 \quad (\underline{59})\ 3\%$$

$$+\ CF_3CFHCF_2CH_2OH \quad (\underline{56})\ 2\%$$

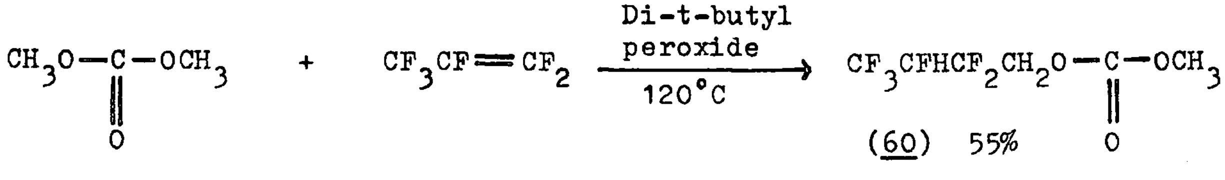
A number of compounds gave no products even at the higher reaction temperature. These were esters substituted with electron withdrawing groups.



$$R-\underset{\underset{O}{\|}}{C}-OCH_3 + CF_3CF{=}CF_2 \xrightarrow[120^\circ C]{\text{Di-t-butyl peroxide.}} \text{No reaction.}$$

$$R = Ph\ ,\ Cl\ ,\ CH_3O\overset{\overset{O}{\|}}{C}CH_2$$

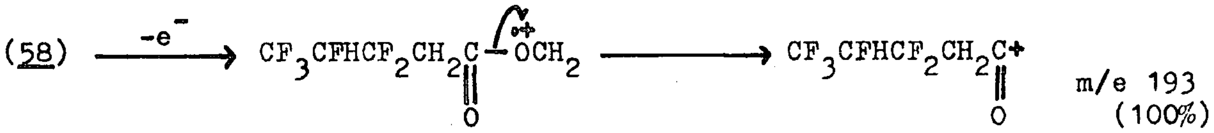
However dimethyl carbonate gave a mono-adduct (60) in moderate yield.



$$CH_3O-\underset{\underset{O}{\|}}{C}-OCH_3 + CF_3CF{=}CF_2 \xrightarrow[120^\circ C]{\text{Di-t-butyl peroxide}} \underset{(\underline{60})\ 55\%}{CF_3CFHCF_2CH_2O}-\underset{\underset{O}{\|}}{C}-OCH_3$$

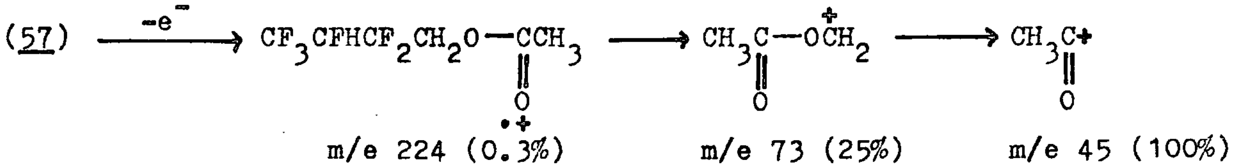
2. IDENTIFICATION OF PRODUCTS.

The infra red spectra of the ester adducts show the carbonyl stretching vibration at 1760 to 1766 cm^{-1} for methoxy substituted adducts and at 1745 cm^{-1} for carboxy substituted adducts. The mass spectra show very small parent peaks and the base peak results usually from cleavage next to the carbonyl group with the charge residing on the carbonyl fragment.



$$(\underline{58}) \xrightarrow{-e^{-}} CF_3CFHCF_2CH_2\underset{\underset{\textstyle O}{\|}}{C}-\overset{\cdot+}{O}CH_2 \longrightarrow CF_3CFHCF_2CH_2\underset{\underset{\textstyle O}{\|}}{C}^{+}$$

m/e 193 (100%)



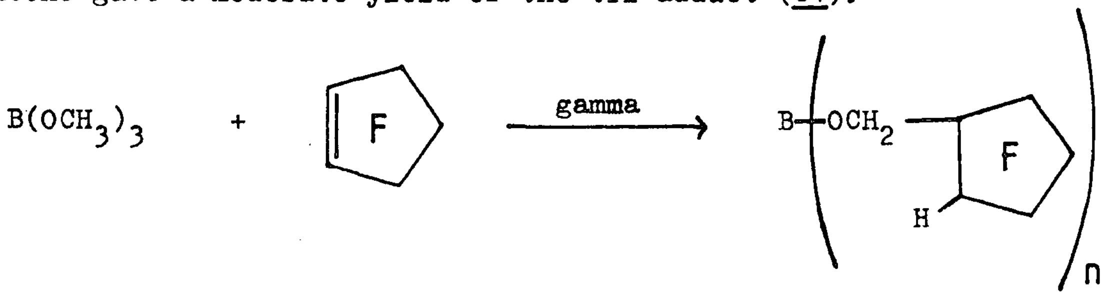
$$(\underline{57}) \xrightarrow{-e^{-}} CF_3CFHCF_2CH_2O-\underset{\underset{\textstyle \overset{}{O}^{\cdot+}}{\|}}{C}CH_3 \longrightarrow CH_3\underset{\underset{\textstyle O}{\|}}{C}-\overset{+}{O}CH_2 \longrightarrow CH_3\underset{\underset{\textstyle O}{\|}}{C}^{+}$$

m/e 224 (0.3%) m/e 73 (25%) m/e 45 (100%)

The proton NMR spectra were useful in identifying methyl groups and aldehydic protons in the adducts.

D. ADDITION OF BORATE ESTERS TO FLUOROALKENES.

A boron atom adjacent to a methoxy group would be expected to have a considerable influence over the reactivity of the carbon-hydrogen bond. The empty p-orbital of the boron may interact with an oxygen lone pair making them less readily available for donation to stabalize the free radical. However the reaction of trimethyl borate with perfluorocyclopentene gave a moderate yield of the tri-adduct (61).[7]



(61) 49%

This reaction has been investigated further by using other fluoroalkenes and by using tri-n-butyl borate.

1. ADDITIONS WITH TRIMETHYL BORATE.

The addition of trimethyl borate to hexafluoropropene gave tri-(2,2,3,4,4,4-hexafluorobutyl) borate (63) in good yield.

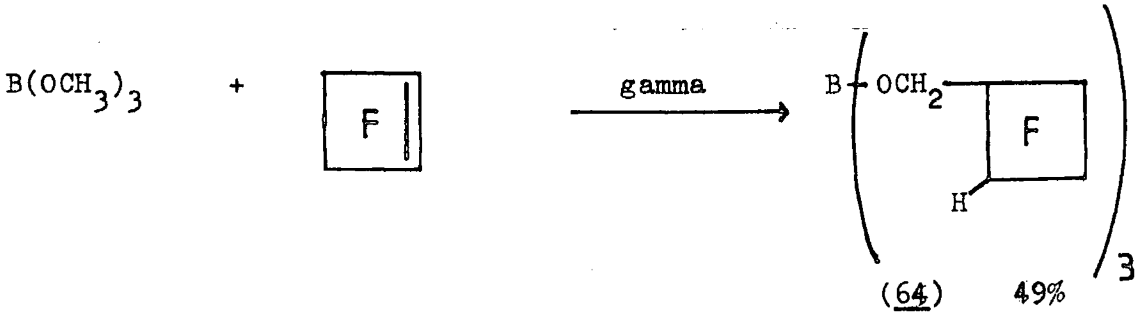
$$B(OCH_3)_3 \quad + \quad CF_3CF{=}CF_2 \xrightarrow{\text{gamma}} B(OCH_2CF_2CFHCF_3)_3$$

(63) 65%

Chlorotrifluoroethene gave a viscous liquid product (62) which could not be purified. However analysis of the mixture was consistent with a telomer adduct type structure.

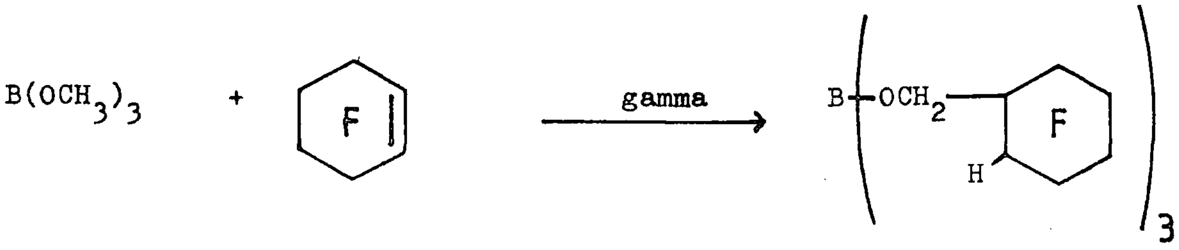
$$B(OCH_3)_3 \quad + \quad CF_2{=}CFCl \xrightarrow{\text{gamma}} \text{Viscous semi-solid telomer adducts. (62)}$$

A moderate yield of tri-adduct (64) was obtained from perfluorocyclobutene and trimethyl borate.



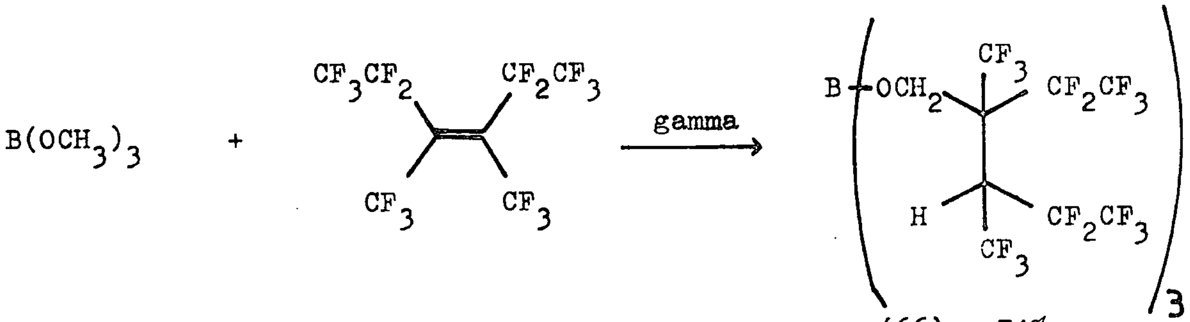
(64) 49%

Similarly perfluorocyclohexene gave a tri-adduct (65)



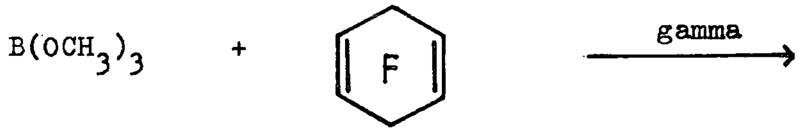
(65) 63%

Surprisingly, a high yield of a tri-adduct (66) was obtained with perfluoro-3,4-dimethylhex-3-ene.



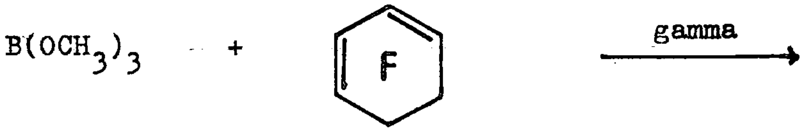
(66) 74%

The addition of perfluorocyclohexa-1,4-diene to trimethyl borate gave a white solid (67) which was very hydroscopic. The analysis of the solid was consistent with an adduct type of structure.



White solid
poly-adduct (67)

However no products were obtained with the isomeric perfluorocyclohexa-1,3-diene.

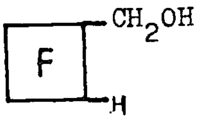


No reaction.

All the borate ester products were viscous high boiling point liquids and they were difficult to isolate quantitatively. This explains why the isolated yields of the tri-adducts were low even though no alkene was recovered. Confirmation of the adduct structures was made by hydrolysis of the borates to their respective alcohols.

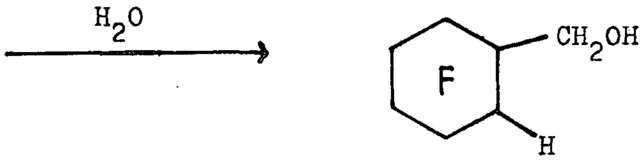
(63) $\xrightarrow{H_2O}$ $CF_3CFHCF_2CH_2OH$ (56)

(64) $\xrightarrow{H_2O}$



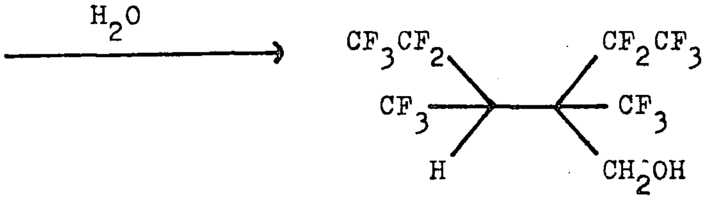
(72)

(65)



(68)

(66)



(73)

2. ADDITIONS WITH TRIBUTYL BORATE.

Tri-n-butyl borate was reacted with hexafluoropropene using a variety of reactant ratios. In all cases an identical borate adduct (69) was obtained with no recovery of alkene. Analytical data onthe adduct suggested approximately a three to one molar ratio of alkene to borate. However the composition of the adduct was not symmetrical because on hydrolysis the major product was 1,1,1,2,3,3-hexafluoro-4-(1,1,2,3,3,3-hexafluoropropyl)heptan-4-ol (71) with a minor amount of 1,1,1,2,3,3,-hexafluoroheptan-4-ol (70).

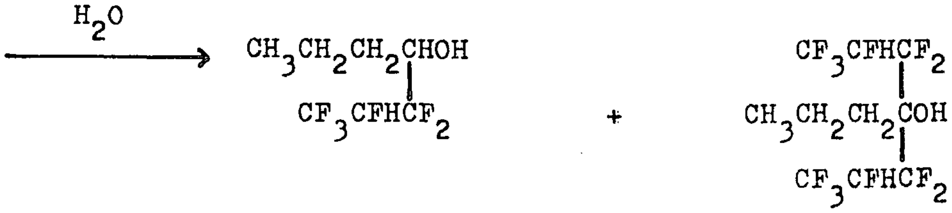
$$B(OCH_2CH_2CH_2CH_3)_3 \quad + \quad CF_3CF{=\!=}CF_2 \xrightarrow{\text{gamma}} \text{Adduct } (69)$$

	$B(OCH_2CH_2CH_2CH_3)_3$		$CF_3CF{=}CF_2$
(i)	2	:	1
(ii)	1	:	3
(iii)	1	:	9

Analysis

Adduct	%C	%H
1:1	47.3	7.1
1:2	40.7	5.0
1:3	37.0	3.9
1:4	34.7	3.2
(69)	36.3	3.6

(69)



$$(69) \xrightarrow{H_2O} CH_3CH_2CH_2CH(OH)CF_2CFHCF_3 + CH_3CH_2CH_2C(OH)(CF_2CFHCF_3)_2$$

(70) 27 %

(71) 67 %

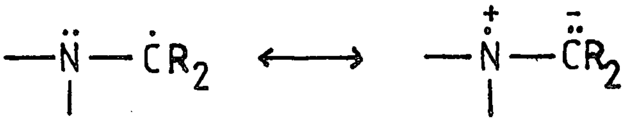
It is likely that the adduct (69) is a mixture of symmetrical adducts rather than an unsymmetrical tri-adduct. The addition of two molecules of alkene to the same carbon atom of the substrate, as demonstrated in structure (71), in tributyl borate but not trimethyl borate, parallels the formation of tri-adducts from dibutyl ether but not from dimethyl ether.

CHAPTER 3

FREE RADICAL ADDITION OF NITROGEN FUNCTION SUBSTRATES TO FLUOROALKENES.

A. INTRODUCTION.

A free radical centre may be stabilized by interaction with the lone pair of electrons on an adjacent nitrogen atom in a similar manner to the interaction with an adjacent oxygen atom.



The higher base strength of nitrogen compounds compared to analogous oxygen compounds indicates that the nitrogen lone pair may be more readily donated to electron deficient systems. Therefore, a nitrogen stabilized radical may be more stable than an oxygen stabilized radical. In order to demonstrate this effect a number of nitrogen functional substrates were reacted with fluoroalkenes. The same standard conditions were used for these reactions as with the oxygen substrates described in Chapter 2.

B. ADDITION OF AMINES TO FLUOROALKENES.

1. DISCUSSION.

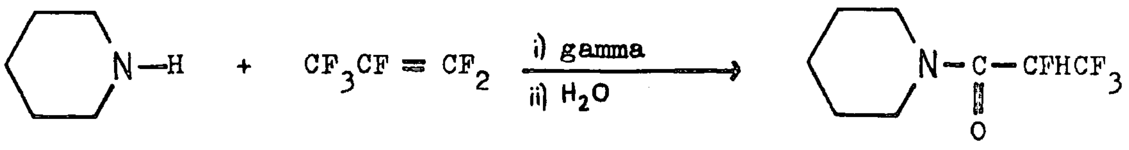
The base strengths of amines are high; therefore they can act as nucleophiles. The nucleophilic addition of the amine to the electron deficient fluoroalkene is often the preferred reaction pathway. Nevertheless, some free radical addition reactions of amines with fluoroalkenes have been reported, Table 12.

During this study, only products of nucleophilic attack were obtained from piperidine and hexafluoropropene.

Table 12.

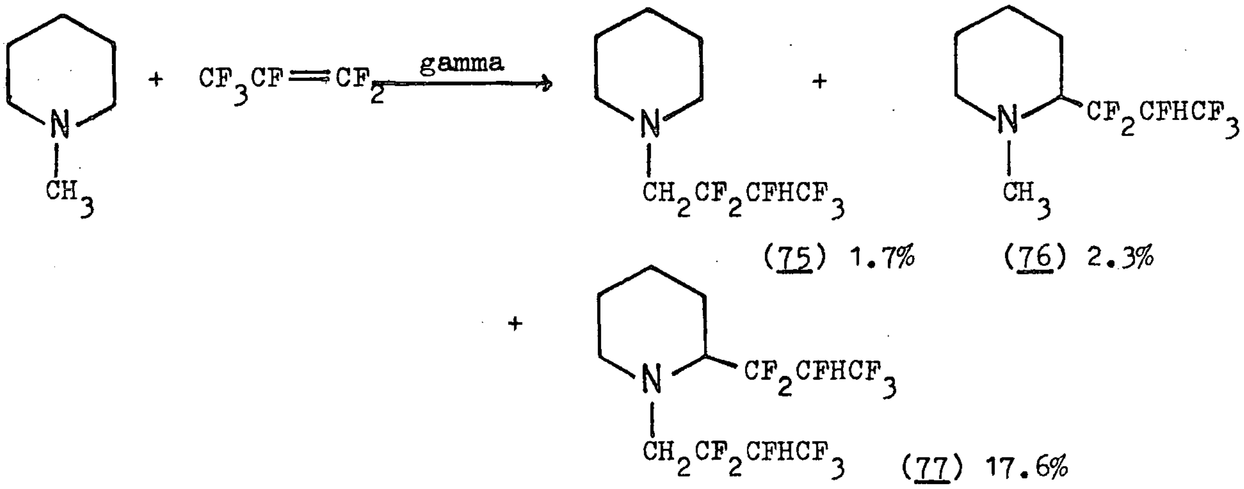
Addition of Amines to Fluoroalkenes

Fluoroalkene	Amine	Reaction Conditions	Products (% yield)	Reference
$CF_2=CFCl$	Me_3N	gamma	$(H(ClFCCF_2)_pCH_2)_nNMe_{(3-n)}$ + $n=1,2;\ p=1,2$ $ClCHFCONMe_2$	[126]
	Et_3N	gamma	Many products	[126]
	Me_2CHNMe_2	gamma	$HCClFCF_2CH_2NMeCHMe_2$ + $HCClFCF_2CMe_2NMe_2$ + $HCClFCF_2CMe_2NMeCH_2CF_2CClFH$	



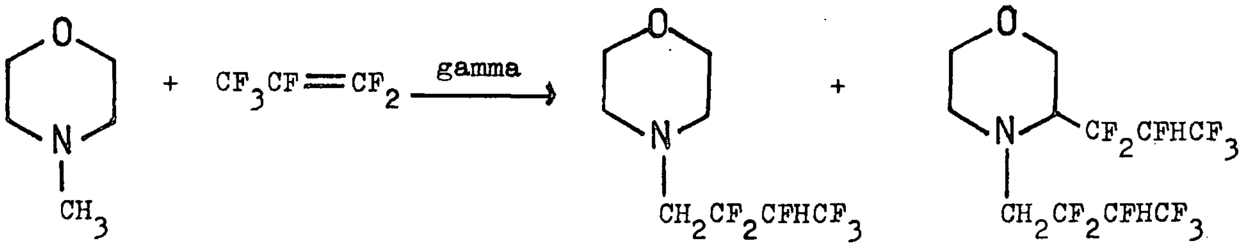
(74) 40%

Tertiary amines have been found to give low yields of adducts. N-Methylpiperidine gave a mixture of mono-adducts (75) and (76) and a di-adduct (77) as the main product.



(75) 1.7% (76) 2.3% (77) 17.6%

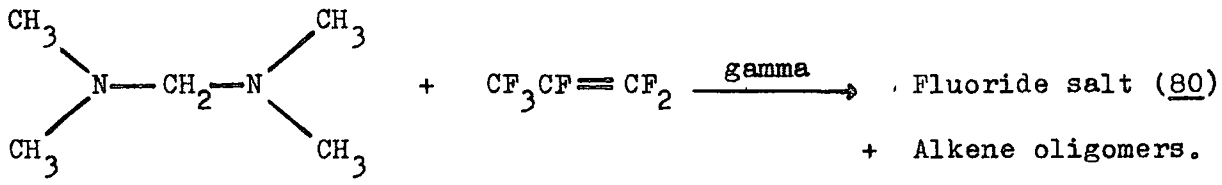
Also, N-methylmorpholine gave the di-adduct (79) as the main product.



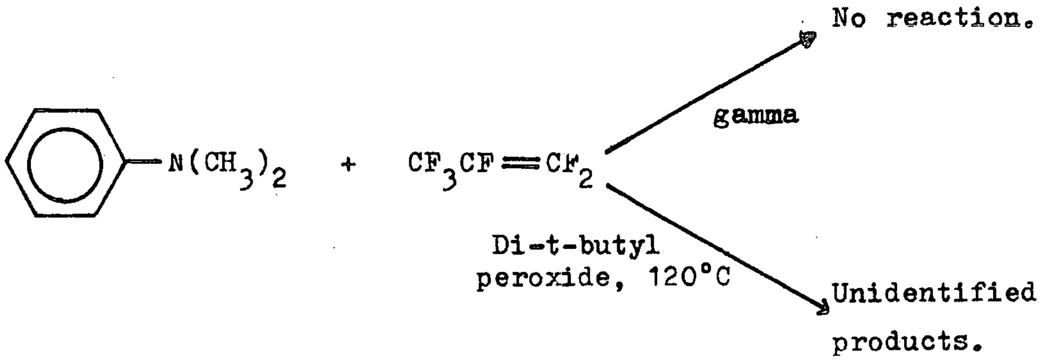
(78) 0.6% (79) 28%

The rest of the alkene in these cases was lost presumably as products of nucleophilic attack. Most of the free radical products were di-adducts which is in contrast to oxane and dioxan which form mainly mono-adducts under these conditions. Another observation was that the N-methylmorpholine adducts were produced mainly adjacent to the nitrogen atom.

A crystalline ionic compound (80) was formed on the addition of tetramethyldiaminomethane to hexafluoropropene, together with extensive oligomerization of the alkene. This shows that a nucleophilic reaction had taken place.



Dimethylaniline did not form any products at 18°C, illustrating the deactivating nature of the phenyl group. When peroxide initiation was used no alkene was recovered but no free radical products were isolated.

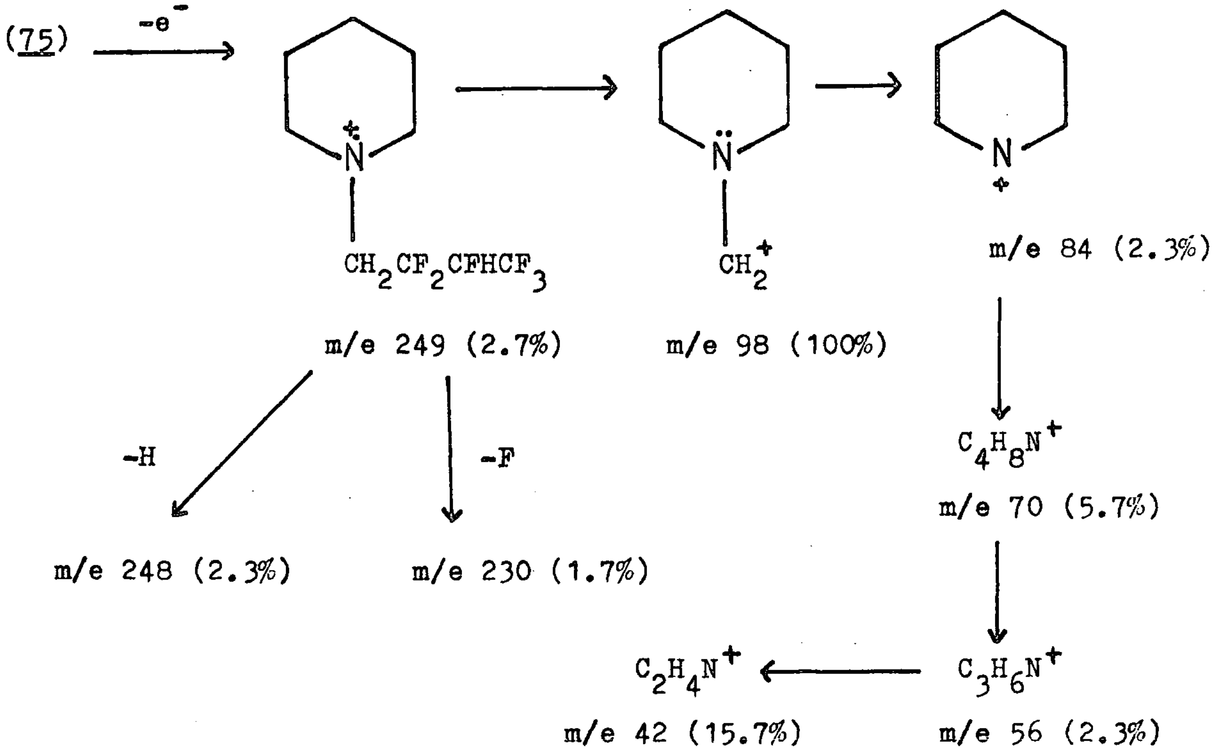


2. IDENTIFICATION OF PRODUCTS.

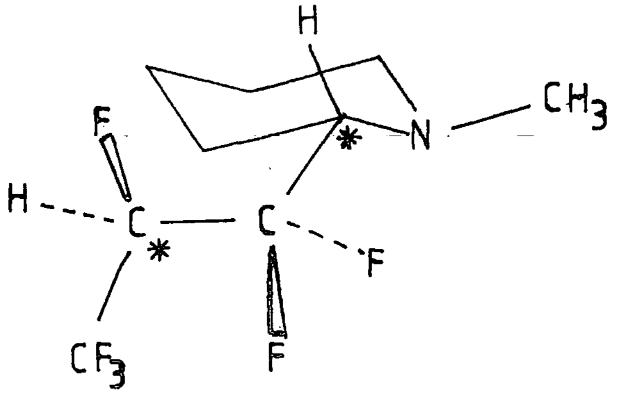
The parent peaks of mass spectra were observed although usually of low intensity. The base peaks were due to the elimination of one of the fluorocarbon fragments by cleavage of the carbon-carbon bond next to nitrogen, Scheme 3.

Two features of the nuclear magnetic resonance spectra were important in the assignment of structures. The absence of a sharp singlet due to the N-methyl groups in the proton spectrum shows that the fluoroalkene has added onto this group. A complementary observation was the appearance of the difluoromethylene resonances of the adducts in the fluorine-19

Scheme 3



spectrum. Two sets of resonances with an AB pattern for the difluoromethylene group indicates that it is attached to a ring position, due to the presence of two asymmetric centres.



(76) (SS isomer)

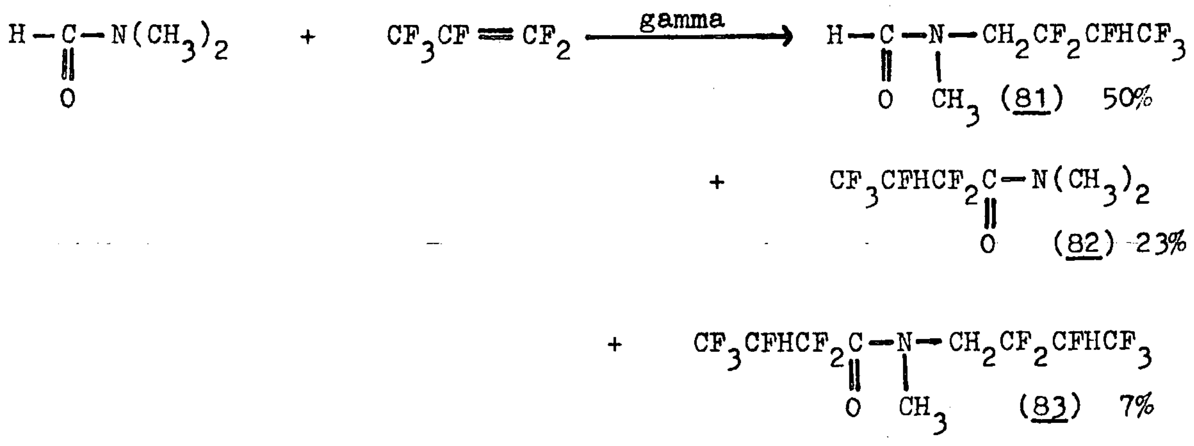
Only one resonance would occur if the group is attached to the methyl side chain because there is then only one asymmetric centre.

C. ADDITION OF AMIDES TO FLUOROALKENES.

The carbonyl group of amides reduces the base strength of the nitrogen atom, making amides less nucleophilic than amines. As a consequence, this may reduce the free radical reactivity of an amide since a similar effect has been demonstrated between the reactivity of esters and ethers. Various free radical reactions between amides and fluoroalkenes have been reported in the literature, Table 13. During this study, amides have been used which have the nitrogen fully substituted by alkyl groups to minimise any possible nucleophilic side reactions.

1. ADDITIONS TO HEXAFLUOROPROPENE.

The addition of N,N-dimethylformamide to hexafluoropropene gave adducts due to hydrogen abstraction from both the N-methyl site (81) and the aldehydic site (82), as well as a di-adduct (83).



$$H{-}\underset{\underset{O}{\|}}{C}{-}N(CH_3)_2 \quad + \quad CF_3CF{=}CF_2 \xrightarrow{\text{gamma}} H{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{CH_3}{|}}{N}{-}CH_2CF_2CFHCF_3 \quad (\underline{81})\ 50\%$$

$$+ \quad CF_3CFHCF_2\underset{\underset{O}{\|}}{C}{-}N(CH_3)_2 \quad (\underline{82})\ 23\%$$

$$+ \quad CF_3CFHCF_2\underset{\underset{O}{\|}}{C}{-}\underset{\underset{CH_3}{|}}{N}{-}CH_2CF_2CFHCF_3 \quad (\underline{83})\ 7\%$$

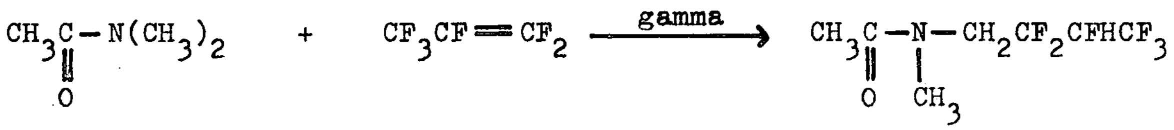
The N-methyl site is the preferred position of attack although allowance must be made of the fact that there are six of these hydrogen atoms compared to one aldehydic hydrogen.

N,N-Dimethylacetamide gave a good yield of the mono-adduct (84) from N-methyl attack.

Table 13

Addition of Amides to Fluoroalkenes.

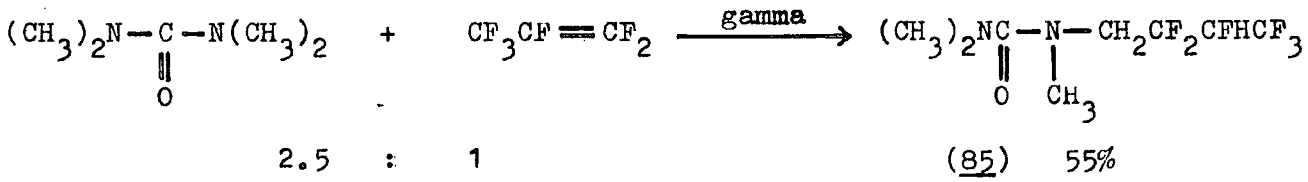
Fluoroalkene	Amide	Reaction Conditions	Products (% yield)	Reference
$CF_2=CF_2$	2-pyrrolidinone N-methyl-2-pyrrolidinone 2-piperidone ε-caprolactam N-hydroxyethyl-2-pyrrolidinone	$(^tBuO)_2$	Mixture of adducts	[128]
$CF_2=CFCl$	$HCONMe_2$	gamma, UV(acetone)	$ClCFHCF_2CCNMe_2$ + (3-11) $H(CClFCF_2)_nCH_2NMeCHO$ n=1(13-51),2(4-6)	[129]
	NHCHO N-methyl-2-pyrrolidinone $Me_2CHNHCHO$ N-formylmorpholine 1-ethyl-2-piperidone N-methyl caprolactam	UV(acetone)	1:1 adducts	[130]
$CF_3CF=CF_2$	2-pyrrolidinone N-methyl-2-pyrrolidinone 2-piperidone ε-caprolactam N-hydroxyethyl-2-pyrrolidinone	$(^tBuO)_2$	1:1 and 2:1 adducts	[128]



$$CH_3C(=O)-N(CH_3)_2 + CF_3CF{=}CF_2 \xrightarrow{\text{gamma}} CH_3C(=O)-N(CH_3)-CH_2CF_2CFHCF_3$$

(84) 82%

With N,N,N',N'-tetramethylurea only a moderate yield of the mono-adduct (85) was obtained, together with other products, using the usual 2.5:1 excess of substrate, however no alkene was recovered.

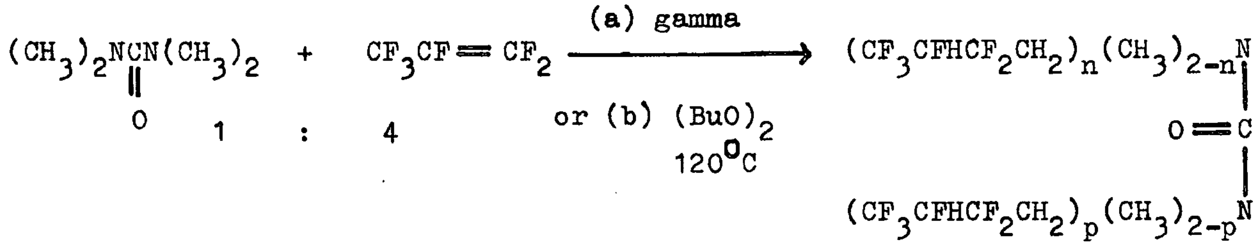


$$(CH_3)_2N-C(=O)-N(CH_3)_2 + CF_3CF{=}CF_2 \xrightarrow{\text{gamma}} (CH_3)_2NC(=O)-N(CH_3)-CH_2CF_2CFHCF_3$$

2.5 : 1

(85) 55%

The experiment was repeated using a 1:4 excess of hexafluoropropene and GLC/mass spectroscopy showed the product as a mixture of mono-, di-, tri-, and tetra-adducts, in quantitative conversion of alkene. The symmetrical di-adduct was the predominant product. To try and obtain a greater proportion of the tetra-adduct (89) the reaction was repeated using peroxide initiation. Although more tetra-adduct was formed,a mixture was still present.

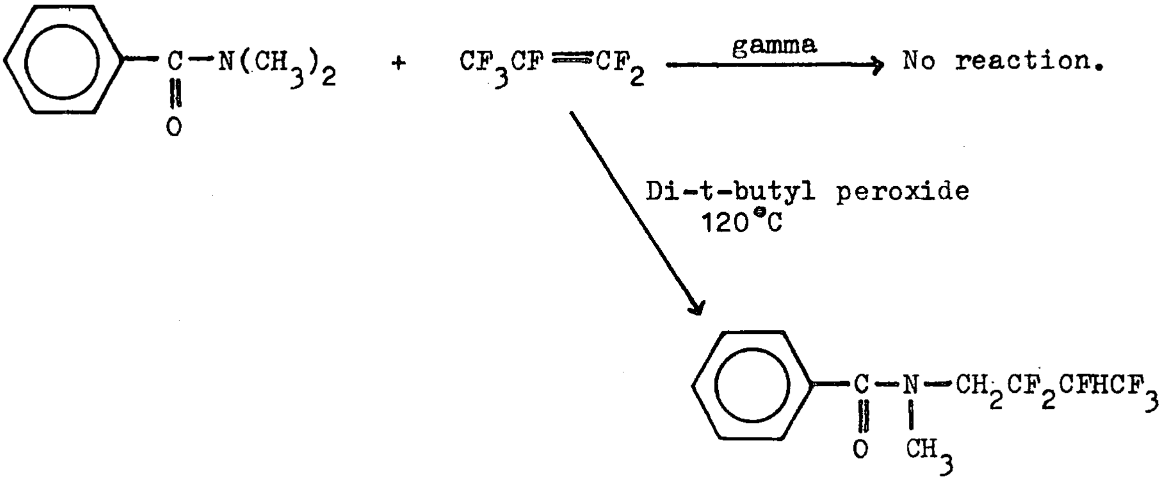


$$(CH_3)_2NC(=O)N(CH_3)_2 + CF_3CF{=}CF_2 \xrightarrow[\text{or (b) } (BuO)_2,\ 120^{o}C]{\text{(a) gamma}} (CF_3CFHCF_2CH_2)_n(CH_3)_{2-n}N-C(=O)-N(CH_3)_{2-p}(CH_2CF_2CFHCF_3)_p$$

1 : 4

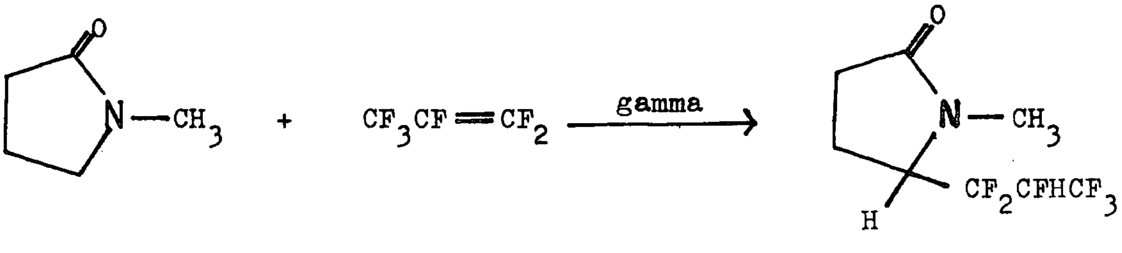
Adduct (n,p)		%Yield (a)	%Yield (b)
(1 , 0)	(85)	10	4
(2 , 0)	(86)	9	5
(1 , 1)	(87)	53	27
(2 , 1)	(88)	24	40
(2 , 2)	(89)	3	24

A phenyl substituent greatly reduces the reactivity of the amide system, for example no adducts were formed from N,N-dimethylbenzamide at a low temperature. However at a higher temperature a small amount of the mono-adduct was obtained.



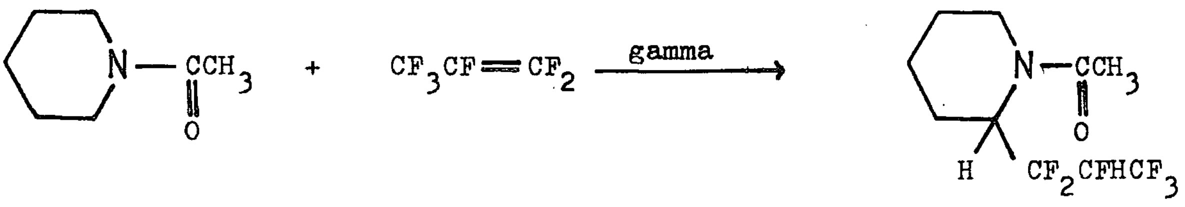
(90) 30%

Cyclic N-substituted amides react with hexafluoropropene to give good yields of adducts. N-Methylpyrrolidinone gave an adduct (91) principally by abstraction of a ring hydrogen atom adjacent to the nitrogen. Conclusive evidence for this assignment was obtained from carbon-13 NMR spectroscopy.



(91) 66%

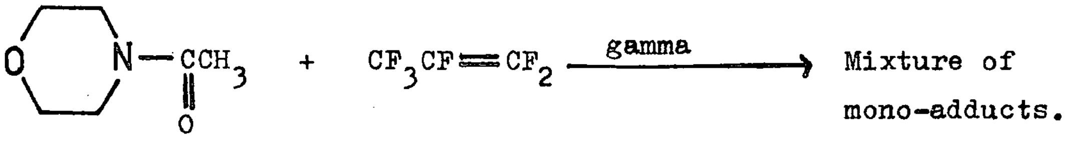
N-Acetylpiperidine gave both a mono-adduct (92) and a mixture of di-adducts. The structure of the di-adducts could not be assigned.



(92) 40%

+ Di-adducts 17%

With N-acetylmorpholine a mixture of mono-adducts was obtained. These were assigned by GLC/mass spectra because they could not be separated.



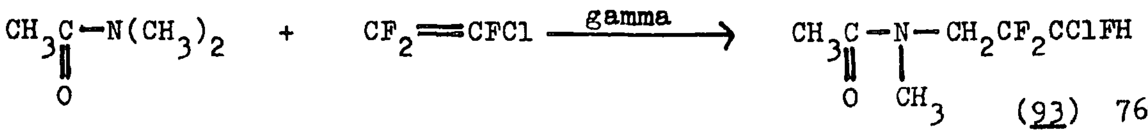
Mixture of mono-adducts.

(35%)

2. ADDITIONS WITH N,N-DIMETHYLACETAMIDE.

N,N-Dimethylacetamide was chosen as a standard amide substrate because there is only one type of easily abstractable hydrogen atom. A range of different fluoroalkenes were used in this study and yields of adduct varied considerably with structure. It was found that in general increased perfluoroalkyl substitution of the fluoroalkene resulted in a lower adduct yield with the amide.

Chlorotrifluoroethene gave a quantitative yield of adducts. Only the mono-adduct (93) was isolated, the higher telomer adducts were identified by GLC/mass spectra but not separated.



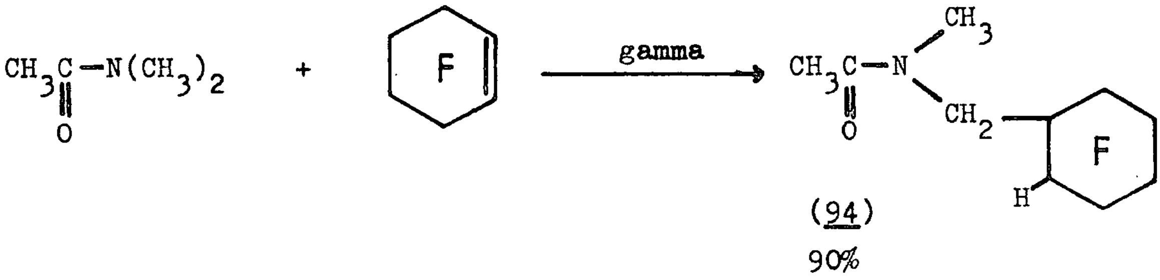
$$CH_3C(=O){-}N(CH_3)_2 + CF_2{=}CFCl \xrightarrow{\text{gamma}} CH_3C(=O){-}N(CH_3){-}CH_2CF_2CClFH$$

(93) 76%

+ Telomer adducts 22%

Hexafluoropropene has been shown above to react very well with N,N-dimethylacetamide.

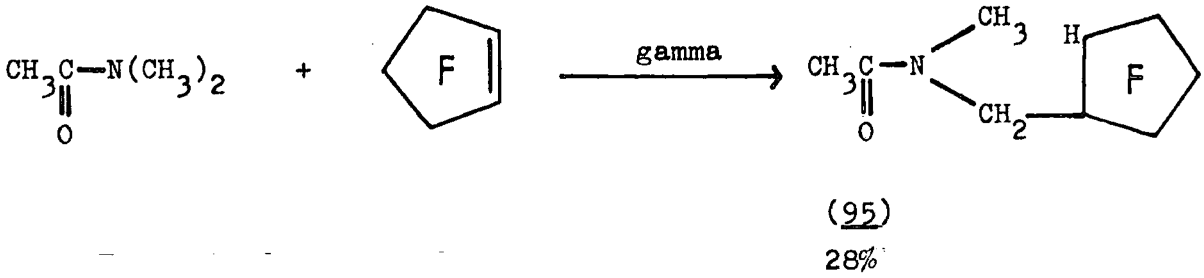
Perfluorocyclohexene was the only alkene of the type $R_fCF{=}CFR_f$ to give a good yield of adduct (94) with N,N-dimethylacetamide.



(94)
90%

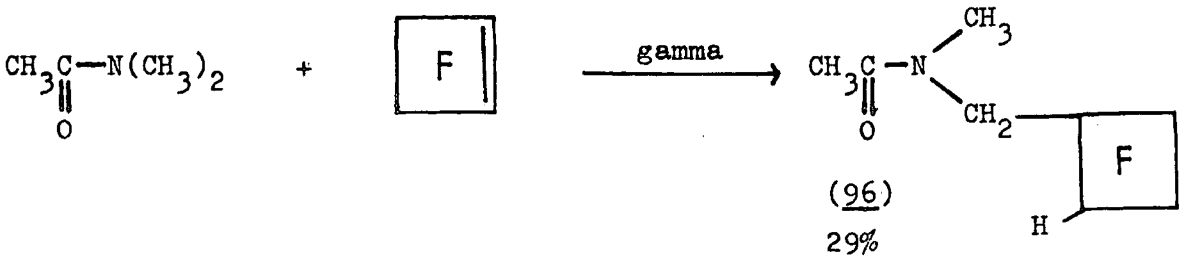
The cis isomer of compound (94) separated as a crystalline solid while the trans isomer remained a viscous liquid.

Perfluorocyclopentene gave a low yield of the mono-adduct (95)



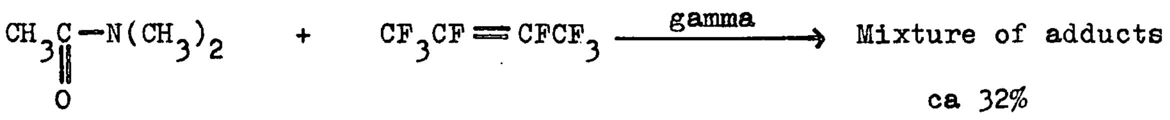
(95)
28%

Similarly a low yield of mono-adduct (96) was obtained with perfluorocyclobutene.



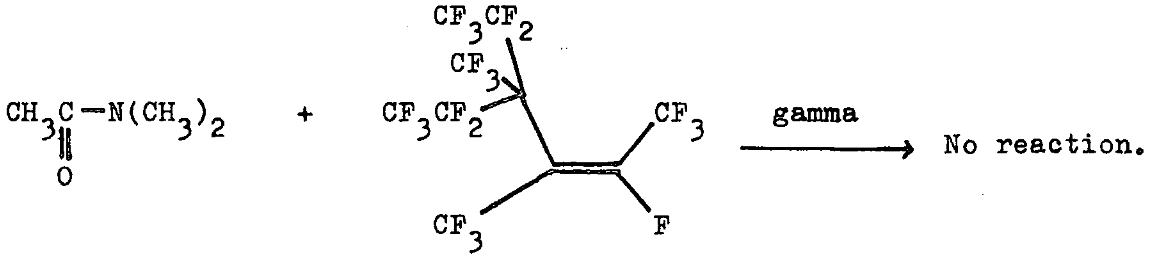
(96)
29%

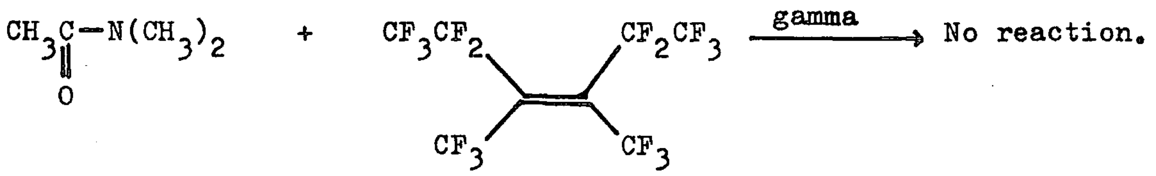
Perfluorobut-2-ene gave a mixture of adducts which were assigned by GLC/mass spectra but could not be separated.



$$CH_3C(=O)-N(CH_3)_2 + CF_3CF=CFCF_3 \xrightarrow{\text{gamma}} \text{Mixture of adducts ca 32\%}$$

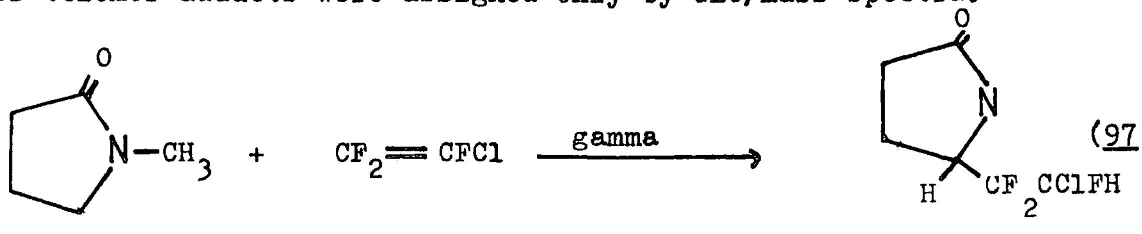
No products were obtained either from perfluoro-3,4-dimethyl-4-ethylhex-2-ene or from perfluoro-3,4-dimethylhex-3-ene with N,N-dimethylacetamide.





3. ADDITIONS WITH N-METHYLPYRROLIDINONE.

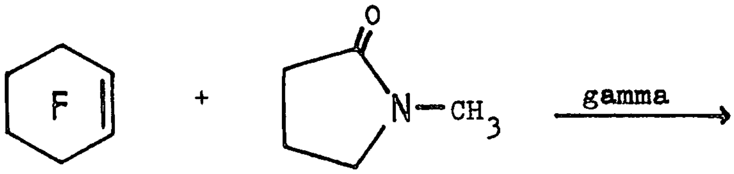
The use of N-methylpyrrolidinone as a standard amide presented problems in some cases due to the high number of products obtained which were difficult to separate. In these cases the extent of reaction was measured from the amount of fluoroalkene recovered. Again lower yields of adducts were obtained with increased substitution of the alkene. The addition of chlorotrifluoroethene to N-methylpyrrolidinone gave a mixture of telomer adducts. The mono-adduct (97) was isolated but the higher telomer adducts were assigned only by GLC/mass spectra.



(97) 75%

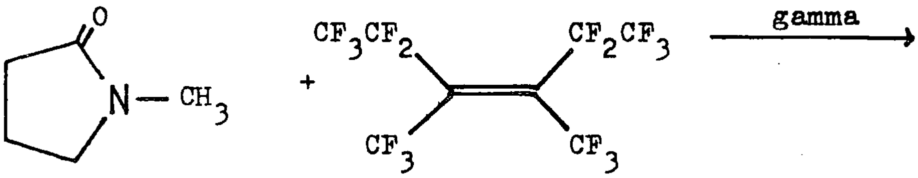
\+ Telomer adducts. ca 24%

Perfluorocyclohexene gave a mixture of adducts which were assigned by GLC/mass spectra only.



Mixture of adducts.
ca 48%

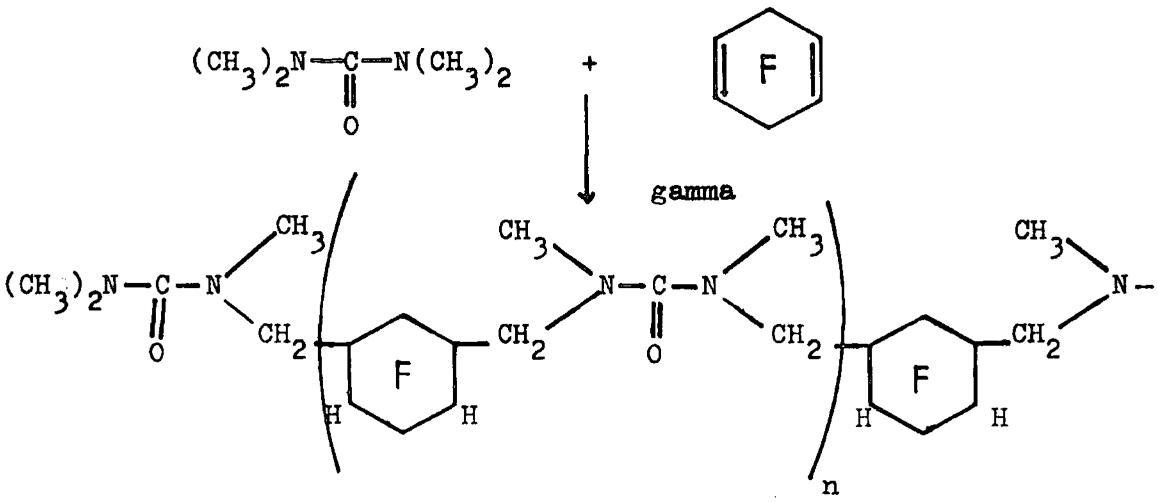
No products were obtained with perfluoro-3,4-dimethylhex-3-ene.



No reaction.

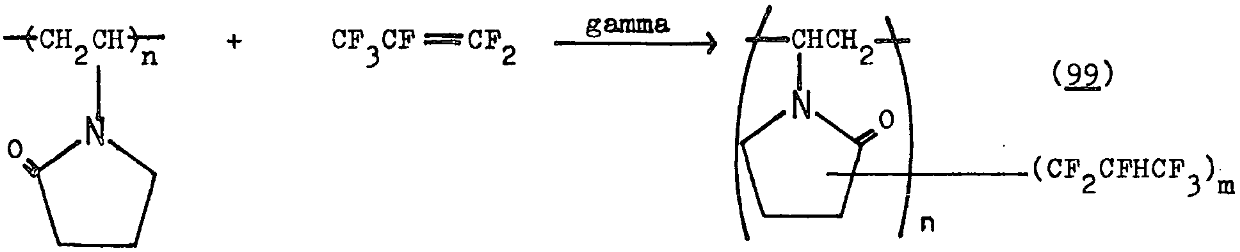
4. MISCELLANEOUS ADDITIONS.

Amide linkages are abundant in nature and the introduction of a fluoroalkyl group often produces interesting biological effects. In view of this, and the high yield of products from free radical addition reactions, the scope of this reaction is worth investigating. N,N,N',N'-Tetramethylurea is a difunctional substrate and reaction with a difunctional fluoroalkene may produce polymers. Perfluorocyclohex-1,4-diene gave a solid which was polymeric in nature. Mass spectrometry indicated an oligomer of at least four monomer units (98) (n=3).



The exact nature of the oligomer was not clear but it would be expected to be a complex mixture of species of different molecular weight with a certain degree of branching.

A solid substrate does not usually react with fluoroalkenes due to insufficient contact between the reagents. In spite of this unfavourable effect, solid poly-N-vinylpyrrolidinone was reacted with hexafluoropropene and incorporation of the alkene into the polymer took place. It was deduced from the amount of alkene recovered that just over one mole of the alkene was absorbed for every monomer unit of the polymer (99).



(99)

m = 1.4n from recovered C_3F_6

Analysis

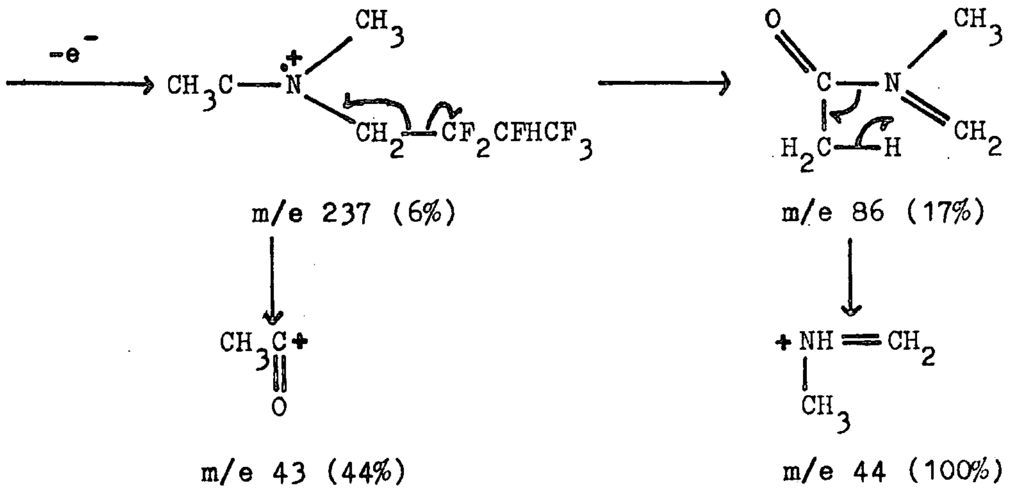
	%C	%H	%N	%F
(99)	33.3	1.3	3.4	52.1
Calc. for m = n,	41.4	3.5	5.4	43.7
Calc. for m = 2n,	35.0	2.2	3.4	55.8
Calc. for m = 3n,	32.1	1.6	2.5	60.1

Therefore a reaction can occur with solid substrates, which indicates that although the reaction may be slower, products will be formed if the substrate is reactive enough.

5. IDENTIFICATION OF PRODUCTS.

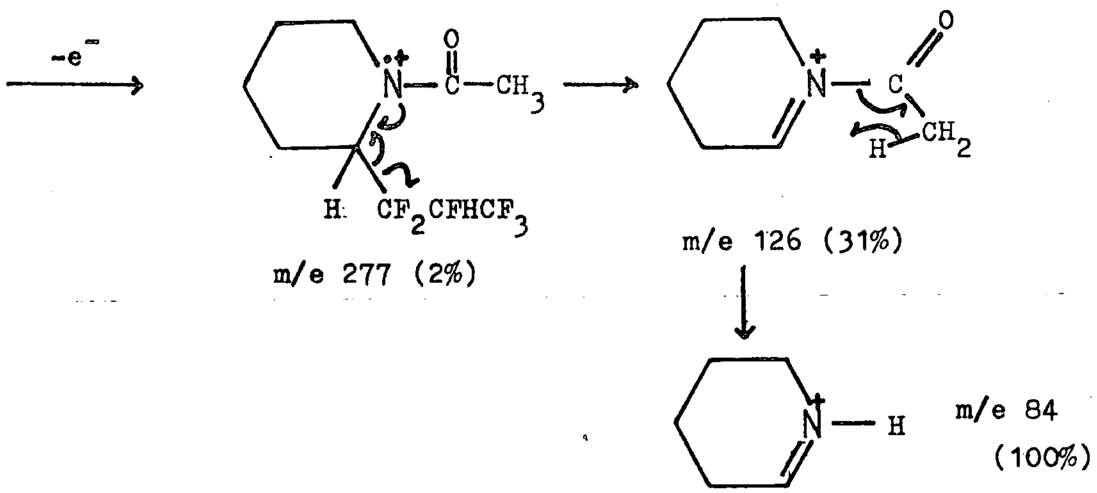
The mass spectra of the acetamide adducts generally showed a parent peak. The cleavage of the fluoroalkyl group at the beta position to the nitrogen atom was a main fragmentation. This fragment cleaved at the carbonyl carbon-nitrogen bond, with rearrangement of an alpha-hydrogen atom from the acyl methyl group, to form the base peak at m/e 44. The second most intense fragment was due to cleavage of the carbonyl-nitrogen bond with loss of the acyl group.

(84)



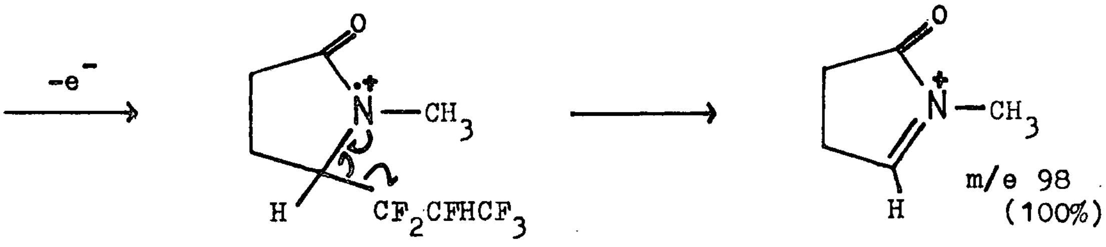
With the N-cycloalkyl amides the base peak mass depends on the size of the ring.

(92)

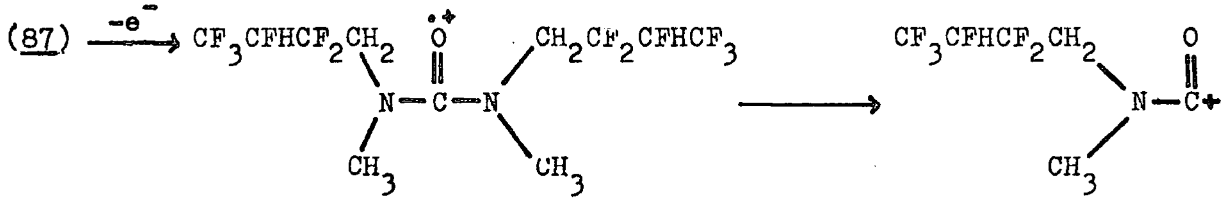


The mass spectra of the N-methylpyrrolidinone adducts were dominated by the cleavage of the fluoroalkyl group. In these cases no alpha-hydrogen atoms from the acyl groups were available for rearrangement because of the stereochemistry of the ring.

(91)



The distinction between the symmetrical (87) and asmmetrical (86) di-adducts of tetramethylurea was possible from their mass spectra. The base peak at m/e 222 for (87) due to the cleavage of the carbonyl-nitrogen bond was absent from the spectrum of (86).



m/e 416 (2%) m/e 222 (100%)

Structural information on the adducts has been obtained from carbon-13 NMR spectra. Comparison of the spectra of N,N-dimethylacetamide and compound (84) confirmed that addition had occurred at the N-methyl site, Figure 2. These spectra were proton broad band decoupled although couplings due to the fluorine atoms were still present. Restricted rotation about the carbonyl-nitrogen bond in dimethylacetamide causes the two N-methyl groups to be inequivalent on the NMR time scale. The presence of only one main resonance due to the N-methyl group of compound (84) implies that one conformation predominates or that there is free rotation. Comparison of the carbon-13 spectra of N-methylpyrrolidinone with compound (91) enabled the attachment of the fluoroalkyl group to the N-methylene group rather than to the N-methyl or carbonyl-methylene groups to be proved, Figure 3.

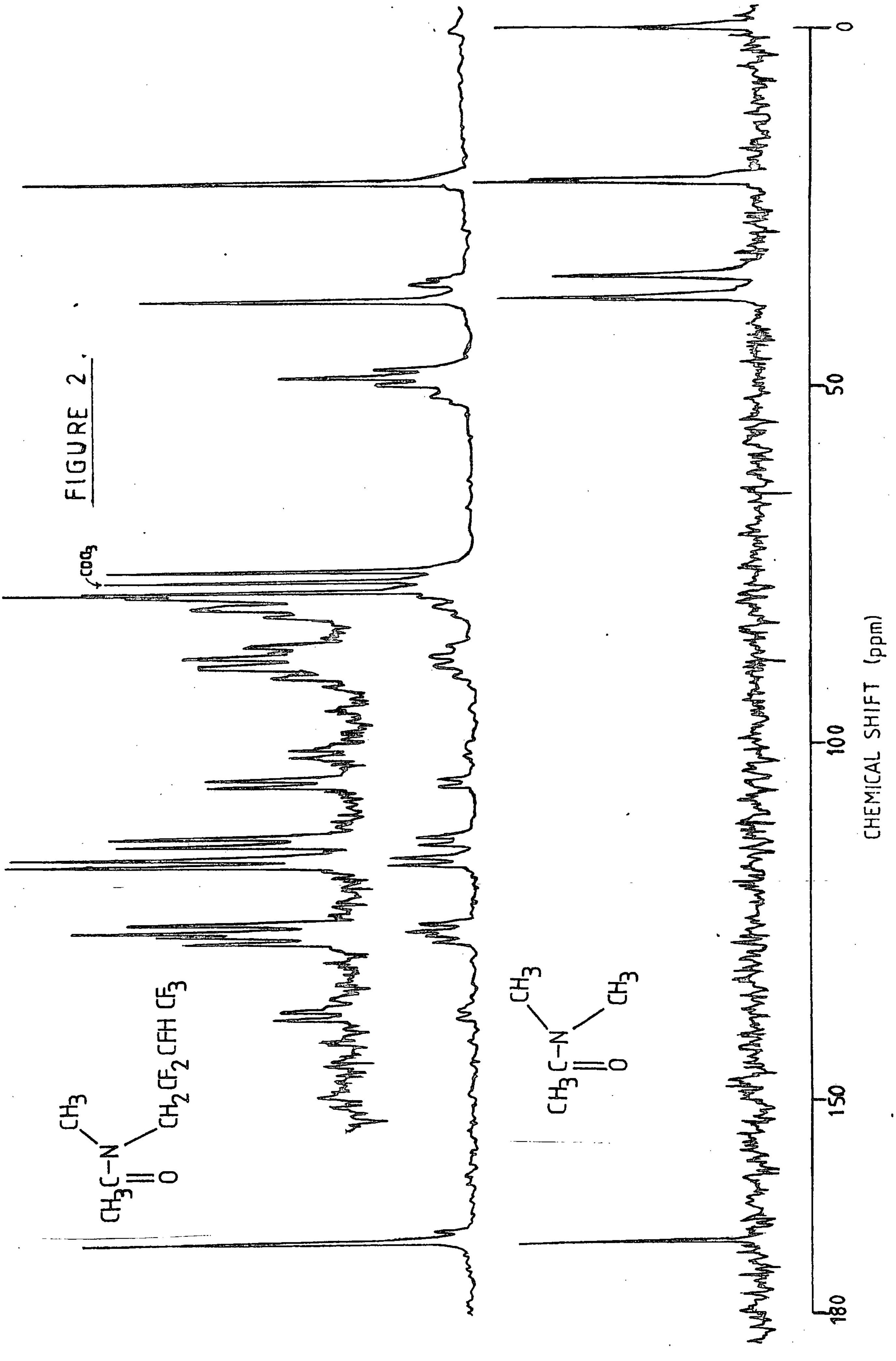
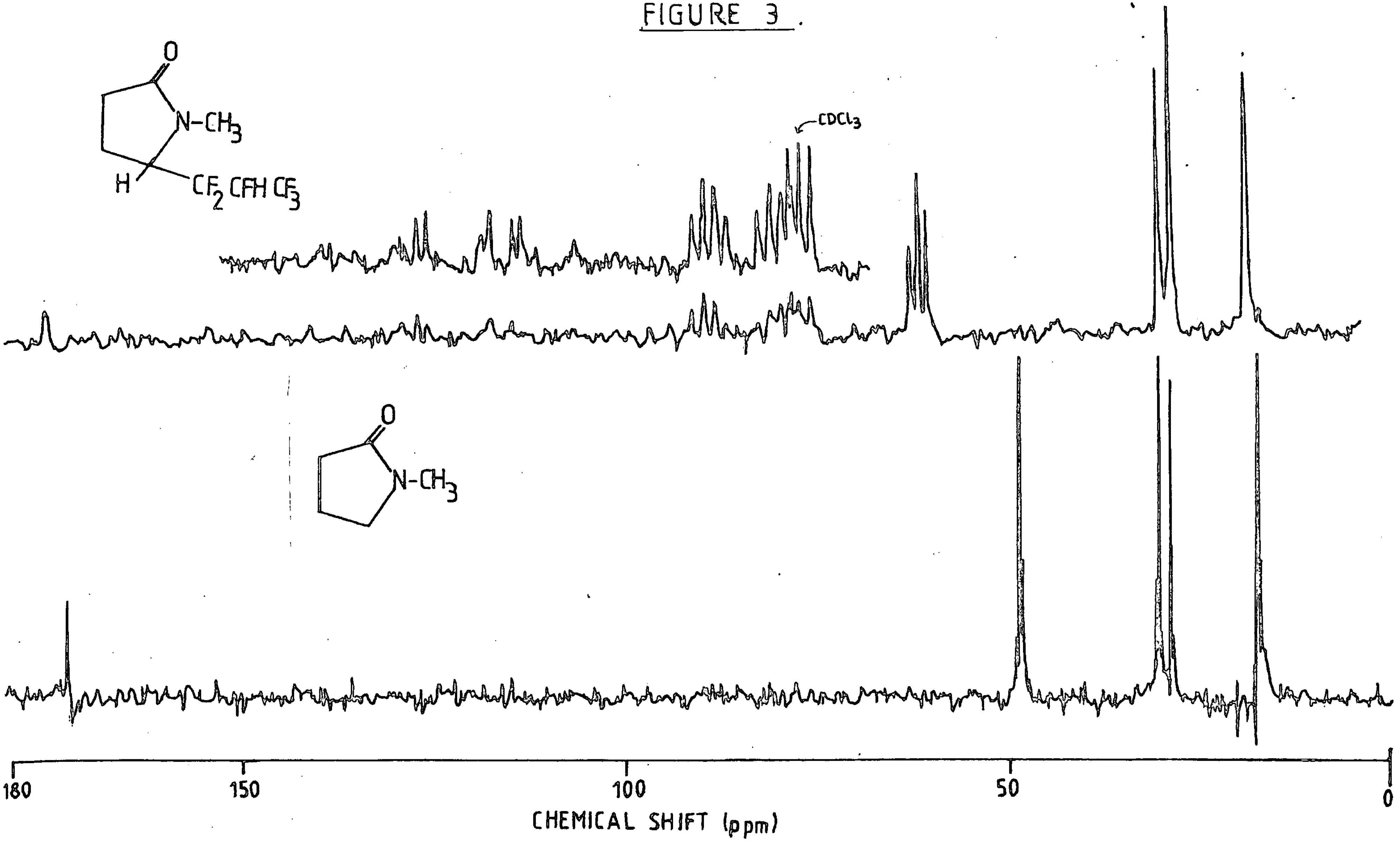


FIGURE 2.

$CDCl_3$
$CH_3C(=O)-N(CH_3)CH_2CF_2CFHCF_3$
$CH_3C(=O)-N(CH_3)CH_3$
0
50
100
150
180
CHEMICAL SHIFT (ppm)

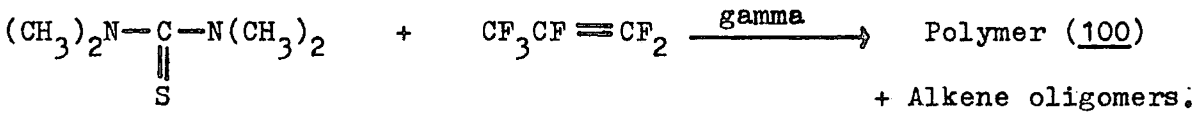
FIGURE 3.


O
N-CH3
H
CF2 CFH CF3
CDCl3
O
N-CH3
180
150
100
50
0
CHEMICAL SHIFT (ppm)

D. MISCELLANEOUS ADDITIONS TO FLUOROALKENES.

The success of tetramethylurea in forming tetra-adducts prompted an investigation into similar systems.

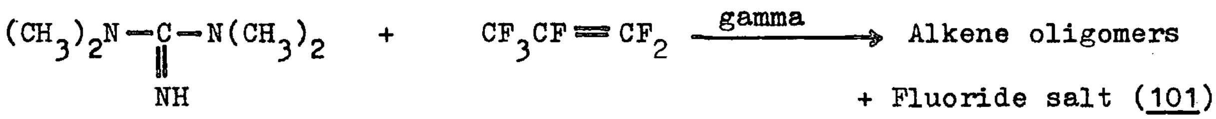
Tetramethylthiourea was reacted with hexafluoropropene but no adducts were obtained. However oligomers of hexafluoropropene and a white powder were isolated. The properties and spectra of the white powder were consistent with a polymer type structure (100) although a firm assignment could not be made.



$$(CH_3)_2N-\underset{\underset{S}{\|}}{C}-N(CH_3)_2 \quad + \quad CF_3CF{=}CF_2 \xrightarrow{\text{gamma}} \text{Polymer } (\underline{100}) + \text{Alkene oligomers.}$$

The sulphur atom must be sufficiently nucleophilic to catalyse the oligomerization of the alkene.

Tetramethylguanidine reacts in a nucleophilic manner with hexafluoropropene to give alkene oligomers and a crystalline fluoriide salt (101).



$$(CH_3)_2N-\underset{\underset{NH}{\|}}{C}-N(CH_3)_2 \quad + \quad CF_3CF{=}CF_2 \xrightarrow{\text{gamma}} \text{Alkene oligomers} + \text{Fluoride salt } (\underline{101})$$

No free radical products were isolated.

CHAPTER 4

CONFORMATION AND SUBSTITUENT EFFECTS IN FLUOROALKENE ADDITION REACTIONS.

A. INTRODUCTION.

A large number of preparative experiments have been discussed in the previous two chapters. They were designed to investigate the influence of substituents on free radical additions to fluoroalkenes. In this chapter the effects observed will be discussed and an explanation proposed.

B. SUBSTITUENT EFFECTS.

The results obtained from the addition of oxygen substrates to hexafluoropropene are summarized in Table 14. The total yields of adducts are quoted for each substrate. This figure will be dependent on the efficiency of the isolation procedure. A more accurate indication of the extent of reaction would be based on the amount of hexafluoropropene recovered, therefore these values are also quoted in Table 14 .

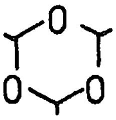
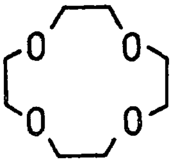
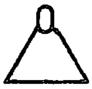
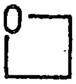
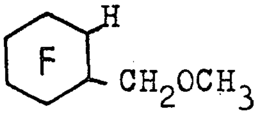
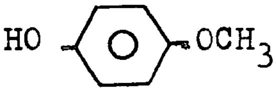
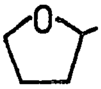
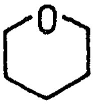
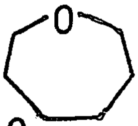
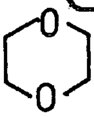
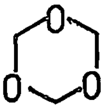
All the substrates have been reacted with a standard alkene under standard conditions, so any difference in reactivity must be due to the reactivity of the substrate. Dimethyl ether may be used as a reference from which the reactivity of other ethers are related. It may also be used as a reference for the study of the effects of substituents on a methoxy group, $R-O-CH_3$. Dimethyl ether forms a primary alkoxyalkyl radical and gives a 68% yield of product.

$$CH_3-O-CH_3 \xrightarrow{\text{gamma}} CH_3-O-\dot{C}H_2$$

Other dialkyl ethers and cyclic ethers containing one oxygen atom all give a quantitative reaction with hexafluoropropene. This greater reactivity may be explained by the formation of more stable secondary

Table 14.

Product Yields from Addition of Oxygen Substrates to Hexafluoropropene Using Gamma Ray Initiation at 18°C

Substrate	Total %Yield[a]	Substrate	Total %yield[a]
$(CH_3)_2O$	68		68[b]
Et_2O	81(100)		
Pr_2O	(80)		-
Bu_2O	(70)	$(ClCH_2CH_2)_2O$	-
$i\text{-}Pr_2O$	5	$(PhCH_2)_2O$	-
	21[b]	$PhOCH_2CH_2CH_2CH_3$	-
	65		-
	95(100)		-
	96(100)	$HCOOCH_3$	-
	95(100)	$(CH_3O)_2CO$	-
	70(100)	$CH_2(COOCH_3)_2$	-
	92(100)	$(COOC_2H_5)_2$	-
	-		

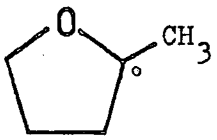
a)Based on isolated yields,figures in brackets allow for recovered C_3F_6

b)Ring opened products

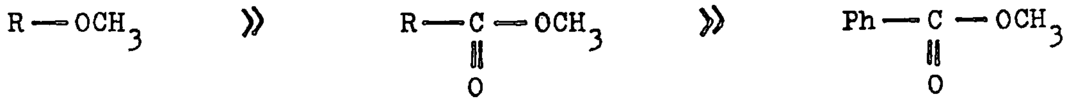
alkoxyalkyl radicals from these substrates.

$$R-O-CH_2-R' \xrightarrow{\text{gamma}} R-O-\dot{C}H-R'$$

Tertiary alkoxyalkyl radicals have been shown to be the most stable from the product distribut-ion with 2-methyloxolane. The product derived from the radical at the 2-position was formed preferentially.



Substitution of methoxy ethers with electron withdrawing chloro- , carboxy- , phenyl- , and polyfluoroalkyl- groups all result in no reaction with the alkene. These substrates will react but a much higher temperature is required. The results for esters are shown in Table 15. The substitution of the ester with electron withdrawing groups result in a further decrease in reactivity of the methoxy group. Therefore electron withdrawing substituents reduce the reactivity of a methoxy group.



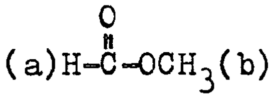
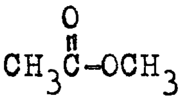
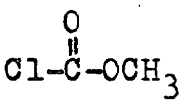
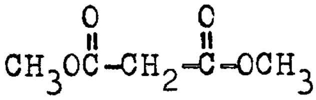
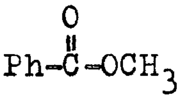
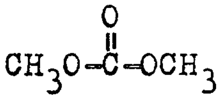
$$R-OCH_3 \gg R-\underset{\underset{O}{\|}}{C}-OCH_3 \gg Ph-\underset{\underset{O}{\|}}{C}-OCH_3$$

This may be explained by the oxygen lone pair being less available for donation to the free radical centre, resulting in a less stable intermediate radical. Also, the intermediate radical will be less nucleophilic in nature so it will not be as reactive towards the electrophilic fluoroalkene.

The results for the nitrogen substrates are in agreement with this conclusion. The total yield of adducts from the nitrogen substrates are

Table 15.

Product Yields from Addition of Oxygen Substrates to Hexafluoropropene Using Di-t-butyl Peroxide Initiation at 120°C

Substrate	% Yield
 $\text{(a)}H-\overset{\overset{O}{\parallel}}{C}-OCH_3\text{(b)}$	(5) (a),(32) (b)
 $CH_3\overset{\overset{O}{\parallel}}{C}-OCH_3$	54
 $Cl-\overset{\overset{O}{\parallel}}{C}-OCH_3$	-
 $CH_3O\overset{\overset{O}{\parallel}}{C}-CH_2-\overset{\overset{O}{\parallel}}{C}-OCH_3$	-
 $Ph-\overset{\overset{O}{\parallel}}{C}-OCH_3$	-
 $CH_3O-\overset{\overset{O}{\parallel}}{C}-OCH_3$	55

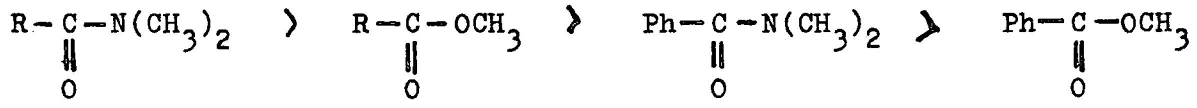
listed in Table 16. The yields from amines are low because of the competing nucleophilic reactions. However most of the products were di-adducts compared to mono-adducts for the analogous ether systems. Therefore radical stabilization by nitrogen is more effective than by oxygen.

$$R-\overset{\bullet +}{\underset{CH_3}{N}}-\overset{\bullet\bullet\,-}{C}H_2 \quad > \quad R-\overset{\bullet +}{O}-\overset{\bullet\bullet\,-}{C}H_2$$

This is understandable as nitrogen is more basic than oxygen so the lone pair will be more readily donated. The reactivity of a number of phenyl derivatives towards hydrogen abstraction by t-butoxyl radical confirms this order.[132]

$$ArNCH_3 \; > \; ArCH_3 \; > \; ArSCH_3 \; \hat{=} \; ArOCH_3$$

Also, our results show that amides react at room temperature while esters require elevated temperatures. An electron withdrawing phenyl substituent greatly reduces the reactivity of the amide, although an elevated temperature gave a slight reaction. An order of reactivity may be constructed.

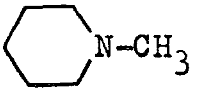
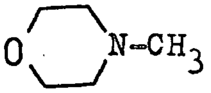
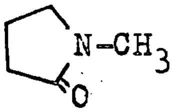
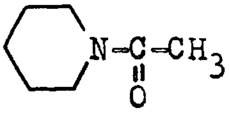
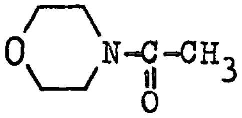


$$R-\underset{\underset{O}{\|}}{C}-N(CH_3)_2 \; > \; R-\underset{\underset{O}{\|}}{C}-OCH_3 \; > \; Ph-\underset{\underset{O}{\|}}{C}-N(CH_3)_2 \; > \; Ph-\underset{\underset{O}{\|}}{C}-OCH_3$$

Therefore the inductive influence of substituents affecting the intermediate radical stability, hence the dissociation energy of the carbon-hydrogen bond, is sufficient to explain most of the results.

Table 16.

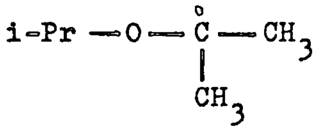
Product Yields from Addition of Nitrogen Substrates to Hexafluoropropene Using Gamma Ray Initiation at 18°C

Substrate	Total % Yield [a]
	22
	29
$Ph-N(CH_3)_2$	-
$HCON(CH_3)_2$	80 (100)
$CH_3CON(CH_3)_2$	82 (100)
$(CH_3)_2NCON(CH_3)_2$	95 (100)
$PhCON(CH_3)_2$	- [30] [b]
	60 (100)
	57
	(35)

a) Based on isolated yields, figures in brackets allow for recovered C_3F_6 (see ether table)

b) Using di-t-butyl peroxide at 120°C

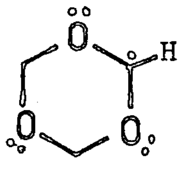
However di-iso-propyl ether and the cyclic ethers containing more than two oxygen atoms cannot be explained in this way. Di-iso-propyl ether would be expected to form a tertiary alkoxyalkyl radical (102) very readily by analogy with 2-methyloxolane.



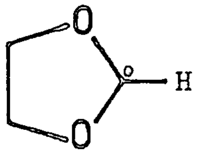
$$\text{i-Pr}-O-\underset{CH_3}{\overset{\circ}{C}}-CH_3$$

(102)

The subsequent chain reaction must not be proceeding very effectively. Trioxan will form a radical (103) that is stabilized by two adjacent oxygen atoms. A similar radical is formed from 1,3-dioxolane (104) which reacts very well with fluoroalkenes.[96] Therefore the inductive effect of the extra oxygen in trioxan must be an important factor in causing it to not react with fluoroalkenes.



(103)



(104)

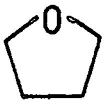
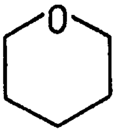
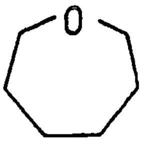
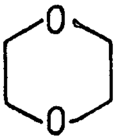
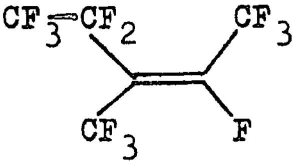
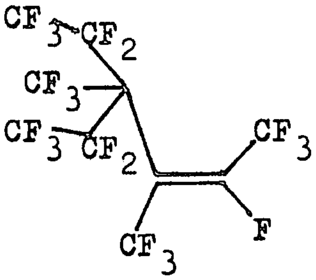
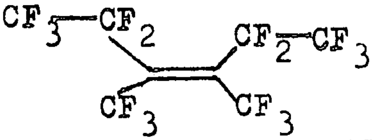
Also 12-crown-4 polyether does not react but has a similar structure to 1,4-dioxan which reacts very well. This effect cannot be explained by inductive arguments.

C. CONFORMATION EFFECTS.

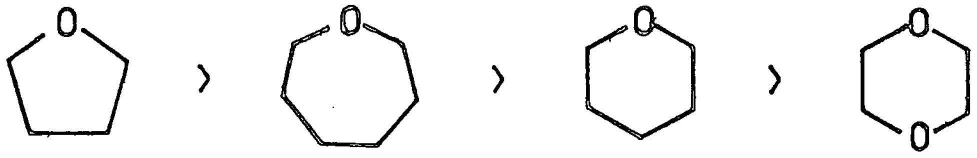
The use of hexafluoropropene has highlighted the difference in reactivity between substituted ethers, esters, and amides. However with this alkene many substrates gave quantitative reactions which makes it impossible to determine their relative reactivity. Differences in reactivity between a number of cyclic ethers in this category were observed by using other fluoroalkenes, as shown in Table 17.

Table 17.

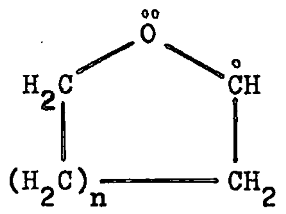
Product Yields from Addition of Cyclic Ethers to Fluoroalkenes Using Gamma Ray Initiation at 18°C

	Total % Yield			
Fluoroalkene				
$CF_2=CFCl$	98			
$CF_2=CFCF_3$	95	95	70	80
	91			
	83	76	71	49
	91			
$CF_3CF=CFCF_3$	89	21	60	34
$CF_3CCl=CClCF_3$	89			
	92			
	10			
	-			

Using octafluorocyclopentene, oxolane and oxepane gave similar yields of products as with hexafluoropropene but oxane gave a slightly decreased yield and dioxan gave a significantly reduced yield. Using octafluorobut-2-ene very poor yields of product were obtained for oxane and dioxan. A series of reactivity of the four cyclic ethers may be derived from these results.



This series cannot be explained by inductive effects, although the extra oxygen atom in dioxan may play an electron withdrawing role causing dioxan to be the least reactive. However the other three ethers have virtually identical substitution about the free radical centre (105).

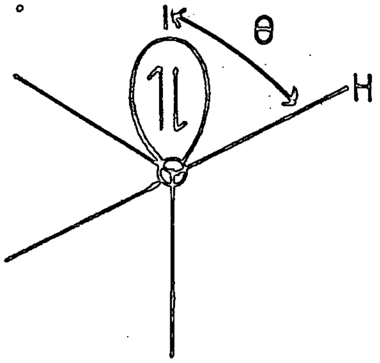


(105)

n = 1 , 2 , 3

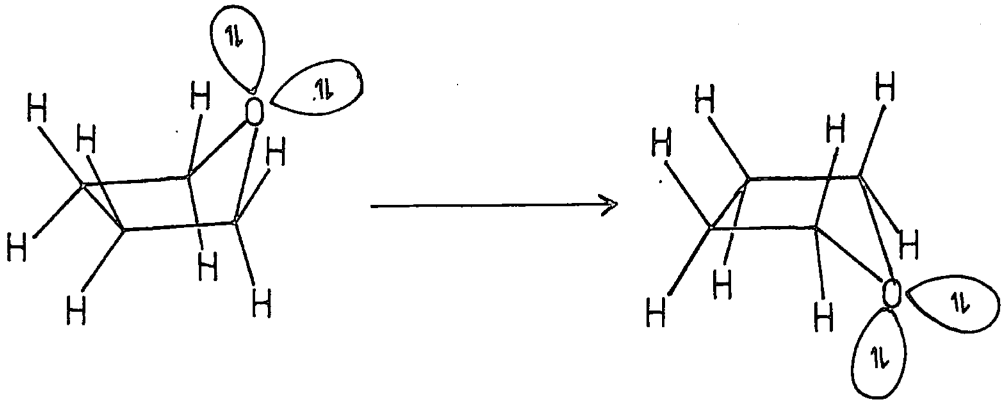
Steric effects are not important because all radicals (105) are similar in size. Also the smallest and largest ring systems are the most reactive while the intermediate ring system is less reactive. The conformation of the intermediate radicals (105) must be important in determining reactivity. Application of the stereoelectronic effect provides an explanation of why the conformation should be important.

The stereo-electronic effect was proposed by Deslongchamps.[133] He showed that molecular reactivities in many heterolytic reactions are determined by the relative orientation of the bond being broken or made and lone pairs on heteroatoms attached to the reaction centre. There have been recent reports that stereo-electronic effects are present in homolytic reactions[134] although to a lesser degree than in heterolytic examples. Electron paramagnetic resonance spectroscopy has been used to determine the relative rates of hydrogen atom abstraction by photo-generated t-butoxyl radical from a variety of cyclic and acyclic ethers, acetals and orthoformates,[135] and from substituted 1,3-dioxanes.[136] In all these reports the relative rates of hydrogen abstraction were higher for those ethers in which the angle between the carbon-hydrogen bond and the oxygen lone pairs was at a minimum. This angle is termed the dihedral angle, θ.

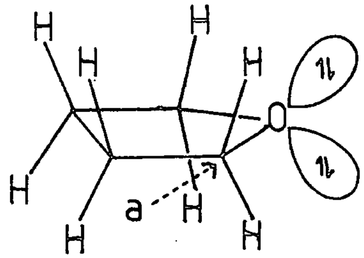


The lower the value of θ the greater would be the orbital overlap between the developing singly occupied radical orbital and the lone pair orbital on the oxygen, hence the more stable the radical. This will result in a lower dissociation energy of the carbon-hydrogen bond. The stereo-electronic effect will be apparent during addition reactions when the substrates have specific values of θ, for example the cyclic ethers. In acyclic ethers rotation of the carbon-oxygen bonds will give usually the best conformation for the most stable overlap. Examination of the conformation of the four cyclic ethers enables their dihedral angles to be calculated.

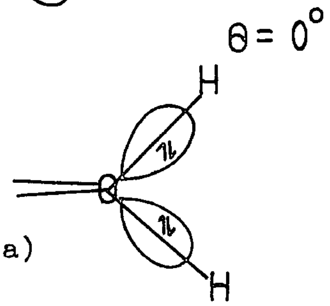
Oxolane has an envelope structure; however pseudo-rotation may occur resulting in the equivalence of the hydrogen atoms. Therefore the average structure may be considered as planar. Assuming that the oxygen lone pairs are tetrahedrally spaced then the average di-hedral angle is 0°.



Average

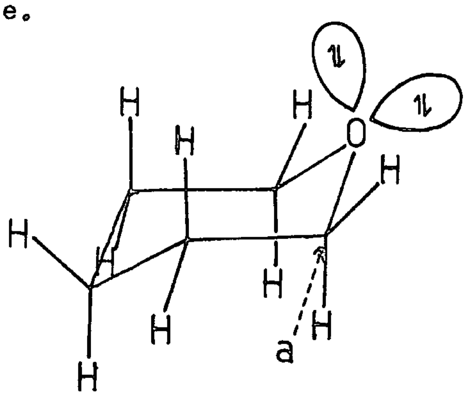


View
down
bond (a)

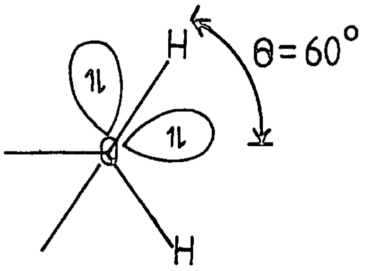


Consequently a very good interaction between the carbon-hydrogen bond and the oxygen lone pair would be expected.

The chair conformation of oxane gives a value of 60°C for the di-hedral angle.

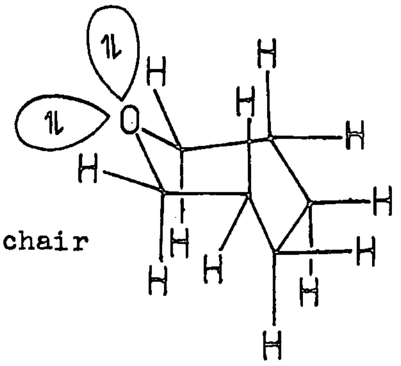


View
down
bond
(a)

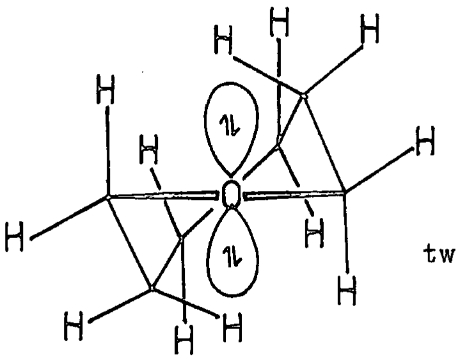


Consequently a relatively poor interaction would be expected between the carbon-hydrogen bond and the oxygen lone pairs.

Oxepane may exist in chair, boat, or twist conformations.



chair

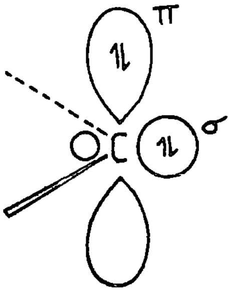


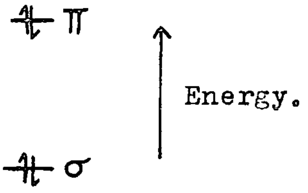
twist

However the ring is relatively very flexible and pseudo-rotation would result in an average value of the di-hedral angle between oxane and oxolane.

Therefore the order of decreasing average value of the di-hedral angle is similar to the order of increasing reactivity of the ether with fluoroalkenes.

Recent photoelectron spectroscopic evidence suggests that the two lone pairs on oxygen are not equivalent[137] and that one lone pair is in a low energy σ-type orbital while the other lone pair is in a high energy π-type orbital.





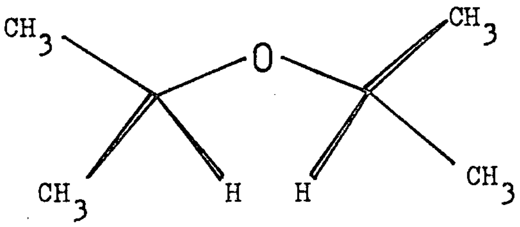
Using this approach similar conclusions may be drawn for the reactivity of the cyclic ethers but they are not so apparent.

Recent data illustrates that the dissociation energy of carbon-hydrogen bonds is determined by the value of the di-hedral angle. Laser flash photolysis techniques were used to determine the absolute rates of hydrogen abstraction by t-butoxyl radicals.[138] These values were roughly proportional to the size of the di-hedral angle, Table 18 . They found that the absolute rate constants decrease along the series of ring size $5 > 7 > 4 > 6 > 3$ which agrees with our pattern of reactivity. Di-iso-propyl ether has a particularly low rate of abstraction which was explained by the most stable rotamer being an all-gauche conformation (105), rather than the more sterically crowded all-anti conformation (105a).

Table 18

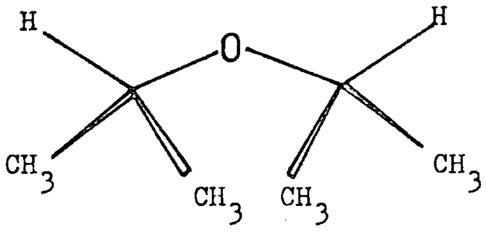
Reactivities of Ethers, Orthoformates and Acetals Toward t-Butoxyl Radicals at 27°C [138]

Substrate	Relative Reactivity (compared to Oxolane=1)
Oxolane	1.0
2-Methyl-1,3-Dioxolane	1.5
1,3-Dioxolane	0.93
Oxepane	0.54
Oxetane	0.48
Diethyl Ether	0.47
3,3-Dimethyl-1-Oxetane	0.39
cis-1,4,5,8-Tetraoxadecaline	0.41
Oxane	0.33
1,1-Dimethoxyethane	0.27
1,3,5-Trioxane	0.24
1,4-Dioxane	0.18
2-Propanol	0.22
Diisopropyl Ether	0.14
Ethylene Oxide	0.13
2-Methoxy-1,3-Dioxolane	0.12
Dimethoxymethane	0.10
Trimethoxymethane	0.06
7-Oxabicyclo [2,2,1] Heptane	0.04
Trioxaadamantane	no reaction



all - gauche

(105)



all anti

(105a)

The large average value of the di-hedral angle in rotamer (105) may account for the low reactivity of di-iso-propyl ether with hexafluoropropene.

A satisfactory explanation for the cyclic ether results may therefore be suggested on the basis of the stereoelectronic effect. This was a preliminary study and more information, especially using polycyclic ethers, is required to investigate this effect further.

Stereoelectronic effects may be observed in nitrogen systems.[139] Refering to Table 16, N-methylpyrrolidin-2-one was more reactive than either N-acetylpiperidine or N-acetylmorpholine. Although these systems are not directly comparable the five membered ring, with a lower average value of the di-hedral angle, is more reactive than the six membered rings.

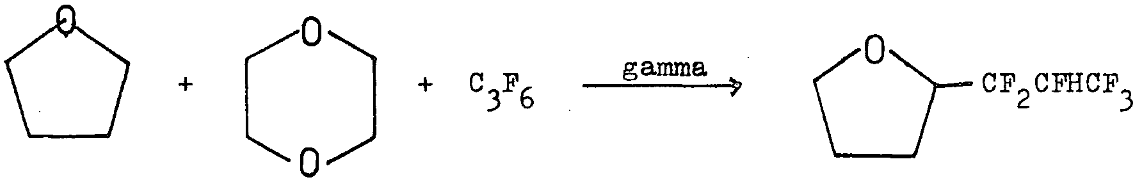
D. EXPERIMENTAL EVIDENCE.

It has been concluded that the reactivity of a substrate towards addition to a fluoroalkene is determined primarily by the inductive effects of substituents and secondarily by the conformation of the substrate. A number of approaches have been investigated in order to obtain confirmatory evidence for these conclusions.

1. COMPETITION EXPERIMENTS.

One way of comparing the reactivity of two substrates is to react a mixture with a deficiency of fluoroalkene and determine the ratio of the two products. This approach has been attempted with a number of the cyclic ethers.

A mixture of oxolane, 1,4-dioxan, and hexafluoropropene gave the oxolane adduct (21) only.

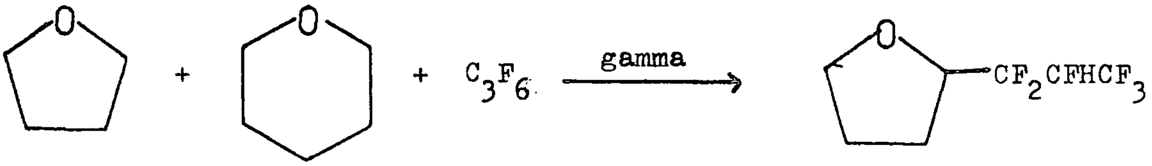


3 : 3 : 1

(21)

This is very clear evidence that oxolane is more reactive than dioxan, especially as dioxan has twice the number of active hydrogen sites.

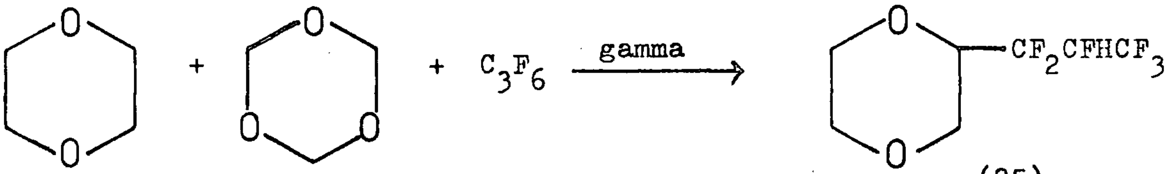
Similarly a mixture of oxolane, oxane, and hexafluoropropene gave the oxolane product only.



3 : 3 : 1

(21)

Also dioxan, trioxan, and hexafluoropropene gave the dioxan product only.

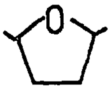
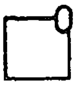
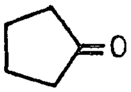
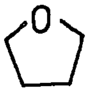
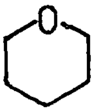
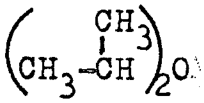
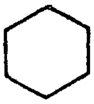
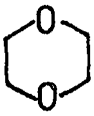
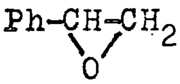
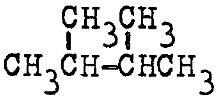


3 : 3 : 1

(25)

Using these data the order of reactivity is;

Table 19[140]

Substrate	Relative Reactivity	Substrate	Relative Reactivity
	50.5	$CH_3O\,^tBu$	3.22
	33.6	$HCOOCH_3$	2.14
	33.5		1.53
	23.0	$CHCl_3$	1.08
Et_2O	16.3	$PhOCH_3$	1.01
	13.1	$PhCH_3$	1.00
	10.8	EtCOEt	0.92
 $(CH_3-\overset{CH_3}{\overset{\vert}{C}}H)_2O$	10.6	$^tBu_2O$	0.311
	8.04	$PhO\,^tBu$	0.300
	6.66	 $Ph-\underbrace{CH-CH_2}_{O}$	0.235
 $CH_3\overset{CH_3}{\overset{\vert}{C}}H-\overset{CH_3}{\overset{\vert}{C}}HCH_3$	5.35	CH_2Cl_2	0.234
		CH_3COCH_3	0.17
		$Ph\,^tBu$	0.17
		CH_3COOEt	0.156
		^tBu-OH	0.129
		$PhCOCH_3$	0.107
		$PhCOOEt$	0.093
		$PhCOOCH_3$	0.040

which is in agreement with the product yield results.

This approach has been applied by other workers to the reactivity of substrates towards t-butoxyl radical, derived from t-butyl hypochlorite, relative to toluene as a standard, Table 19[140]. These results correlate well with the reactivity of the substrates towards fluoroalkenes. The results of Muramatsu et al discussed in Chapter 1 show a similar order of reactivity.[94]

2. ACETONE/t-BUTANOL RATIOS FROM THE DECOMPOSITION OF DI-t-BUTYL PEROXIDE.

A method was needed to determine the ease of hydrogen abstraction from the substrates. The technique that was attempted was based on the thermal decomposition of di-t-butyl peroxide with the substrate as solvent[141]. The t-butoxyl radical produced may either abstract a hydrogen atom from the substrate (106) or decompose (107).

$$(CH_3)_3CO\cdot \quad + \quad R-H \xrightarrow{K_H} (CH_3)_3COH \quad + \quad R\cdot \qquad (\underline{106})$$

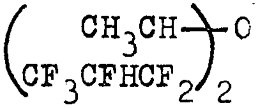
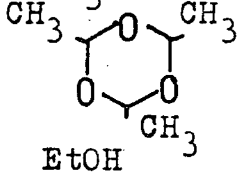
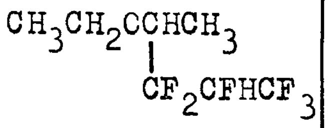
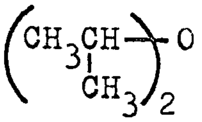
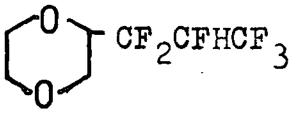
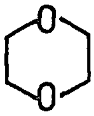
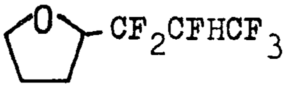
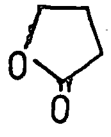
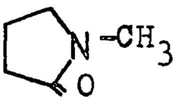
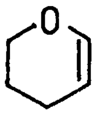
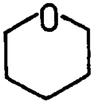
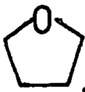
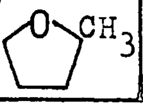
$$(CH_3)_3CO\cdot \xrightarrow{k_D} CH_3\cdot \quad + \quad CH_3COCH_3 \qquad (\underline{107})$$

$$\frac{k_D}{k_H} \propto \frac{\%CH_3COCH_3}{\%(CH_3)_3COH}$$

At a particular temperature, k_D will be independent of the solvent while k_H will depend on the ease of hydrogen abstraction from the solvent. Therefore the ratio of the amount of acetone produced to the amount of t-butanol will be a measure of the ease of hydrogen abstraction. A large number of these experiments were run and the results are shown in Table 20. The acetone / t-butanol ratios refer to the whole substrate molecule not just to specific hydrogen sites. It is not possible to eliminate any other effects which may be present, eg. solvent effects,

Table 20.

Ratio of Acetone to t-Butanol Products from the Thermal Decomposition of Di-t-Butyl Peroxide in a Variety of Solvents[a]

Solvent	Acetone/^{t}Butanol Ratio	Solvent	Acetone/^{t}Butanol Ratio
 $\left(\begin{matrix}CH_3CH\\CF_3CFHCF_2\end{matrix}\right)_2O$	100	iPrOH	0.46
$(^tBuO)_2$	3.6	Bu_2O	0.40
$PhCOOCH_3$	2.91	CH_3OH	0.36
			0.36
 $CH_3CH_2\underset{\displaystyle CF_2CFHCF_3}{C}HCH_3$	2.42	EtOH	0.22
 $\left(\underset{\displaystyle CH_3}{CH_3CH}\right)_2O$	2.23	$CH_3OCH_2OCH_3$	0.21
		PrOH	0.16
$EtCOCH_3$	2.21	$CH_3OCH_2CH_2OCH_3$	0.15
CH_3COOCH_3	1.92	$CH_3OCH_2CH_2OH$	0.15
$(ClCH_2CH_2)_2O$	1.59	BuOH	0.15
	1.48	12-Crown-4 polyether	0.14
			0.14
	1.00	Pr_2O	0.10
	0.97		0.10
$(CH_3CH_2)_2S$	0.61	$HCON(CH_3)_2$	0.09
		$[(CH_3)_2N]_2CO$	0.08
	0.54	Et_2O	0.08
PhOBu	0.50		0.08
			0.07
$PhOCH_3$	0.47		0.07

a) At 120°C for 8 hours in 5ml sealed Carius tubes, Peroxide:Solvent = 1:10

from the ease of hydrogen abstraction. Despite the limitations of the method thereis a very clear correlation between the ease of reaction of the substrate with a fluoroalkene and the acetone / t-butanol ratio. This is best shown as a graph of product yield with fluoroalkene against the acetone / t-butanol ratio, Figure 4 . Substrates that have an acetone / t-butanol ratio below approximately 0.4 all react well with hexafluoropropene at room temperature while those above this value do not react.

The range of acetone / t-butanol ratios were such that they are useful for investigating the less reactive substrates. The more reactive substrates give a very low yield of acetone, consequently the experimental error in the ratio is too great to distinguish small differences between them. The development of a different radical system may be of use in these cases.

The order of reactivity of substrates deduced from the acetone / t-butanol ratios in Table 20 is very similar to that produced by using the relative reactivity data shown in Table 19 . This is expected because the two procedures are measuring the same parameter, ie. the ease of hydrogen abstraction.

12-Crown-4 polyether is the only substrate which does not fit onto Figure 4 . It has a low ratio but is unreactive. A flexible ring conformation would appear to rule out stereoelectronic effects but it may be possible that the ring is fixed in an un-favourable conformation. A crystal structure of 18-crown-6 polyether shows that the most stable conformation has the oxygen atoms pointing towards the centre of the ring, and held by hydrogen bonds,[156] Figure 5 . In this conformation the values of the di-hedral angles are at their maximum. Similarly the crystal structure of 12-crown-4 polyether shows that the dihedral angles for most of the oxygen atoms are large.[157]

Figure 4.

Graph of % Yield of Adduct with C_3F_6 against the Acetone/t-Butanol ratio for the Substrate.

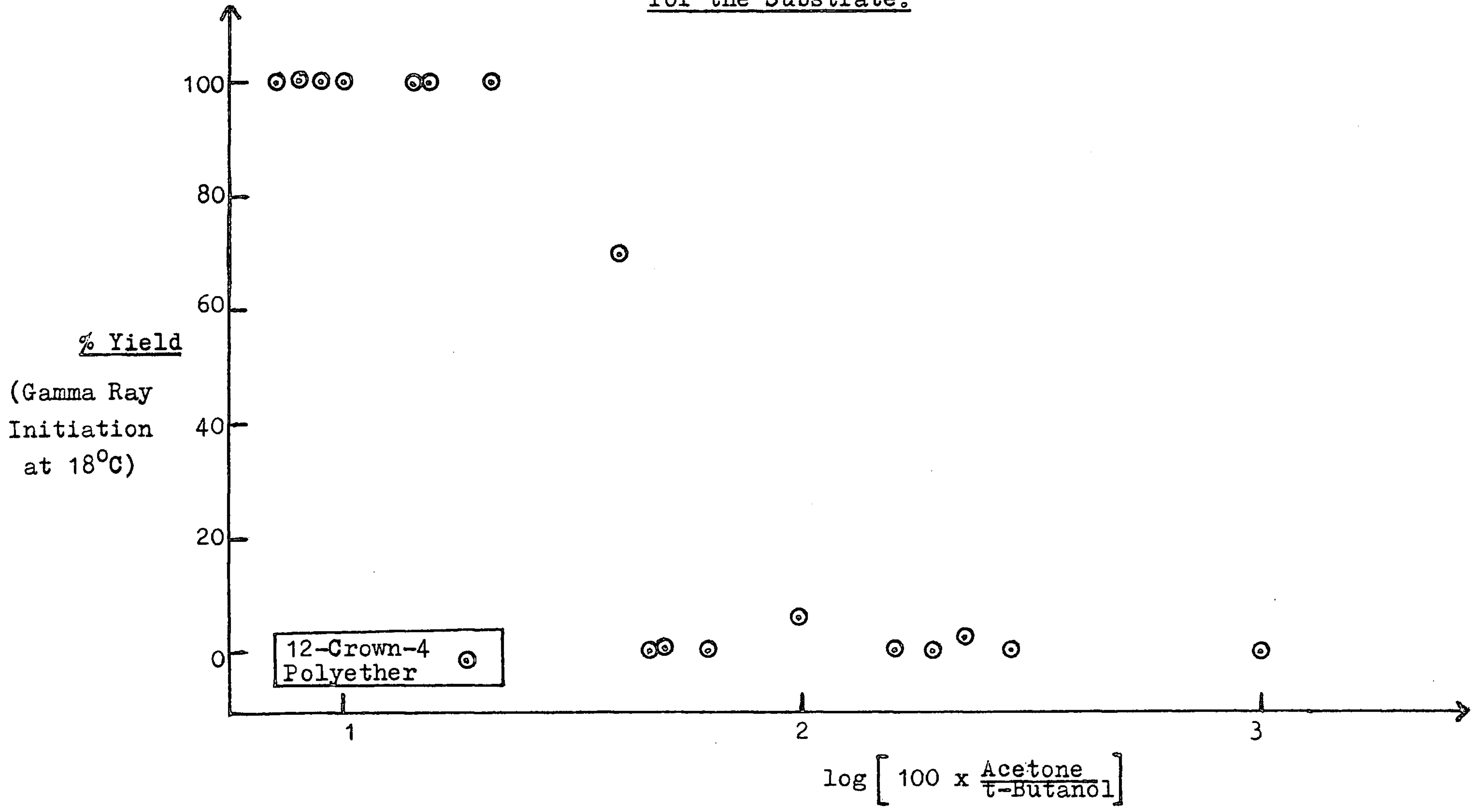
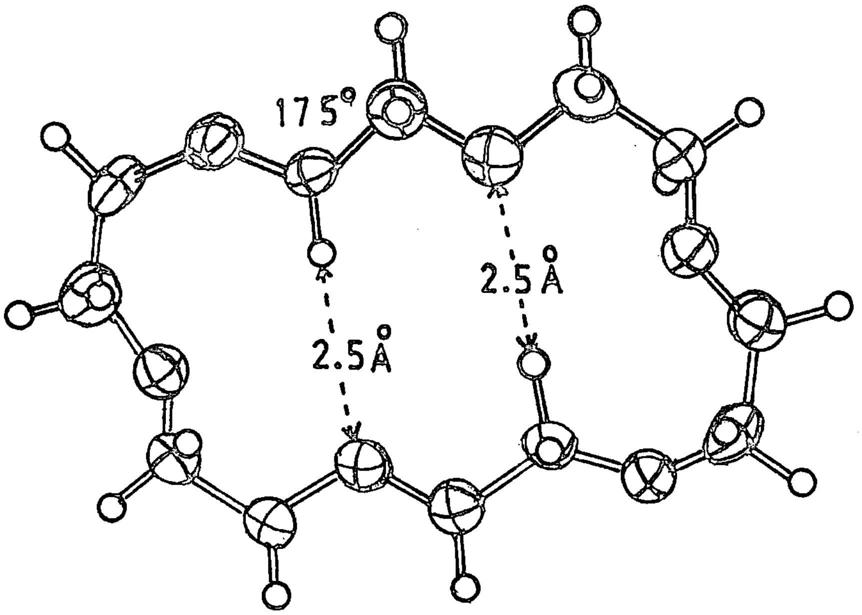


Figure 5



E. CONCLUSION.

Our results show that the ease of hydrogen abstraction from the substrates is related to the inductive effects of substituents and to conformation in a predictable manner. The ease of hydrogen abstraction must directly affect the rate of addition to fluoroalkenes.

Considering the mechanism of the chain reaction, the initiation step must be assumed to proceed whatever the dissociation energy of the carbon-hydrogen bond.

$$\mathrm{ROCH_3} \xrightarrow{\text{gamma}} \mathrm{RO\dot{C}H_2}$$

This is because gamma rays are high energy initiators and are able to break most activated bonds.

The first chain propagation step will depend on the nucleophilicity of the substrate radical (<u>108</u>) because the radical must add to the electrophilic alkene.

$$\underset{(\underline{108})}{\mathrm{RO\dot{C}H_2}} \quad + \quad \mathrm{CF_2{=}\ CFR_f} \longrightarrow \underset{(\underline{109})}{\mathrm{ROCH_2CF_2\dot{C}FR_f}}$$

An electron withdrawing substituent would reduce the nucleophilicity of radical (108) hence the rate of the reaction.

The second chain propagation step will depend on the ability of the intermediate radical (109) to abstract a hydrogen from the substrate. The radical (109) is of low reactivity and will not be able necessarily to abstract the hydrogen.

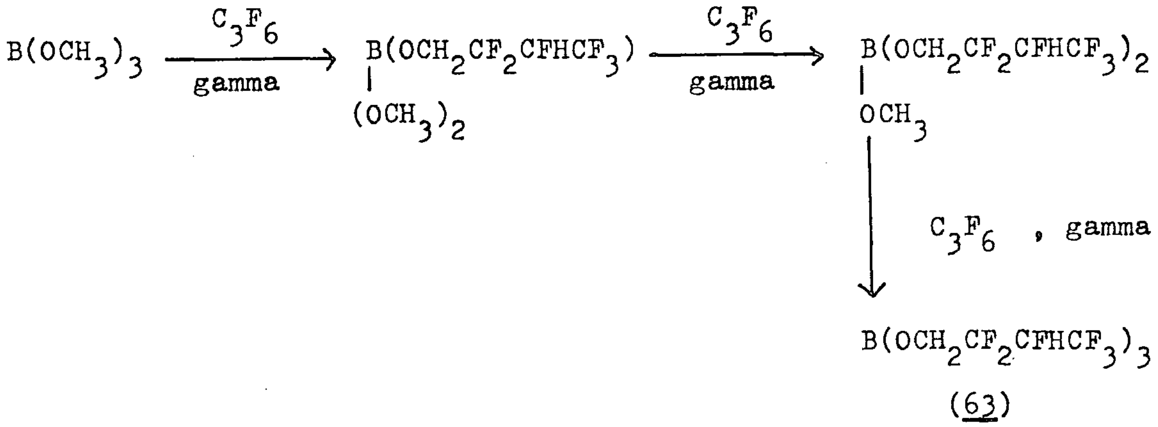
$$\underset{(\underline{109})}{\mathrm{ROCH_2CF_2\dot{C}FR_f}} \quad + \quad \mathrm{ROCH_3} \longrightarrow \mathrm{ROCH_2CF_2CFHR_f} \quad + \quad \mathrm{RO\dot{C}H_2}$$

With a constant fluoroalkene, the energy of radical (109) must be very similar whatever substrate is used, because the R group is remote from the radical centre. Therefore this step of the chain will be very dependent on the ease of hydrogen abstraction. In fact there must be a particular carbon-hydrogen dissociation energy above which radical (109) would be unable to abstract the hydrogen. This would explain the sudden drop in reactivity of the substrate with decreasing ease of hydrogen abstraction shown by acetone / t-butanol ratios in Figure 4 .

F. MECHANISM OF ADDITION OF BORATES TO FLUOROALKENES.

The formation of tri-adducts in good yield from the addition of trimethyl borate to fluoroalkenes was unexpected. The empty orbital on boron was expected to have a very good conjugative electron withdrawing effect that would cause the borate to be unreactive towards fluoroalkenes. These results questioned whether a free radical mechanism was operating in the borate reactions. There are three plausible mechanisms which may be considered.

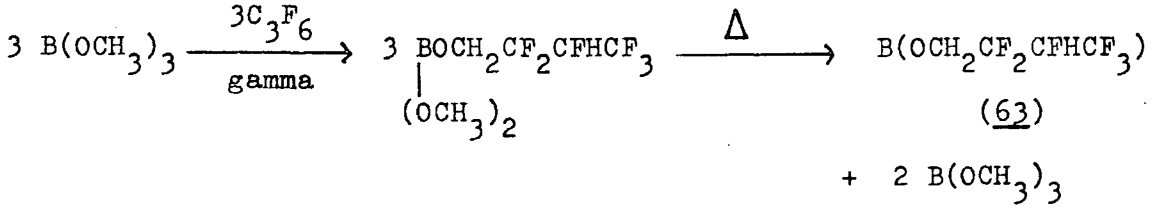
(a) The tri-adducts are formed by three consecutive free radical addition reactions.



$$\begin{tikzcd} B(OCH_3)_3 \arrow[r, "C_3F_6", "gamma"'] & \underset{(OCH_3)_2}{B(OCH_2CF_2CFHCF_3)} \arrow[r, "C_3F_6", "gamma"'] & \underset{OCH_3}{B(OCH_2CF_2CFHCF_3)_2} \arrow[d, "{C_3F_6\ ,\ gamma}"] \\ & & B(OCH_2CF_2CFHCF_3)_3 \end{tikzcd}$$

(63)

(b) A free radical addition reaction occurs to form a mono-adduct which disproportionates to form the tri-adduct and trimethyl borate on isolation. Disproportionation readily occurs for unsymmetrical borates and very few have been isolated.[125]



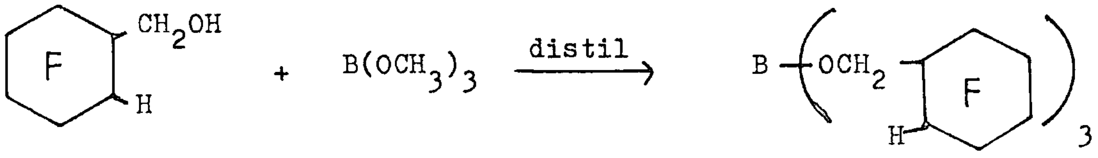
$$3\ B(OCH_3)_3 \xrightarrow[gamma]{3C_3F_6} 3\ \underset{(OCH_3)_2}{BOCH_2CF_2CFHCF_3} \xrightarrow{\Delta} B(OCH_2CF_2CFHCF_3)\ (\underline{63}) + 2\ B(OCH_3)_3$$

(c) The free radical addition of methanol to the fluoroalkene occurs, followed by alcohol exchange with trimethyl borate on isolation, or during the reaction.

$$3\ CH_3OH \xrightarrow[gamma]{3C_3F_6} 3\ CF_3CFHCF_2CH_2OH \xrightarrow[heat]{B(OCH_3)_3} B(OCH_2CF_2CFHCF_3)_3\ (\underline{63}) + 3\ CH_3OH$$

The methanol may be produced by the hydrolysis of trimethyl borate, with which it forms an azeotrope. Alcohol exchange is a well documented reaction between borate esters and higher molecular weight alcohols than the alkoxy moiety of the borate.[125]

Alcohol exchange was tested by distilling a mixture of the alcohol adduct (68) with trimethyl borate. The higher molecular weight borate was formed.



(68)

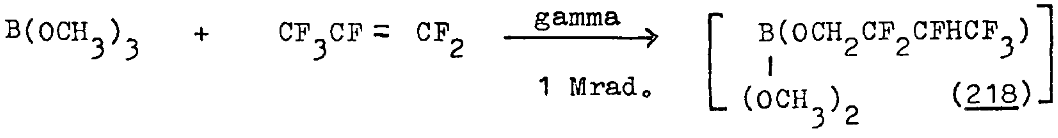
(65) 71%

A series of control reactions were carried out in order to try to distinguish between the three possible mechanisms.

A sealed mixture of trimethyl borate and hexafluoropropene were left in the dark. No product was formed, indicating that the reaction is free radical in nature. A three to one mixture of methanol and hexafluoropropene was irradiated with gamma rays for a set period of time. The crude product was analysed by GLC and shown to contain a large proportion of the methanol adduct (56)

$$CH_3OH \quad + \quad CF_3CF=CF_2 \xrightarrow[\text{1 Mrad.}]{\text{gamma}} \underset{(56)}{CF_3CFHCF_2CH_2OH}$$

A similar three to one mixture of trimethyl borate and hexafluoropropene was irradiated for the same time. The crude product showed neither the methanol adduct (56) nor the borate tri-adduct (63); the only products had GLC retention times which would be expected for a borate mono-adduct, (218)



$$B(OCH_3)_3 \quad + \quad CF_3CF=CF_2 \xrightarrow[\text{1 Mrad.}]{\text{gamma}} \left[\begin{array}{l} B(OCH_2CF_2CFHCF_3) \\ \ \ | \\ (OCH_3)_2 \qquad (218) \end{array} \right]$$

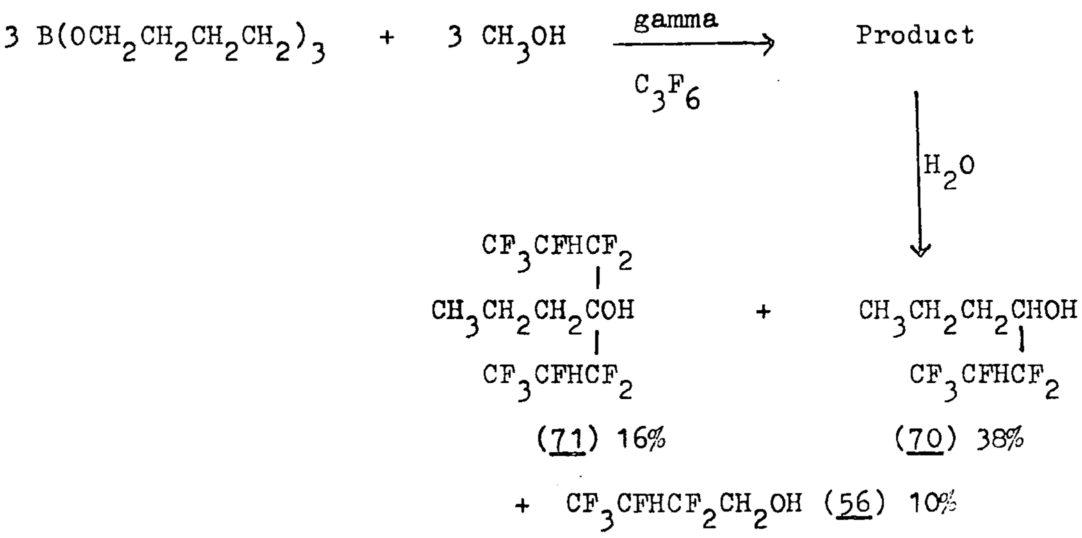
Distillation of this mixture gave a product containing some of the borate tri-adduct (63).

$$\text{Product } (\underline{218}) \xrightarrow{\text{distil}} B(OCH_2CF_2CFHCF_3)_3 \quad (\underline{63})$$

This suggests that borate mono-adducts are formed which disproportionate on distillation.

Finally a three to three to one mixture of methanol, trimethyl borate, and hexafluoropropene respectively was irradiated for the standard time. The product gave an almost identical GLC trace to that obtained using trimethyl borate only with hexafluoropropene.

These observations indicate that a borate mono-adduct is formed which disproportionates on isolation to givethe tri-adducts, ie mechanism (b). However these results are not conclusive and more evidence is needed. A borate ester that on hydrolysis does not produce the methanol adduct (56) from itself, or any potential adduct, was needed to help decide between the three mechanisms. Also the borate ester would have to have a big enough alkoxy group to prevent exchange with the methanol adduct (56). A suitable candidate was tri-n-butyl borate which is easy to separate from n-butyl alcohol by distillation as an azeotrope is not formed. The reaction of tri-n-butyl borate with hexafluoropropene was shown in Chapter 2 to give a complex adduct product which on hydrolysis gave the mono- (70) and di-adducts (71) of n-butyl alcohol and hexafluoropropene. A competition reaction was carried out using a mixture of three to three to one molar ratio of tri-n-butyl borate, methanol, and hexafluoropropene respectively. Hydrolysis of the crude product gave mainly the butyl alcohol adducts (70) and (71) and very little of the methanol adduct (56) as analysed by GLC.



$$3\ B(OCH_2CH_2CH_2CH_2)_3 \quad + \quad 3\ CH_3OH \xrightarrow[C_3F_6]{gamma} \text{Product} \xrightarrow{H_2O}$$

$$\begin{array}{c} CF_3CFHCF_2 \\ | \\ CH_3CH_2CH_2COH \\ | \\ CF_3CFHCF_2 \\ (\underline{71})\ 16\% \end{array} \quad + \quad \begin{array}{c} CH_3CH_2CH_2CHOH \\ | \\ CF_3CFHCF_2 \\ (\underline{70})\ 38\% \end{array}$$

$$+ \quad CF_3CFHCF_2CH_2OH\ (\underline{56})\ 10\%$$

This indicates that most of the reaction has occurred with the borate and not with the methanol. Methanol would not be expected to exchange with the borate under these conditions to produce n-butyl alcohol which would react with the alkene.

In summary, the evidence appears to suggest mechanism (b) as the most likely mechanism of the formation of the borate tri-adducts. However there is a degree of uncertainty in these conclusions due to the difficulty in ruling out conclusively exchange reactions.

CHAPTER 5

REACTIONS OF FREE RADICAL ADDUCTS

A. INTRODUCTION.

Many fluorinated compounds have been prepared by free radical additions to fluoroalkenes. However there have been very few reports in the literature on further reactions of the adducts. The aim of this work was to use free radical addition reactions to introduce functionality into fluoroalkenes. The reactions of the adducts produced during the mechanistic studies have been investigated in an attempt to form other functional fluorocarbons which may have useful applications. In this chapter the results of this investigation are presented, with the exception of cobalt trifluoride fluorination which is discussed in Chapter 6.

B. FREE RADICAL HALOGENATION.

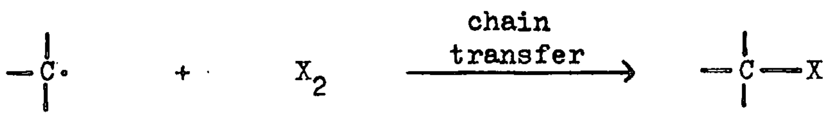
The photoinduced halogenation of adduct compounds will result in the introduction of halogen substituents. The reactivity of the various hydrogen atoms within an adduct would be expected to be influenced greatly by the electronic effects of the fluorine atoms. At this point it is worth discussing the mechanism of halogenation.

1. GENERAL MECHANISM.

The halogenation of an organic substrate proceeds via a chain mechanism.[142]

$$X_2 \xrightarrow{h\nu} 2\,X\cdot \qquad -(\underline{110})$$

$$X\cdot \;+\; -\underset{|}{\overset{|}{C}}-H \xrightarrow{\text{abstraction}} -\underset{|}{\overset{|}{C}}\cdot \;+\; HX \qquad -(\underline{111})$$



$$-\overset{|}{\underset{|}{C}}\cdot \quad + \quad X_2 \xrightarrow{\text{chain transfer}} -\overset{|}{\underset{|}{C}}-X \quad + \quad X\cdot \qquad -(\underline{112})$$

$$X\cdot \quad + \quad X\cdot \quad + \quad M \xrightarrow{\text{termination}} X_2 \quad + \quad M \qquad -(\underline{113})$$

ΔH° (kJ/mol) [142]

X =	F	Cl	Br	I
Reaction (111)	-160	-20	+46	+113
Reaction (112)	-285	-97	-92	-71

The thermochemistry of the abstraction (111) and chain transfer (112) steps depend critically on the nature of the halogen. The abstraction step is exothermic for fluorine and chlorine, but endothermic for bromine and iodine. The chain transfer step is exothermic for all of the halogens but decreases from fluorine to iodine; therefore the ease of halogenation decreases from fluorination to iodination. For iodination the reverse reaction is often more favourable.

Halogenation of a hydrocarbon derivative gives a mixture of all possible halides formed by abstraction of the various hydrogen atoms present in the molecule. The rate of abstraction of the hydrogen atoms will depend onthe chemical environment of the hydrogen and the type of halogen atom. The relative reactivities of hydrogen atoms are expressed usually in terms of their Relative Selectivity, a quantity defined as the relative rate of abstraction per hydrogen atom of position Y compared to position X.

$$\text{Relative Selectivity, } RS_X^Y = \frac{k_Y}{k_X} \times \frac{x}{y}$$

where k_X, k_Y are the rate constants of hydrogen abstraction at positions X and Y respectively.

x, y are the number of hydrogen atoms at positions X and Y.

The RS_X^Y values for primary , secondary , and tertiary hydrogen atoms are given in Table 21[142] which show that the order of reactivity is tertiary > secondary > primary. Also Table 21 shows that fluorine atoms are not very selective and show little discrimination between the various types of hydrogen atoms. In contrast iodine atoms are very selective and react almost exclusively with tertiary hydrogen atoms. Therefore the more reactive the halogen atom, the less selective it is during halogenation. Absolute Arrhenius parameters for hydrogen abstraction by halogen atoms are given in Table 22 . For each alkane the activation energy increases from fluorine to iodine which would be expected as the reaction becomes less exothermic. The less exothermic the reaction, the more the reaction will be controlled by the strength of the carbon-hydrogen bond being broken. The figures in Table 22 are in good agreement with the Polanyi equation (114).

$$E = \alpha.\Delta H + C \qquad -(\underline{114})$$

where E = activation energy
ΔH = enthalpy of reaction
α , C = constants

The constant α may have a value between 0 and 1 and the higher the value, the greater the influence the bond being broken will have on the course of the reaction. Values of α are 0.0 for fluorine, 0.45 for chlorine, 0.86 for bromine, and 0.91 for iodine. So endothermic brominations and iodinations will have transition states which resemble the products more than the reactants (115). Conversely exothermic chlorinations and fluorinations will have transition states which resemble the reactants more than the products (116).

Table21 [142]

Relative Selectivities(RSx^y) for Hydrogen Abstraction by Halogen Atoms at 300K

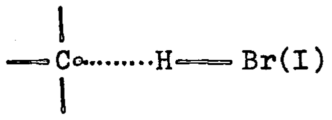
Halogen	$-CH_3$	$=CH_2$	$\equiv CH$
F	1	1.3	1.8
Cl	1	4.4	6.7
Br	1	80	1600
I	1	1850	210,000

Table22

Arrhenius Parameters for Hydrogen Abstraction from Alkanes by Halogen Atoms

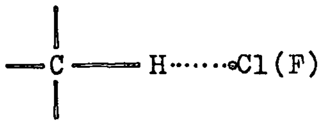
$R-H + X^\circ \longrightarrow R^\circ + HX$								
R-H	F		Cl		Br		I	
	logA^a	E^b	logA	E	logA	E	logA	E
H_2	10.7	7.1	10.9	23.1	11.5	82.7	11.4	143
CH_3-H	10.5	5.0	10.6	16.0	11.0	78.1	11.5	141
C_2H_5-H	10.0	1.3	11.0	4.2	11.6	58.8	11.6	115
C_3H_7-H	9.7	0.0	11.0	4.2	-	-	11.6	121
$(CH_3)_2CH$-H	9.8	0.0	10.9	2.9	11.0	43.7	11.3	102
$(CH_3)_3C$-H	9.8	0.0	10.3	0.4	10.6	32.8	11.0	92

[a] in L/mol/s [b] in kJ/mol



$-\overset{|}{\underset{|}{C}}\cdots\cdots H - Br(I)$

(115)



$-\overset{|}{\underset{|}{C}} - H\cdots\cdots Cl(F)$

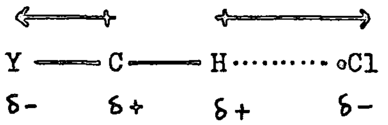
(116)

This is a statement of the Hammond Postulate.

2. HALOGENATION OF SUBSTITUTED ALKANES.

The presence of a substituent greatly influences the relative selectivity values during halogenation. A large amount of data is available using substituted n-butanes. A selection of this data is given in Tables 23 , 24 , and 25 for fluorination, chlorination, and bromination respectively. [142]

During chlorination the hydrogen atoms at the alpha and beta positions of the n-butanes are deactivated by electron withdrawing substituents. This may be explained by the small extent of bond breaking in the transition state and the influence of the bond dissociation energies will be small. The polar inductive effect of the substituent will be the important factor and will cause dipole-dipole repulsions within the transition state (117) which will cause deactivation.



Y = substituent.

(117)

Electron repelling substituents will cause activation of the alpha and beta positions due to a favourable inductive effect. Hydrogen atoms at the gamma position or further from the substituent remain unaffected.

The few fluorination results available show the same pattern as the chlorination results. In these cases the relative selectivities are

Table 23[142]

Relative Selectivities(RSp^X) for the Fluorination of Substituted Butanes at 20°C in the Gas Phase.

X	CH_2X	CH_2	CH_2	CH_3
H	1.0	1.3	1.3	1.0
F	0.3	0.8	1.0	1.0
Cl	-	1.7		1.0

Table 24[142]

Relative Selectivities(RSp^X) for the Chlorination of Substituted Butanes at 50°C in the Gas Phase.

X	CH_2X	CH_2	CH_2	CH_3
H-	1	3.6	3.6	1
F-	0.9	1.7	3.7	1
Cl-	0.8	2.1	3.7	1
CF_3-	0.04	1.2	4.3	1
CH_3O-	3.5	0.7	4.4	1
Me_3C	2.9	3.7	5.3	1
Ph-	6.5	1.0	-	1

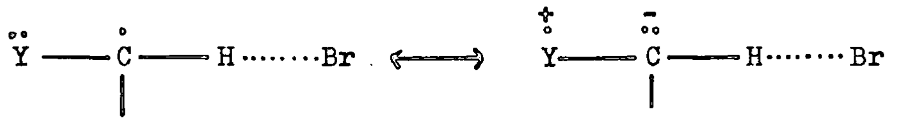
Table 25[142]

Relative Selectivities(RSp^X) for the Bromination of Substituted Butanes at 160°C in the Gas Phase.

X	CH_2X	CH_2	CH_2	CH_3
H-	1	80	80	1
F-	9	7	90	1
Cl-	34	32	80	1
CF_3	1	7	80	1
NC-	20	8	80	1

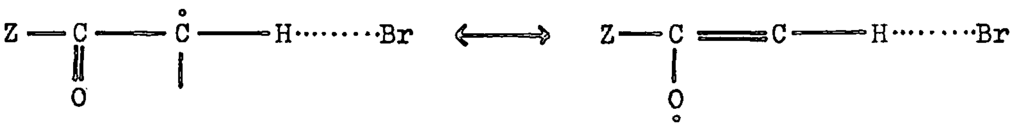
lower due to the greater reactivity of the fluorine atom.

The bromination of substituted n-butanes shows a different pattern to chlorination. Here the amount of bond breaking in the transition state is greater and the bond dissociation energy of the carbon-hydrogen bond is the dominant factor in controlling the reaction. The alpha hydrogen atoms are activated because the bond dissociation energy has been lowered due to the resonance effects of the substituents, eg (118) and (119).



$\ddot{Y}-\dot{C}-H\cdots Br \longleftrightarrow \overset{+}{Y}=\overset{-}{\ddot{C}}-H\cdots Br$

(118)



$Z-C(=O)-\dot{C}-H\cdots Br \longleftrightarrow Z-C(-\dot{O})=C-H\cdots Br$

(119)

These mesomeric effects do not apply to the beta hydrogen atoms which will still be influenced by the inductive effects of the substituents so will be deactivated.

3. SOLVENT EFFECTS.

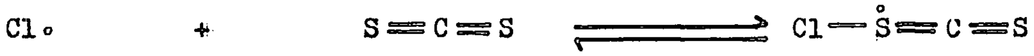
During halogenation a solvent may interact with the halogen atom causing it to be less reactive;hence more selective. Solvent effects have been investigated during the chlorination of 2,3-dimethylbutane by observing changes in the Relative Selectivity between tertiary and primary attack, shown in Table 26 .[142] The influence of the solvents is to make the chlorination more selective and increase the Relative Selectivity. Small effects occur with oxygen solvents due to interaction of the chlorine atom with the oxygen lone pairs. The presence of a sulphur atom in a solvent greatly increases the solvent effect due to

Table 26

Solvent Effects in the Chlorination of 2,3-Dimethyl-Butane

Solvent	Relative Reactivities at 55°C (Tertiary to Primary)
Neat	3.7
CCl_4	3.5
Cyclohexane	3.6
Dioxan	5.6
n-Butyl ether	7.2
Sulphur monochloride	14
Carbon disulphide	33 (at 25°C)
Nitrobenzene	4.9
Chlorobenzene	17.1 (at 25°C)
Iodobenzene	31
Benzene	14.6
Toluene	15.4
Arisole	18.4
Diphenyl sulphide	24

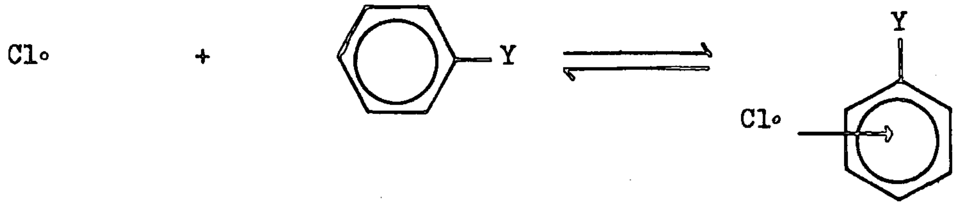
the expansion of the covalency shell of the sulphur to form a complexed radical (120) of low energy with a chlorine atom.



$$Cl^{\circ} \quad + \quad S{=}C{=}S \rightleftharpoons Cl{-}\overset{\circ}{S}{=}C{=}S$$

(120)

Aromatic solvents are good at decreasing the reactivity of a chlorine atom due to formation of π-complexes (121)



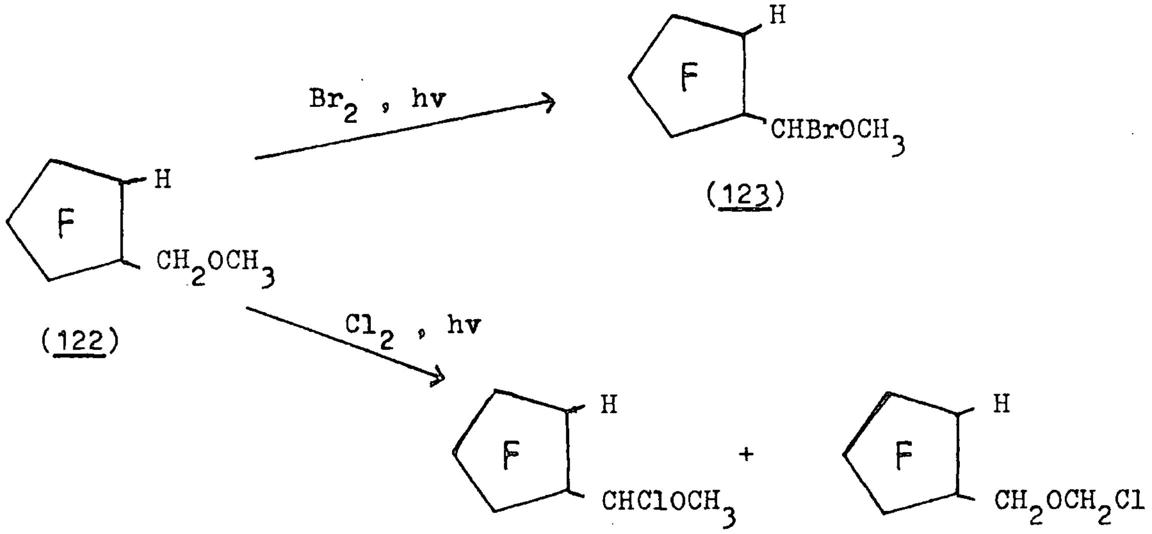
(121)

Electron withdrawing substituents on the benzene ring [Y in (121)] make the ring more electrophilic so forming a weaker complex with the chlorine atom. The opposite effect occurs with electron donating substituents in (121).

4. HALOGENATION OF FLUOROALKENE ETHER ADDUCTS.

a. Introduction.

The halogenation of octafluorocyclopentylmethoxymethane (122) has been investigated previously in this laboratory.[7] Using a one to one molar ratio of reactants, bromine attacked the methylene group of (122) to give compound (123) and chlorine attacked mainly the methyl group to give compound (124a) with some methylene attack to give compound (124). These results were explained by the late transition state during bromination causing resonance effects to be dominant. Therefore methylene attack would be preferred because this forms a secondary radical in the transition state while methyl attack forms a primary radical. Although



(122) (123) (124) (124a)

Solvent.	% Yield. (124)	% Yield. (124a)
Neat	9	91
CCl_4	44	56
CS_2	77	23

the tertiary hydrogen site of (122) would form a tertiary radical there is no resonance stabilization with an oxygen atom. During chlorination inductive effects are dominant because the early transition state means that the more nucleophilic methyl position is more reactive towards the electrophilic chlorine atom. A solvent increases the yield of product from methylene attack (124) due to interaction with the chlorine atom lowering the reactivity to more like the bromine case.

An independant investigation of the chlorination of a polyfluoroether (125) gave attack predominantly at the least electronegative site, in agreement with the above results.[143]

$$\begin{array}{lcclr} \mathrm{CHF_2CHFOCH_3} & \xrightarrow[55\ -\ 96^{\circ}C]{Cl_2} & & \mathrm{CF2HCHFOCHCl_2} & 78\% \\ (125) & & + & \mathrm{CHF_2CClFOCH_2Cl} & 10\% \\ & & + & \mathrm{CHF_2CHFOCH_2Cl} & 3\% \\ & & + & \left.\begin{array}{l} \mathrm{CHF_2CClFOCHCl_2} \\ \mathrm{CHF_2CHFOCCl_3} \end{array}\right\} & 9\% \end{array}$$

The halogenation of 2,2,3,4,4,4-hexafluorobutyl methyl ether has been carried out to investigate further the orientation of halogen attack on a polyfluoroether.

b. Halogenation of 2,2,3,4,4,4-Hexafluorobutyl methyl ether.

i. Chlorination.

The chlorination of 2,2,3,4,4,4-hexafluorobutyl methyl ether (9) using equimolar quantities of reactants in a sealed pyrex flask gave three major components. They were the products from methylene group attack (126), from methyl group attack (127), and a mixture of di-chlorinated species (128).

$$\underset{(9)}{CF_3CFHCF_2CH_2OCH_3} \xrightarrow[\text{sealed pyrex vessel, UV.}]{Cl_2} \underset{(126)\quad 6.8\%}{CF_3CFHCF_2CHClOCH_3}$$

$$+ \underset{(127)\quad 45.5\%}{CF_3CFHCF_2CH_2OCH_2Cl}$$

$$+ \underset{(128)}{\left\{\begin{array}{ll} CF_3CFHCF_2CH_2OCHCl_2 & 36.7\% \\ CF_3CFHCF_2CHClOCH_2Cl & 11.0\% \end{array}\right.}$$

This result shows that chlorination of compound (9) occurs preferentially at the methyl group. An interesting structural identification feature was based on the presence of two asymmetric centres in compound (126) and one in compound (127). Two sets of fluorine-19 NMR resonances are observed for each fluorine environment of compound (126) while compound (127) shows only one set. The formation of di-chlorinated species was a problem to the determination of the preferred site of attack. Therefore the chlorination of compound (9) was repeated using an excess of (9) however the dichlorinated species were still present in comparable amounts. The effect of solvent on the position of attack was investigated and the results shown in Table 27 . Two conclusions may be drawn;

(a) The methyl group was always the preferred position of attack.

(b) The quantity of dichlorinated species decreased on using a solvent. Therefore compound (9) appears to be a much more reactive system than octafluorocyclopentylmethoxymethane (122) towards chlorination. A competitive chlorination reaction between (9) and (122) gave products from compound (9) only, confirming this conclusion. It is not clear at present why compound (9) should be much more reactive than compound (122).

Iodine monochloride was used to chlorinate 2,2,3,4,4,4-hexafluorobutyl methyl ether (9) . Chlorination products (126) , (127) , and (128) were formed together with a compound (129) that was assigned as a dimer of (9).

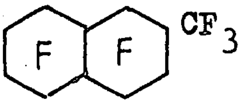
$$\begin{array}{lllll} CF_3CFHCF_2CH_2OCH_3 & \xrightarrow[UV]{ICl} & & CF_3CFHCF_2CHClOCH_3 & (\underline{126})\ 1.6\% \\ & & + & CF_3CFHCF_2CH_2OCH_2Cl & (\underline{127})\ 49\% \\ & & + & C_5H_4OF_6Cl_2 & (\underline{128})\ 10\% \\ & & + & [\text{Dimer of } (\underline{9})] & (\underline{129})\ 39\% \end{array}$$

ii. Bromination.

The bromination of 2,2,3,4,4,4-hexafluorobutyl methyl ether (9) was carried out using similar conditions to those used for the chlorination reactions. The two reagents were mixed in a one to one molar ratio in a sealed pyrex flask and exposed to ultra violet light. The main product was the alcohol (56), presumably from hydrolysis of a bromomethyl ether resulting from attack of bromine on the methyl group of compound (9). Only a small amount of products were formed from bromine attack on the methylene group of compound (9). Non-bromine containing products (131) and (132) have been assigned as dimers of compound (9).

Table 27

Effect of Solvent on the Chlorination of 2,2,3,4,4,4-HEXAFLUOROBUTYL METHYL ETHER(9).

Molar Ratio [(9)/Cl_2]	Solvent	%(126)	%(127)	%(128)
0.62	Neat	6.8	45.5	47.7
2.01	Neat	12.7	39.9	47.4
1.94	Neat	13.5	50.4	36.1
0.71	CCl_4	4.8	49.5	45.7
2.07		17.6	67.0	15.4
0.84	CS_2	16	76.5	7.5
2.90	CS_2	19.9	80.1	-

$$\underset{(\underline{9})}{\mathrm{CF_3CFHCF_2CH_2OCH_3}} \xrightarrow[\substack{\text{sunlight}\\ \text{3 days.}}]{\mathrm{Br_2}} \begin{array}{llll} & \mathrm{CF_3CFHCF_2CHBrOCH_3} & (\underline{130}) & 12\% \\ + & \mathrm{CF_3CFHCF_2CH_2OH} & (\underline{56}) & 38\% \\ + & \text{Dimer of } (\underline{9})\ \text{I} & (\underline{131}) & 27\% \\ + & \text{Dimer of } (\underline{9})\ \text{II} & (\underline{132}) & 23\% \end{array}$$

Therefore it is not clear from this experiment which is the preferred position of attack by bromine.

The bromination was repeated using carbon disulphide as a solvent. In this case the main product was from methylene group attack (<u>130</u>), with only a small amount of the alcohol (<u>56</u>).

$$\underset{(\underline{9})}{\mathrm{CF_3CFHCF_2CH_2OCH_3}} \xrightarrow[\substack{\mathrm{CS_2}\\ \text{sunlight}\\ \text{72 hrs.}}]{\mathrm{Br_2}} \begin{array}{llll} & \mathrm{CF_3CFHCF_2CHBrOCH_3} & (\underline{130}) & 81\% \\ + & \mathrm{CF_3CFHCF_2CH_2OH} & (\underline{56}) & 9\% \\ + & \text{Dimer of } (\underline{9})\ \text{I} & (\underline{131}) & 9\% \end{array}$$

The yield of dimers was greatly reduced giving a more accurate picture of the preferred position of attack.

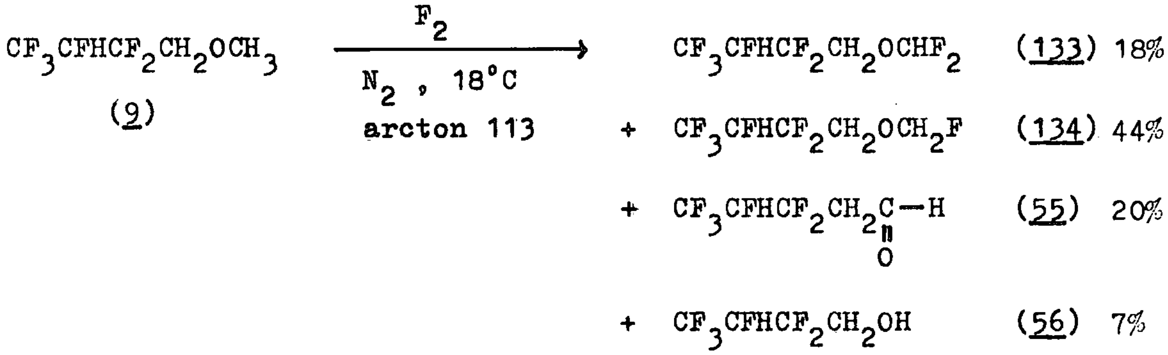
Another bromination reaction was attempted using thermal initiation. This will give a greater proportion of gas phase reaction and perhaps reduce the amount of dimerization. This was found to be the case and the main product was again from methylene attack.

$$\underset{(\underline{9})}{\mathrm{CF_3CFHCF_2CH_2OCH_3}} \xrightarrow[220^{\circ}\mathrm{C}]{\mathrm{Br_2}} \begin{array}{llll} & \mathrm{CF_3CFHCF_2CHBrOCH_3} & (\underline{130}) & 57\% \\ + & \mathrm{CF_3CFHCF_2CH_2OH} & (\underline{56}) & 8\% \\ + & \text{Dimer of } (\underline{9}) & (\underline{131}) & 34\% \end{array}$$

From the limited data it may be concluded that the preferred position of bromination of compound (<u>9</u>) is at the methylene position.

iii. Fluorination.

An equimolar quantity of fluorine, diluted with nitrogen, was bubbled through the adduct in $CF_2ClCFCl_2$ as solvent. The products were isolated by preparative GLC. A few non-ether products (55) and (56) were formed that may be explained by the hydrolysis of the ether products during the isolation proceedure.



$$
\begin{array}{llll}
\underset{(9)}{CF_3CFHCF_2CH_2OCH_3} & \xrightarrow[N_2\text{ , }18^\circ C\text{ arcton }113]{F_2} & CF_3CFHCF_2CH_2OCHF_2 & (133)\ 18\% \\
 & + & CF_3CFHCF_2CH_2OCH_2F & (134)\ 44\% \\
 & + & CF_3CFHCF_2CH_2\underset{\|\atop O}{C}-H & (55)\ 20\% \\
 & + & CF_3CFHCF_2CH_2OH & (56)\ 7\%
\end{array}
$$

No products were formed from methylene group attack. This shows that fluorine attacks preferentially the methyl group of compound (9) which is the least electronegative site, in agreement with the chlorination results.

C. OXIDATIVE CHLORINATION.

1. BORATE ADDUCTS.

The chlorination of trimethyl borate results in cleavage and oxidation of the methoxy groups to form carbonyl chloride.[144]

$$B(OCH_3)_3 \quad + \quad 9Cl_2 \longrightarrow BCl_3 \quad + \quad 3COCl_2 \quad + \quad 9HCl$$

It appeared possible, therefore, to produce fluoroalkanoyl chlorides from the fluoroalkyl borate adducts discussed in Chapter 2. A number of fluoroalkyl borates (135) have been chlorinated using gaseous chlorine to give chlorinated species (136) and a small amount of boron-oxygen bond cleavage to form compound (137).[145]

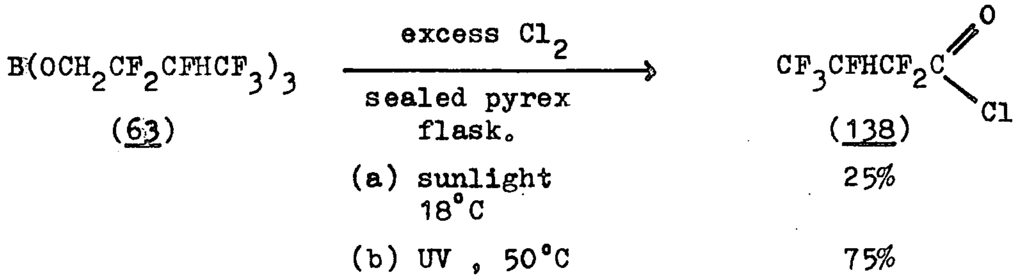
$$(R_fCH_2O)_3B \xrightarrow{Cl_2} (R_fCHClO)_3B \xrightarrow{Cl_2} (R_fCHClO)_2BCl$$

(135) (136) (137)

$R_f = CF_3 , C_2F_5 , C_3F_7$

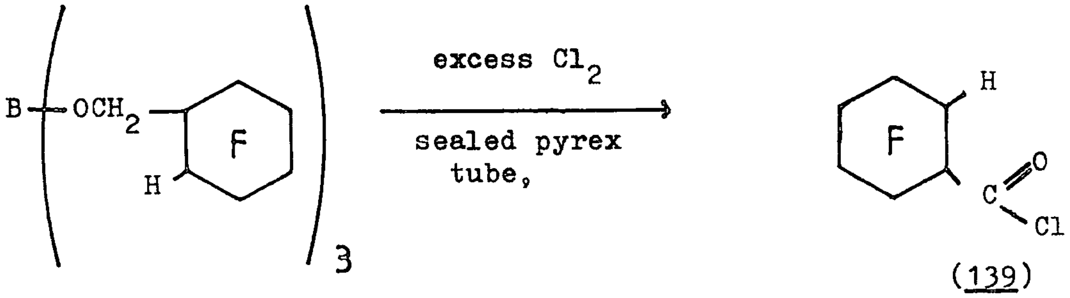
The fate of the cleaved fluoroalkyl group was not discussed. This work shows that more forceful conditions are needed to give fluoroalkanoyl chlorides from borate adducts.

Tri(2,2,3,4,4,4-hexafluorobutyl) borate was sealed in a pyrex flask with an excess of chlorine and left in the sunlight. On opening, a copious amount of hydrogen chloride was liberated and the volatile product mixture was mainly 2,2,3,4,4,4-hexafluorobutanoyl chloride (138).



The experiment was repeated using UV initiation to give a better yield of the acid chloride. A few other borate esters have been chlorinated in this manner to investigate whether this is a general reaction. Each borate ester was chlorinated using both sunlight and UV initiation but the latter usually gave the best yield of products.

Tri(1,2,3,3,4,4,5,5,6,6-decafluorocyclohexyl) borate gave very good yields of the acid chloride (139).

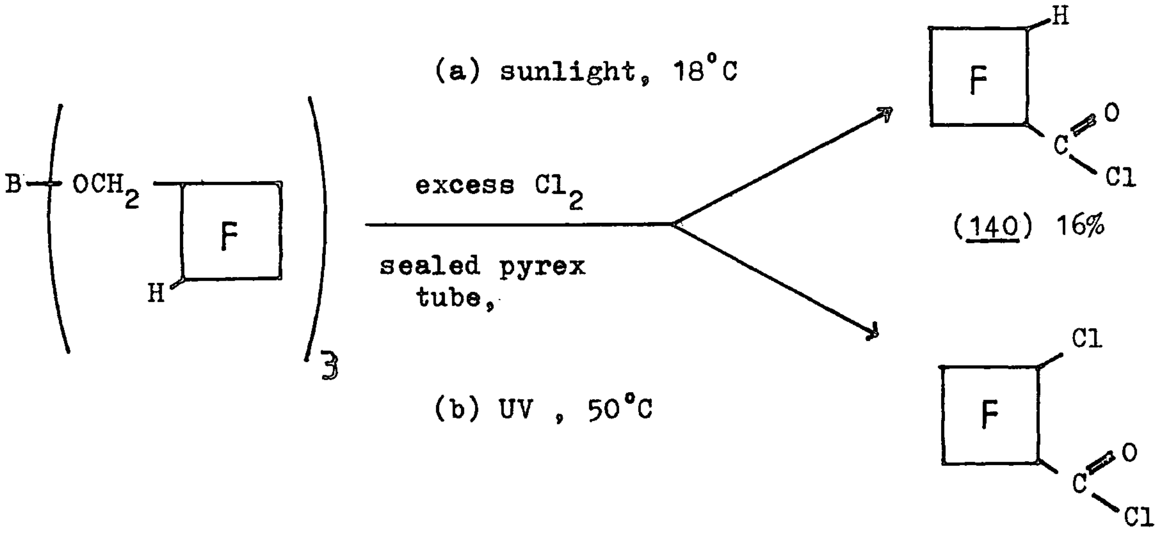


(139)

(a) sunlight, 18°C 85%

(b) UV, 50°C 83%

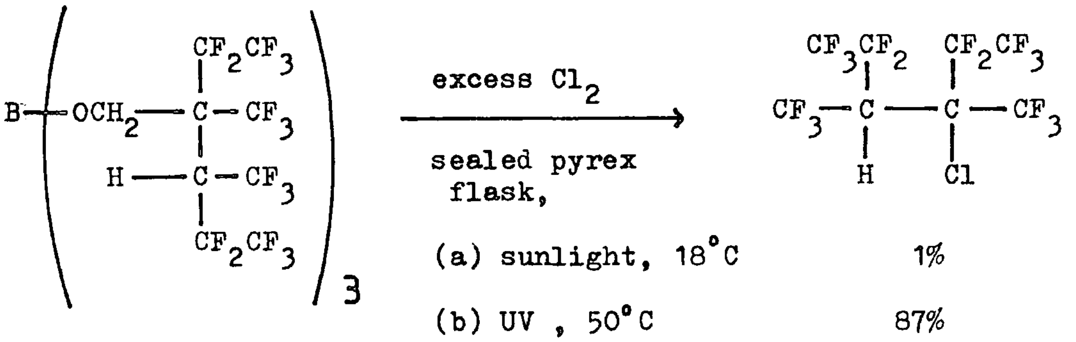
Two different products were obtained from tri(1,2,3,3,4,4-hexafluorocyclobutyl) borate depending on the method of initiation used. Sunlight gave the expected acid chloride (140) as the main product although in a low yield, while UV gave the chlorinated acid chloride (141)



(140) 16%

(141) 63%

An acid chloride was not detected from the chlorination of tri(2-pentafluoroethyl-4,4,5,5,5-pentafluoro-2,3-di(trifluoromethyl)pentyl) borate but compound (142) was the main product. It is probable that the acid chloride is decarbonylated readily due to the highly stable tertiary radical intermediate.



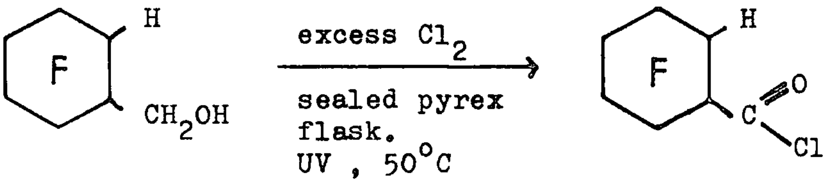
(142)

These preliminary results show that polyfluorinated acid chlorides may be prepared in good yields by the oxidative chlorination of borate esters.

2. ALCOHOL ADDUCTS.

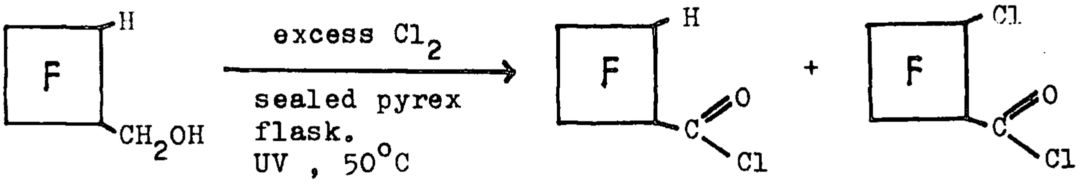
It would be more useful if acid chlorides could be prepared from alcohol adducts rather than from borate adducts. Therefore alcohol adducts analogous to the borate adducts discussed above have been chlorinated using our vigorous conditions.

1,2,3,3,4,4,5,5,6,6-Decafluorocyclohexylmethanol gave the acid chloride (139) in a similar yield to the analogous borate adduct reaction.



(139) 86%

A mixture of acid chlorides (140) and (141) was formed on chlorination of 1,2,3,3,4,4-hexafluorocyclobutylmethanol.



(140) 17% (141) 20%

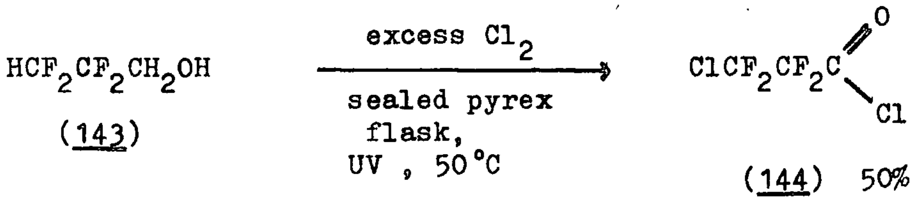
Tetrafluoroethene and methanol telomer adducts are prepared industrially and the preparation of acid chlorides from these compounds would be a valuable process. The chlorination of α,α,ω-trihydroperfluoroalkanols has been described to give a mixture of products including aldehydes and esters but very little acid chlorides.[146]

$$\underset{n= 1,2,3}{H(CF_2CF_2)_nCH_2OH} \xrightarrow[20-80°C]{Cl_2} \underset{1-55\%}{H(CF_2)_{2n}Cl} + \underset{24-84\%}{H(CF_2CF_2)_nCHO}$$

$$+ \underset{2-8\%}{H(CF_2CF_2)_nCOOH} + \underset{6-25\%}{H(CF_2)_{2n}COOCH_2(CF_2)_{2n}H}$$

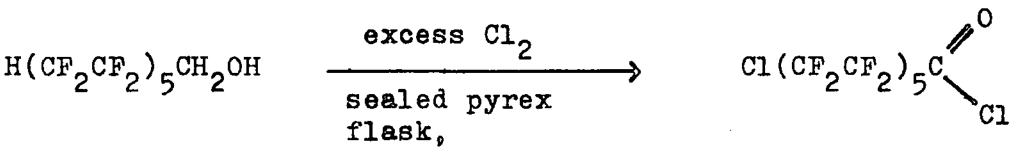
These chlorinations were carried out by bubbling chlorine through the substrates at a high temperature. A few α,α,ω-trihydroperfluoroalkanols have been subjected to chlorination by our sealed vessel technique.

1,1,3-Trihydrotetrafluoropropan-1-ol (143) gave a good yield of 3-chloro tetrafluoropropanoyl chloride (144). The volatile (144) was separated readily from a mixture of less volatile products.



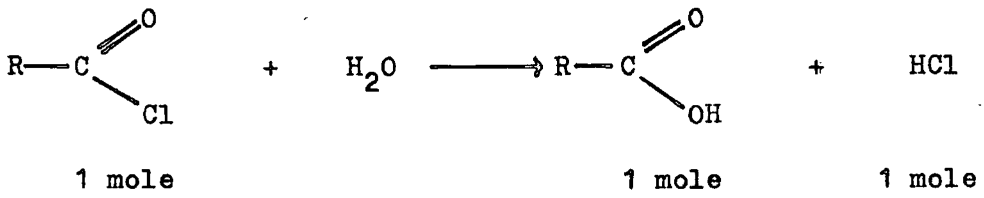
It is of interest that the ω-hydrogen was chlorinated during this reaction.

1,1,11-Trihydroeicosafluoroundecan-1-ol (145) was chlorinated as an example of a higher molecular weight member of this class of adducts. The crystalline (145) dissolved in the liquid chlorine during the reaction and after the excess gases had been left to evaporate a white amorphous solid remained. The white solid was very moisture sensitive and analytical evidence was in favour of it being mainly 11-chloroeicosafluoroundecanoyl chloride (146)



(146)

The available chromatographic and spectroscopic techniques were not very suitable for determining the purity of compound (146). To try and obtain more information a volumetric technique was applied. A weighed amount of compound (146) was hydrolysed and dissolved in distilled water and the resulting acid solution titrated with standard alkali solution. An acid chloride ought to give two moles of acid from one of acid chloride.



In practice 86% of the theoretical acid was formed and 89% using a back titration method by dissolving compound (146) in a standard alkali solution.

Chlorination of 1,1,5-trihydro-octafluoropentan-1-ol (147) gave a complex mixture of products including acid chlorides.

$$H(CF_2CF_2)_2CH_2OH \xrightarrow[\text{sealed pyrex flask, UV , 18°C}]{\text{excess } Cl_2} \text{Product mixture.}$$

However this reaction was run at a lower temperature than that used above.

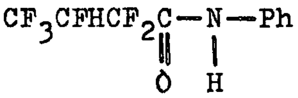
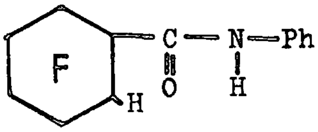
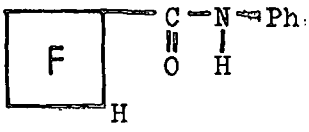
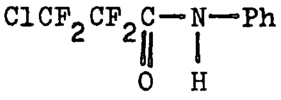
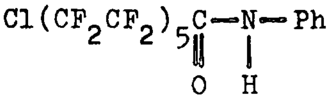
3. CONCLUSION.

These results show that acid chlorides may be prepared from fluoroalkene-borate and -alcohol adducts in good yields. A high reaction temperature was preferred, however the experimental apparatus was working to the pressure limit. Therefore a new apparatus would have to be designed to cope with higher pressures generated when using higher reaction temperatures in order to maximize the yield of acid chlorides.

4. IDENTIFICATION OF PRODUCTS.

Anilide derivatives were prepared for some of the acid chlorides and their melting points are given below.

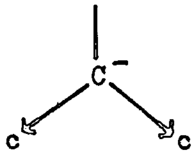
Anilide Derivatives of Acid Chlorides

Structure.		Melting Point.(°C)
 $CF_3CFHCF_2\underset{\underset{O}{\Vert}}{C}-\underset{\underset{H}{\vert}}{N}-Ph$	(148)	79.5 - 81.5
	(149)	129.5 - 131
	(150)	141.5 - 143
 $ClCF_2CF_2\underset{\underset{O}{\Vert}}{C}-\underset{\underset{H}{\vert}}{N}-Ph$	(151)	87.5 - 88.5
 $Cl(CF_2CF_2)_5\underset{\underset{O}{\Vert}}{C}-\underset{\underset{H}{\vert}}{N}-Ph$	(152)	136 - 137

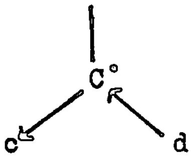
D. FREE RADICAL DEHYDRODIMERIZATION.

1. INTRODUCTION.

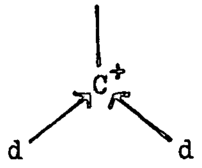
From recent experiments on the stability of free radicals the concept of capto-dative resonance stabilization has been developed.[147] This theory is an extension of the principles determining the stability of ionic species. Carbanions are stabilized by electron accepting or capto-substituents (153) and carbocations are stabilized by electron donating or dative substituents (154). Therefore free radicals are stabilized by a combination of a capto and a dative substituent (155).



(153)



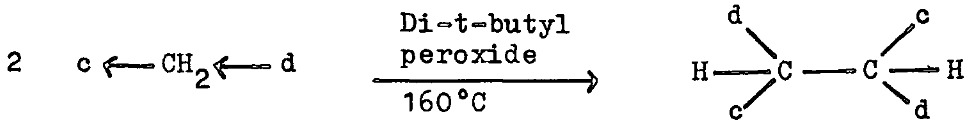
(155)



(154)

c = capto group.   d = dative group

A review of the development and application of capto-dative stabilization is available.[147] One particular application of this theory we have investigated is the dehydrodimerization or oxidative coupling of methylene compounds. This reaction involves the dimerization of a methylene unit substituted with both a capto and a dative group (156). A much lower yield of dimer product is produced if the methylene unit is substituted by any other combination of groups.



(156)

25-91%

c= CO_2Me , CN , $CONMe_2$; d = MeO , Me_2N , $MeCO_2$

This reaction has been reported using capto groups that are conjugatively electron withdrawing. Fluoroalkene-ether adducts contain a methylene group that is substituted by an inductively electron withdrawing polyfluoroalkyl group and a donating methoxy group.

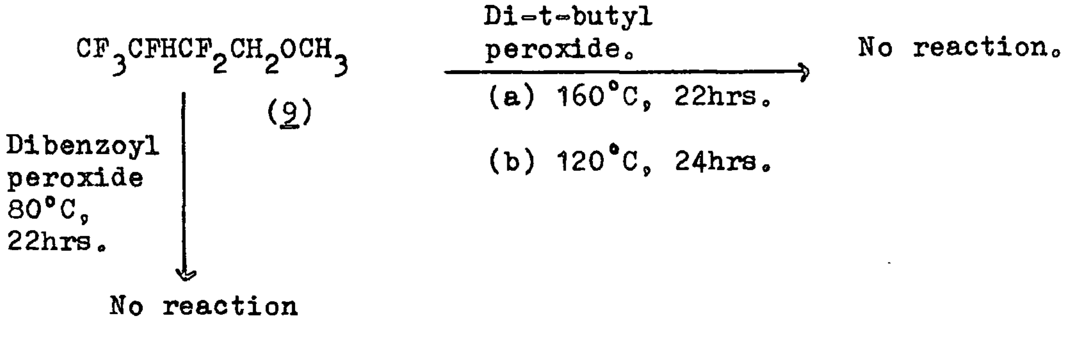
$$CH_3O \longrightarrow CH_2 \longrightarrow CF_2CFHCF_3$$

dative- -inductively capto

Experiments have been attempted to try and dimerize a number of these adducts. This would be useful both to investigate the capto-dative theory and as a synthetic procedure to produce further functionally substituted fluorocarbons.

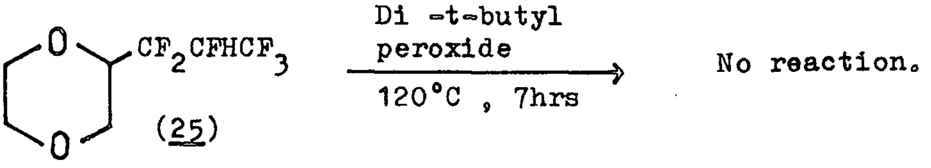
2. RESULTS.

2,2,3,4,4,4-Hexafluorobutyl methyl ether was heated with di-t-butyl peroxide in a sealed tube; however no products were observed by GLC.

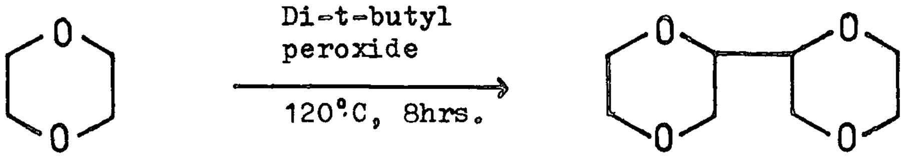


The reaction was repeated using dibenzoyl peroxide as an alternative radical initiator however the ether was recovered unchanged.

Another adduct (25) was tried but the dimerization was still unsuccessful.

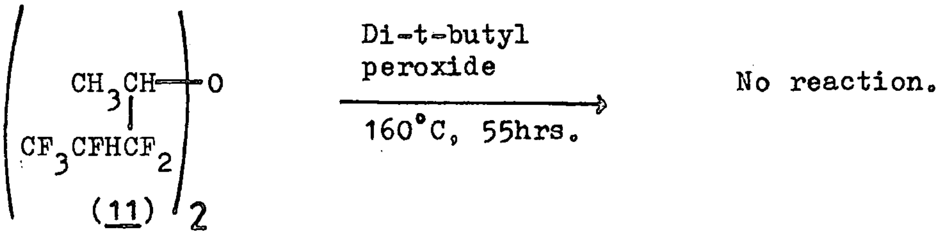


To check on the experimental conditions 1,4-dioxan was successfully dimerized.



(156) 25%

A final reaction was tried using the di-adduct (11) but it was recovered quantitatively.



(11)

Therefore in every case no dimer was formed from the fluoroalkene-ether adducts. It must be concluded that inductively electron withdrawing perfluoroalkyl groups do not represent good capto groups. The strong influence of the fluoroalkyl group on the rest of the adduct molecule is demonstrated by the absence of dimers from the dioxan adduct (25) even at the remote 5-position.

CHAPTER 6

COBALT TRIFLUORIDE FLUORINATION OF FLUOROALKENE ETHER ADDUCTS.

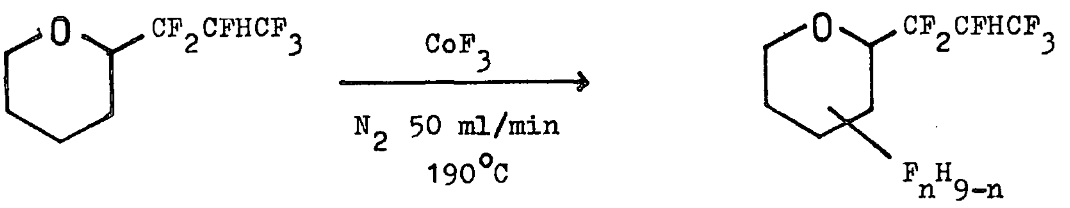
A. INTRODUCTION.

A range of methods exist for the synthesis of highly fluorinated ethers which have been discussed in Chapter 1. These syntheses fall into two categories. Either complex multistep procedures are used with expensive starting materials or a one step procedure is used that gives very low yields of product. No high yield synthesis of highly fluorinated ethers exists using simple procedures and inexpensive starting materials. It would be useful to develop such a synthesis because fluoroethers exhibit useful properties.

Many partially fluorinated ether adducts were obtained during the mechanistic investigation discussed in the previous chapters. The cobalt trifluoride fluorination of these adducts was investigated as a potential route to highly fluorinated ethers.

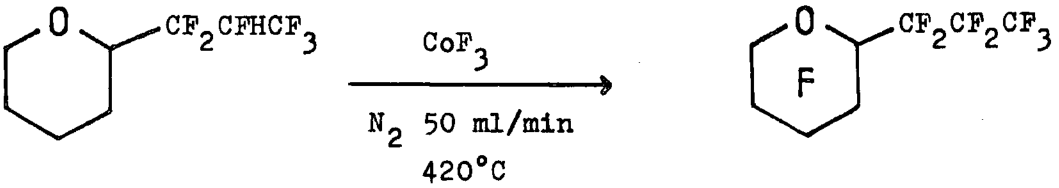
B. DEVELOPMENT.

It is usual to carry out the cobalt trifluoride fluorination of a compound at a temperature just above the boiling point. These conditions were used in a previous study in this laboratory to fluorinate dimethyl ether adducts of fluoroalkenes.[7] Polyfluorinated products were obtained but this did not include any of the fully fluorinated ether. No fragmentation products were obtained and it was concluded that a fluorine containing substituent stabilized the ether during fluorination. To build on these results some fluoroalkene ether adducts were fluorinated using cobalt trifluoride. The fluorination was attempted first with 2-(1,1,2,3,3,3-hexafluoropropyl)oxane(<u>22</u>) at 190°C. A good recovery of material was obtained but the product (<u>214</u>) was a complex mixture of polyfluoro species by GLC/mass spectrum analysis.



(214) 69% n= 1 to 9

The incomplete reaction may have been due to exhaustion of the cobalt trifluoride. Therefore the cobalt trifluoride was regenerated with fluorine and the reaction repeated with mixture(214). The product (215) consisted of a similar ratio of components as in mixture (214) by GLC. Therefore the cobalt trifluoride bed had not been exhausted. In an attempt to obtain a greater degree of fluorination the reaction was repeated with mixture (215) at 250°C. GLC showed that, although the components of this product mixture (216) were the same as for the previous two mixtures (214) and (215) , there were significant amounts of the more highly fluorinated products. This was encouraging and the temperature was increased in stages until, at 420°C, a product was obtained that consisted of the perfluorinated ether (156) in greater than 90% of the product mixture. The total yield of (156) is very good in comparison to any other available synthesis of (156) shown in Chapter 1.



(156) 62%

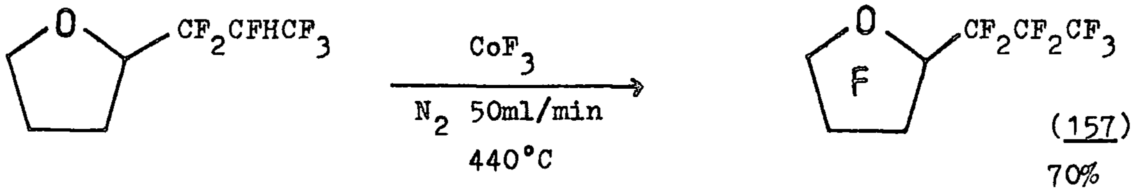
This discovery opened up the possibility of a new high yield general synthesis of perfluoroethers. Therefore a systematic study of the high temperature cobalt trifluoride fluorination of ether adducts has been carried out.

C. TEMPERATURE DEPENDENCE STUDIES.

The preliminary experiments described above showed that a temperature of at least 420°C is required for complete fluorination of an ether adduct. It was necessary to obtain quantitative results and, consequently, the fluorination of a number of ether adducts were done at a variety of temperatures to determine the optimum temperature. The extent of fluorination at each temperature was calculated from GLC peak area measurements and GLC/mass spectra were used to identify the products. Intermediate polyfluoroethers were isolated by preparative GLC where possible.

1. USING 2-(1,1,2,3,3,3-HEXAFLUOROPROPYL)OXOLANE.

The cobalt trifluoride fluorination of 2-(1,1,2,3,3,3-hexafluoropropyl) oxolane (21) at 440°C gave perfluoro-2-propyloxolane (157) as the major product.



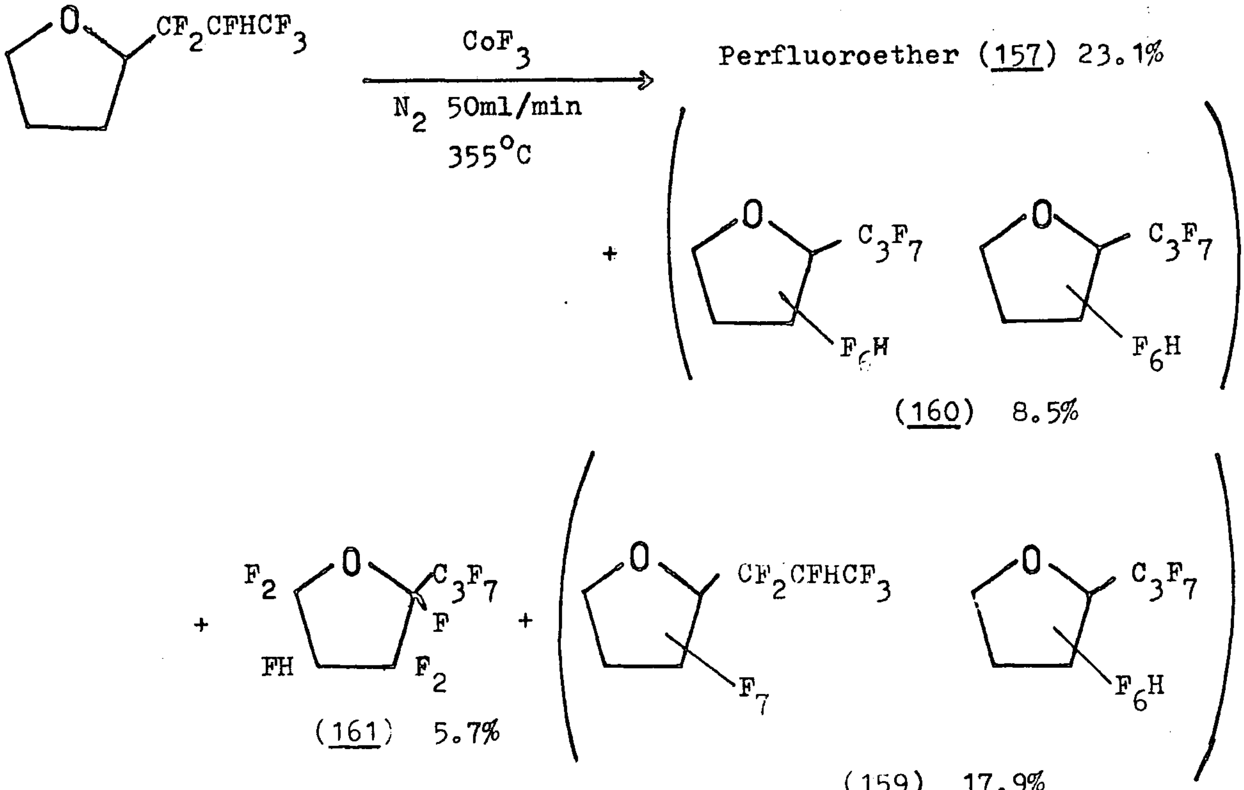
(157)
70%

+ $CF_3CF_2CF_2CF_2CF_2CF_3$ (158)
3%

(Total yield 73%)

Perfluorohexane (158) was isolated as a minor decomposition product due to carbon-oxygen bond fission of the ether.

Fluorination at 355°C gave some of the perfluoroether (157) but most of the products contained one hydrogen atom. Various isomer mixtures were isolated from the product.



Perfluoroether (157) 23.1%

(160) 8.5%

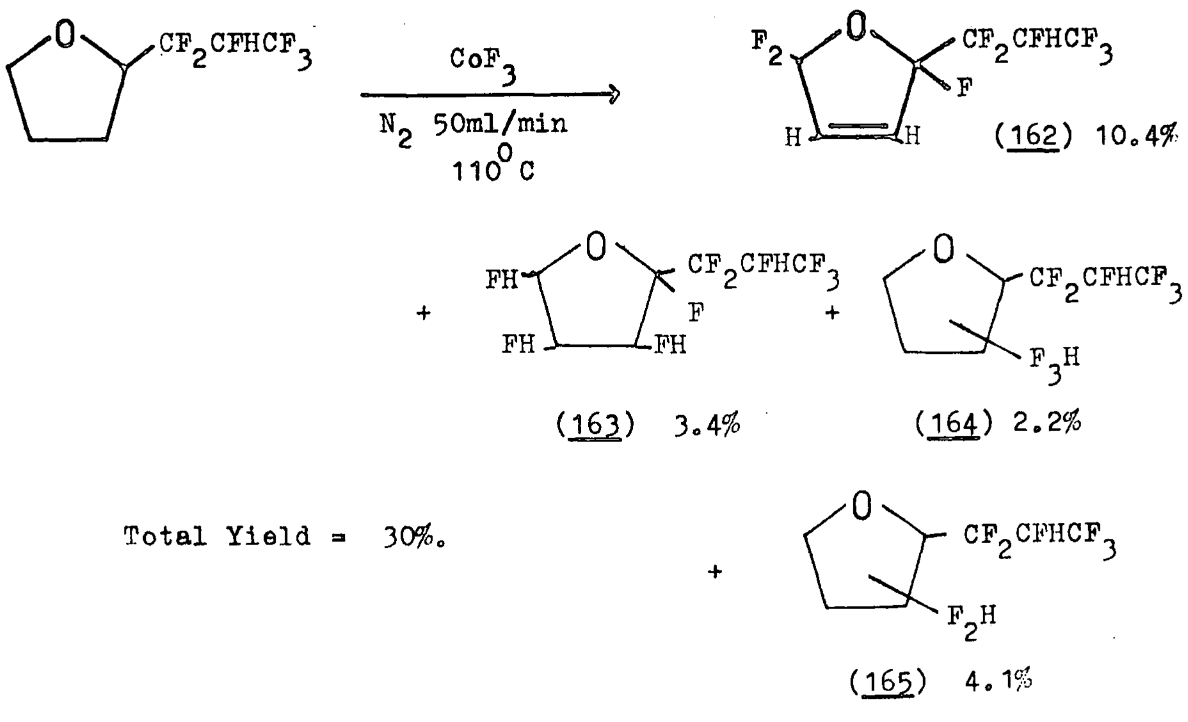
(161) 5.7%

(159) 17.9%

(Total Yield = 73%)

Fluorination at temperatures of 270°C , 240°C , and 180°C gave complex mixtures of products.

The major products from fluorination at 110°C contained a double bond and were assigned as isomers of 2,5,5-trifluoro-2-(1,1,2,3,3,3-hexafluoropropyl)oxolen (159).



(162) 10.4%

(163) 3.4%

(164) 2.2%

Total Yield = 30%.

(165) 4.1%

Table28

Extent of Cobalt Trifluoride Fluorination of 2-(1,1,2,3,3,3-Hexafluoropropyl)Oxolane at Various Temperatures

Temperature (°C)	%Yield	%Composition of Product					%Fluorination[a]
		$\%C_7F_{14}O$	$\%C_7F_{13}HO$	$\%C_7F_{12}H_2O$	$\%C_7F_{11}H_3O$	$\%C_7F_{14-n}H_nO$ $n=4-8$	
110	30[b]	trace	1.3	3.7	24.3	71.1	45.5
180	49[c]	trace	1.5	7.5	69.8	21.2	54.8
240	79[c]	0.4	1.2	14.8	63.7	19.7	62.2
270	70[d]	2.8	20.9	29.2	42.9	2.4	71.0
355	73[e]	31.6	46.3	14.2	7.8	-	87.6
440	~73[f]	~95	~1	-	-	-	96

a)Calculated from

$$\%\text{Fluorination} = \frac{\sum_{n=1}^{8} n(\%C_7F_{6+n}H_{8-n}O)}{800} \times 100\%$$

b)Based on $C_7F_{10}H_4O$

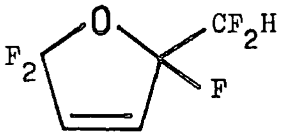
c)Based on $C_7F_{11}H_3O$

d)Based on $C_7F_{12}H_2O$

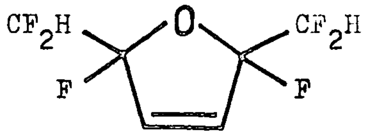
e)Based on $C_7F_{13}HO$

f)Based on $C_7F_{14}O$

The extent of fluorination at each of the above temperatures are summarized in Table 28 and illustrated in Figure 6. It can be concluded from the structures of the isolated compounds that fluorination occurred first at the positions adjacent to the oxygen atom. Also the isolation of oxolen products indicates that the initial stages of the fluorination involves elimination steps. Similar oxolen type compounds have been isolated by Tatlow et al[148] from the potassium tetrafluorocobaltate(III) fluorination of 2-methyloxolane and 2,5-dimethyloxolane at 200°C to give (166) and (167) respectively.



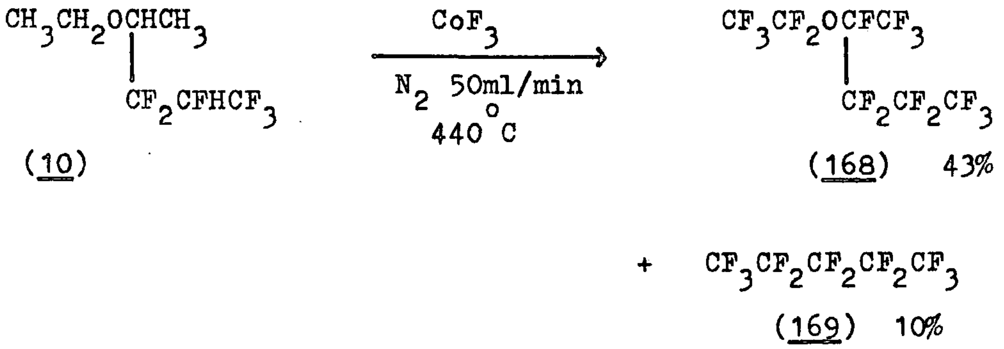
(166)



(167)

2. USING 2,2,3,4,4,4-HEXAFLUORO-1-METHYLBUTYL ETHYL ETHER.

The fluorination of 2,2,3,4,4,4-hexafluoro-1-methylbutyl ethyl ether (10) at 440°C gave the perfluoroether (168) as the main product.



$$CH_3CH_2OCH(CF_2CFHCF_3)CH_3 \xrightarrow[N_2\ 50ml/min,\ 440^{\circ}C]{CoF_3} CF_3CF_2OCF(CF_2CF_2CF_3)CF_3 + CF_3CF_2CF_2CF_2CF_3$$

(10)

(168) 43%

(169) 10%

A variety of temperatures were used for this fluorination but no attempt was made to isolate individual polyfluoroethers. The extent of fluorination at each temperature is presented in Table 29 and Figure 6. A similar pattern of reactivity was observed with this system as compared with the oxolane system, although the total yield of products is lower, ie.ca 50% compared to ca 70% respectively. Also a much greater

Table29

Extent of Cobalt Trifluoride Fluorination of 2,2,3,4,4,4-Hexafluoro-1-Methylbutyl Ethyl Ether at Various Temperatures

Temperature (°C)	%Yield	%Composition of Product					%Fluorination[a]
		%$C_7F_{16}O$	%$C_7F_{15}HO$	%$C_7F_{14}H_2O$	%$C_7F_{13}H_3O$	%$C_7F_{16-n}H_nO$ n=4to10	
240	42[b]	1.0	5.4	43.5	34.9	15.4	74.3
320	46[c]	27.7	28.0	35.8	8.4	-	87.4
410	50[d]	60.7	21.0	16.1	2.3	-	94.1
440	53[d]	78.0 + 18.4Decomp	3.6	-	-	-	99.6

a) Calculated from

$$\%\text{Fluorination} = \frac{\sum_{n=1}^{10} n(\%\ C_7F_{6+n}H_{10-n})}{1000} \times 100\%$$

b) Based on $C_7F_{14}H_2O$

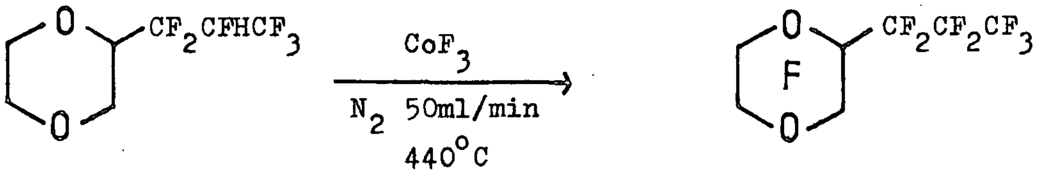
c) Based on $C_7F_{15}HO$

d) Based on $C_7F_{16}O$

proportion of decomposition products was observed for this system at 440°C. Therefore the high temperature fluorination of an acyclic ether adduct is not as good as for a cyclic ether adduct.

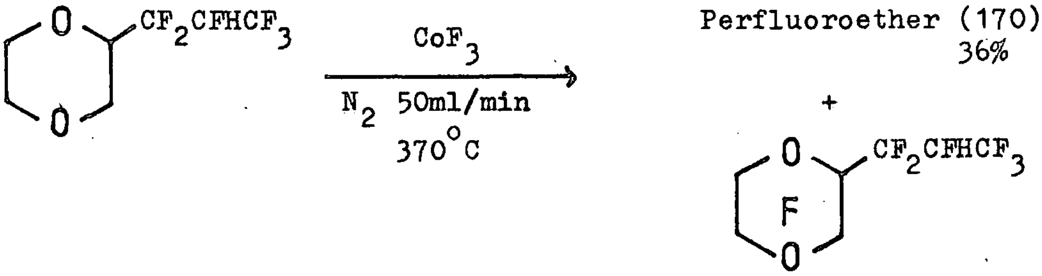
3. USING 2-(1,1,2,3,3,3-HEXAFLUOROPROPYL)-1,4-DIOXAN.

The fluorination of 2-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dioxan (25) at 440°C gave the perfluoroether (170) with little decomposition.



(170) 68%

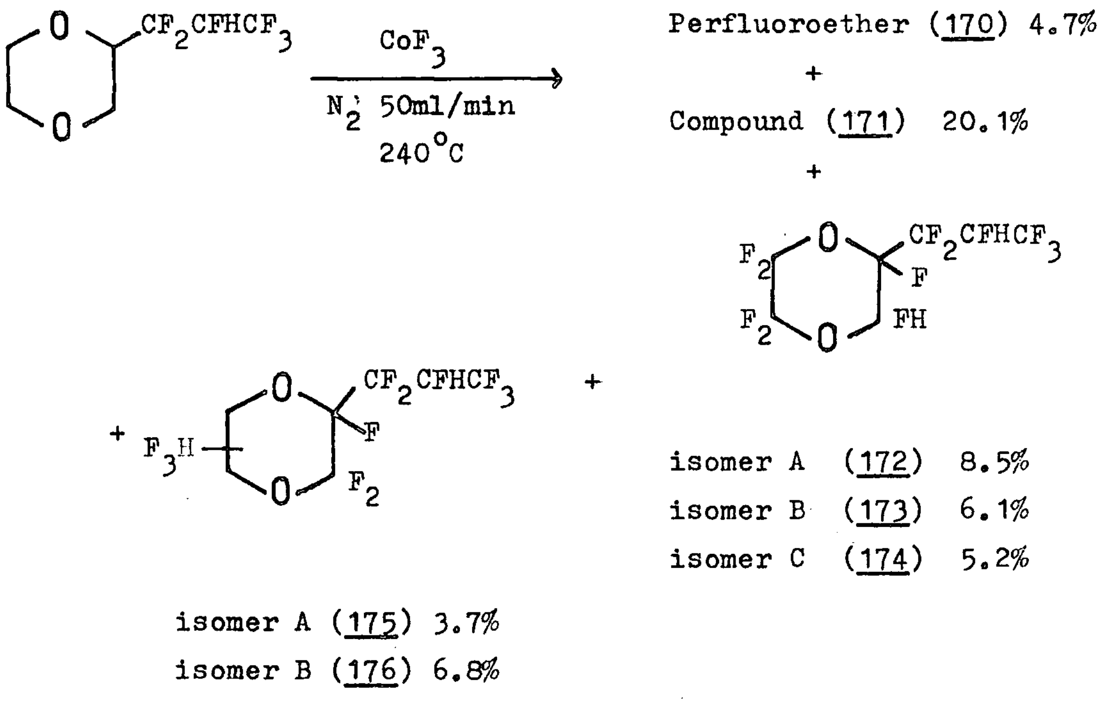
Fluorination at a slightly lower temperature gave a significant amount of heptafluoro-2-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dioxan (171) although the main product was still the perfluoroether (170).



(171) 21%

(Total Yield = 70%)

Using a fluorination temperature of 240°C a product mixture was obtained from which was isolated a number of polyfluorodioxan compounds containing two hydrogen atoms. However it was not possible to assign the stereochemistry of each isomer. The main product at this temperature was (171).



Perfluoroether (170) 4.7%
+
Compound (171) 20.1%
+

isomer A (172) 8.5%
isomer B (173) 6.1%
isomer C (174) 5.2%

+

isomer A (175) 3.7%
isomer B (176) 6.8%
isomer C (177) 2.4%

(Total Yield = 74%)

The extent of fluorination at each temperature is given in Table 30 and illustrated in Figure 6. These results show that hydrogen atoms adjacent to an oxygen atom are fluorinated more readily. This can be concluded from the high yield of compound (171) formed at the relatively low temperature of 240°C. The diethyl ether and oxolane adducts gave only small amounts of products containing one hydrogen atom at 240°C. These two adducts have three hydrogen sites that are not adjacent to an oxygen atom and these will all require a higher temperature to be fluorinated. This is apparent from Figure 6 where at any one temperature the extent of fluorination of the dioxan adduct is greater than for the diethyl ether and oxolane adducts.

4. CONCLUSION.

The temperature dependance studies have shown that fluorination at 440 °C was required to obtain mainly the perfluorinated ether. Good yields of products are formed with cyclic ether adducts although they are less with acyclic ether adducts.

Table 30

Extent of Cobalt Trifluoride Fluorination of 2-(1,1,2,3,3,3-Hexafluoropropyl)-1,4-Dioxane at Various Temperatures

Temperature (°C)	%Yield	%Composition of Product					%Fluorination[a]
		%$C_7F_{14}O$	%$C_7F_{13}HO_2$	%$C_7F_{12}H_2O_2$	%$C_7F_{11}H_3O_2$	%$C_7F_{14-n}H_nO_2$ n=4to8	
130	40[b]	0.5	1.9	12.0	59.3	26.3	64.4
240	74[c]	6.4	35.1	47.9	10.4	-	79.5
370	70[d]	51.8	35.5	12.6	-	-	92.3
440	68[e]	~97	~1	-	-	-	97

a) Calculated from $$\%\text{Fluorination} = \frac{\sum_{n=1}^{8} n(\%C_7F_{6+n}H_{8-n}O_2)}{800} \times 100\%$$

b) Based on $C_7F_{11}H_3O_2$

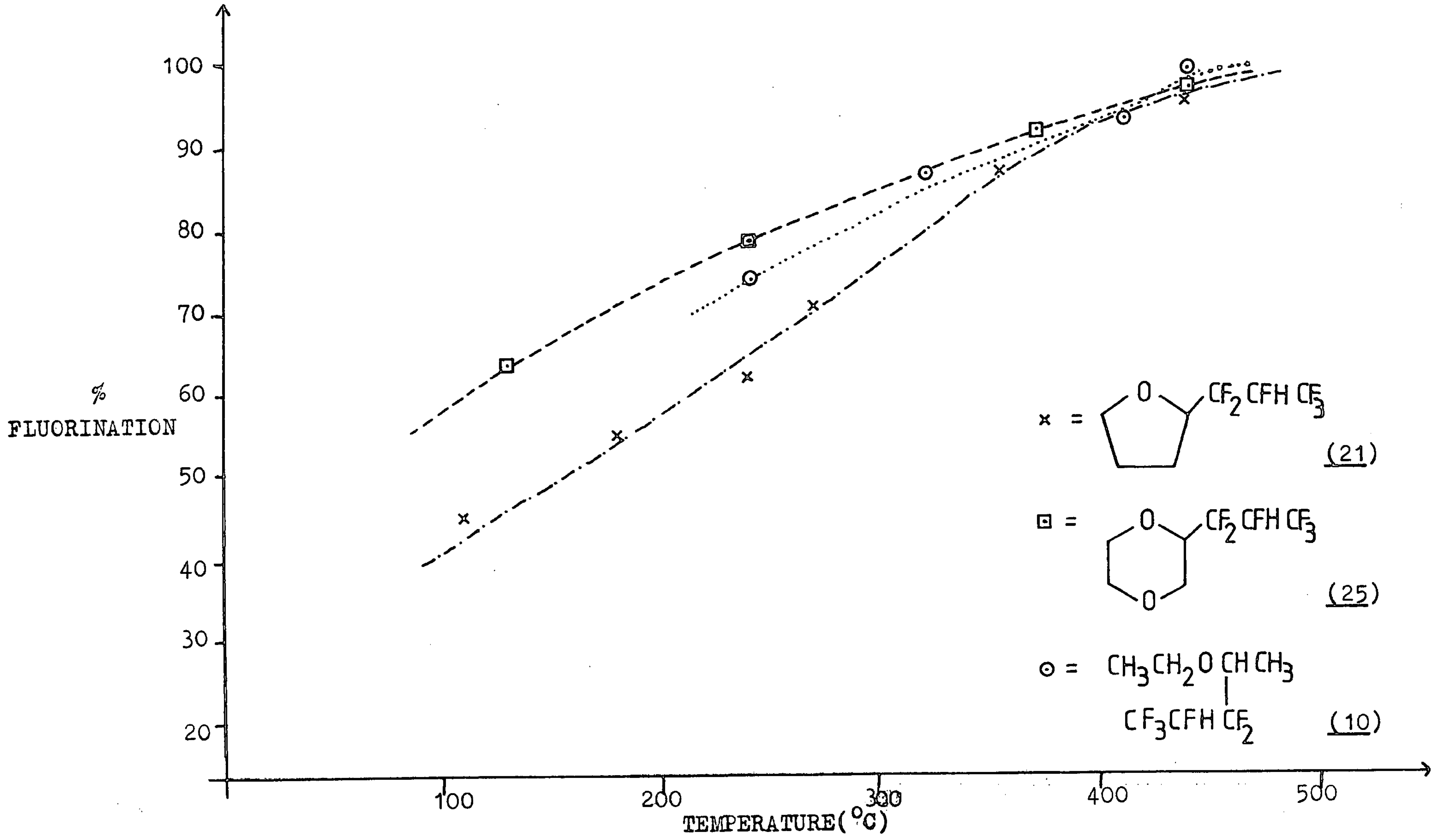
c) Based on $C_7F_{12}Fl_2O_2$

d) Based on $C_7F_{13}HO_2$

e) Based on $C_7F_{14}O_2$

FIGURE 6

Graph of Extent of Fluorination against Temperature for Compounds (10),(21),and(25).



D. FLUORINATION OF ACYCLIC ETHER ADDUCTS.

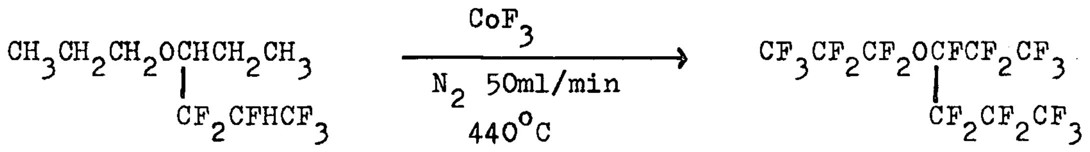
Although the high temperature fluorination of the few ether adducts discussed above gave high yields of products, it was important to assess the scope of this reaction by varying the structure of the adduct. A standard temperature of 440°C was used.

Fluorination of 2,2,3,4,4,4-hexafluorobutylmethyl ether gave two gaseous products which were not separated but GLC/mass spectra identified them as perfluorobutyl methyl ether (178) and perfluorobutane (179).

$$\underset{(\underline{9})}{CF_3CFHCF_2CH_2OCH_3} \xrightarrow[N_2\ 50ml/min,\ 440^{o}C]{CoF_3} \underset{(\underline{178})\ 36\%}{CF_3CF_2CF_2CF_2OCF_3} + \underset{(\underline{179})\ 44\%}{CF_3CF_2CF_2CF_3}$$

Therefore a significant amount of carbon-oxygen bond cleavage of the ether had occurred with the loss of the methoxy group.

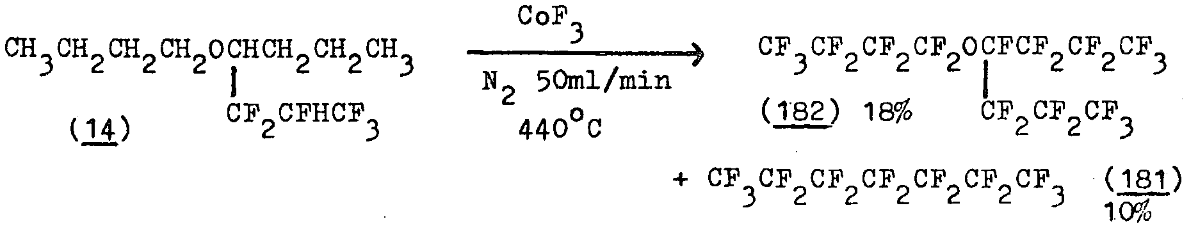
2,2,3,4,4,4-Hexafluoro-1-ethylbutyl propyl ether gave a mixture of mainly perfluoro-1-ethylbutyl propyl ether (180).



$$\underset{CF_2CFHCF_3}{CH_3CH_2CH_2OCHCH_2CH_3} \xrightarrow[N_2\ 50ml/min,\ 440^{o}C]{CoF_3} \underset{CF_2CF_2CF_3}{CF_3CF_2CF_2OCFCF_2CF_3}$$

(12) (180) 32%

A significant amount of carbon-oxygen bond fission of the ether occurred on the fluorination of 2,2,3,4,4,4-hexafluoro-1-propylbutyl butyl ether to give perfluoroheptane (181) as well as the perfluoroether (182).

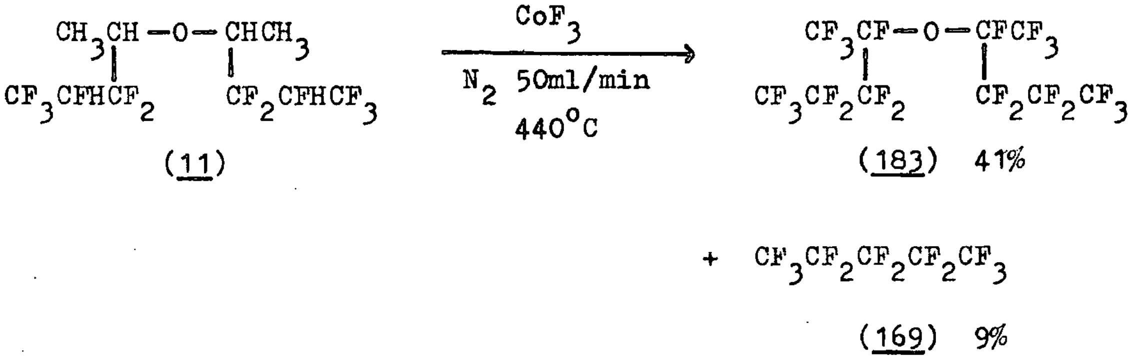


$$\underset{CF_2CFHCF_3}{CH_3CH_2CH_2CH_2OCHCH_2CH_2CH_3} \xrightarrow[N_2\ 50ml/min,\ 440^{o}C]{CoF_3} \underset{CF_2CF_2CF_3}{CF_3CF_2CF_2CF_2OCFCF_2CF_2CF_3} + CF_3CF_2CF_2CF_2CF_2CF_2CF_3$$

(14) (182) 18% (181) 10%

Therefore optimum hydrocarbon chains on an ether adduct appear to be ethyl and propyl. It is possible that decomposition occurred because one fluoroalkyl substituent on the ether adduct is not sufficient to stabilize the whole ether molecule during fluorination. To investigate this hypothesis ether di-adducts were fluorinated.

Di-(2,2,3,4,4,4-hexafluoro-1-methylbutyl) ether gave a moderate yield of perfluoroether (183) together with perfluoropentane (169) derived from carbon-oxygen bond cleavage.



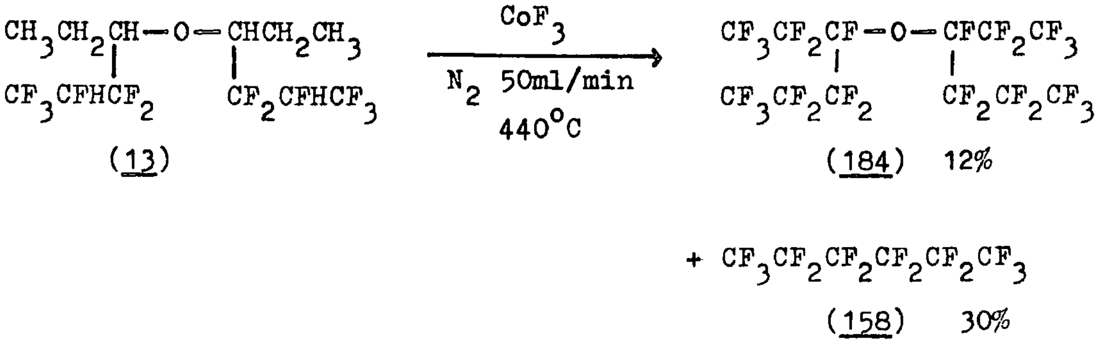
(11)

(183) 41%

+ $CF_3CF_2CF_2CF_2CF_3$

(169) 9%

Fluorination of di-adduct (13) gave a low yield of the perfluoroether (184) but the main product was perfluorohexane (158).



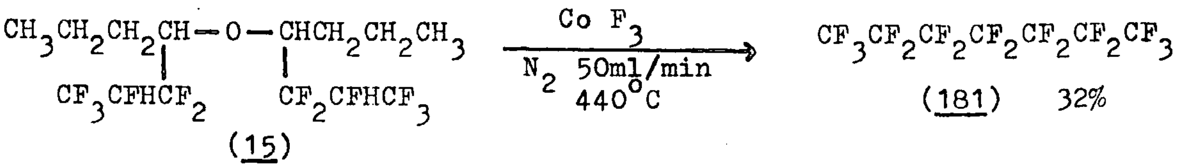
(13)

(184) 12%

+ $CF_3CF_2CF_2CF_2CF_2CF_3$

(158) 30%

Only perfluoroheptane (181) was formed from the fluorination of di-(2,2,3,4,4,4-hexafluoro-2-propylbutyl) ether.



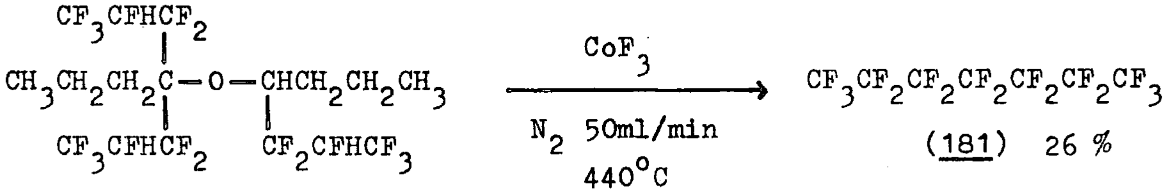
(15)

$CF_3CF_2CF_2CF_2CF_2CF_2CF_3$

(181) 32%

These results show that the extra fluoroalkyl group does not increase the stability of the ether adduct and does not give higher yields of perfluoroethers. In fact lower yields of perfluoroethers are obtained possibly due to increased branching causing carbon-oxygen bond cleavage to predominate.

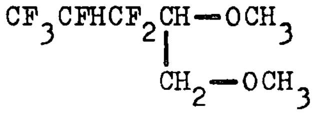
This effect was confirmed by fluorinating the tri-adduct (16) from which only perfluoroheptane was isolated in a low yield.



$$CH_3CH_2CH_2C(CF_2CFHCF_3)_2-O-CH(CF_2CFHCF_3)CH_2CH_2CH_3 \xrightarrow[N_2\ 50ml/min,\ 440^{\circ}C]{CoF_3} CF_3CF_2CF_2CF_2CF_2CF_2CF_3$$

(16) (181) 26 %

It was shown above that a methoxy group was readily lost during fluorination, therefore an ether adduct containing two methoxy groups would be expected to decompose easily. Fluorination of compound (185) gave a complex mixture of products in very low yield which were not isolated but were shown to be fully fluorinated by GLC/mass spectra.



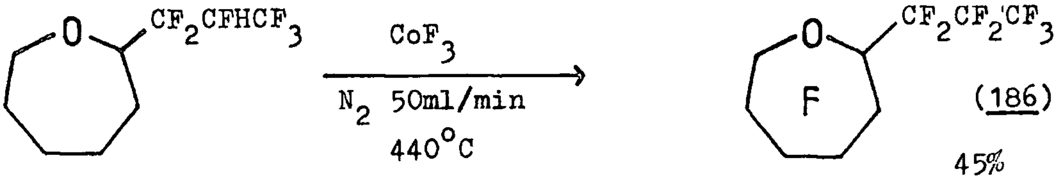
$$CF_3CFHCF_2CH(OCH_3)CH_2-OCH_3$$

(185)

E. FLUORINATION OF CYCLIC ETHER ADDUCTS.

The fluorination of a series of cyclic ether adducts was carried out to study the effect of ring size. Oxolane (21) , oxane (22) , and dioxan (25) adducts with hexafluoropropene are discussed above and all gave the corresponding perfluoroether in approximately 70% yield.

2-(1,1,2,3,3,3-Hexafluoropropyl)oxepane gave a moderate yield of perfluoro-2-propyloxepane (186). In addition perfluoro-octane (187) was formed which shows that carbon-oxygen bond fission of the ether had occurred.

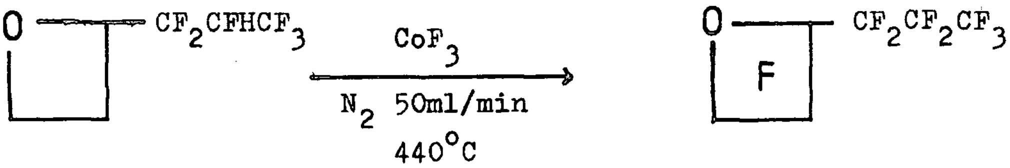


(24)

(186) 45%

+ $CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_3$ (187) 12%

Fluorination of the oxetane adduct (20) gave only a low yield of perfluoro-2-propyloxetane (188) due to facile cleavage of the four membered ring.



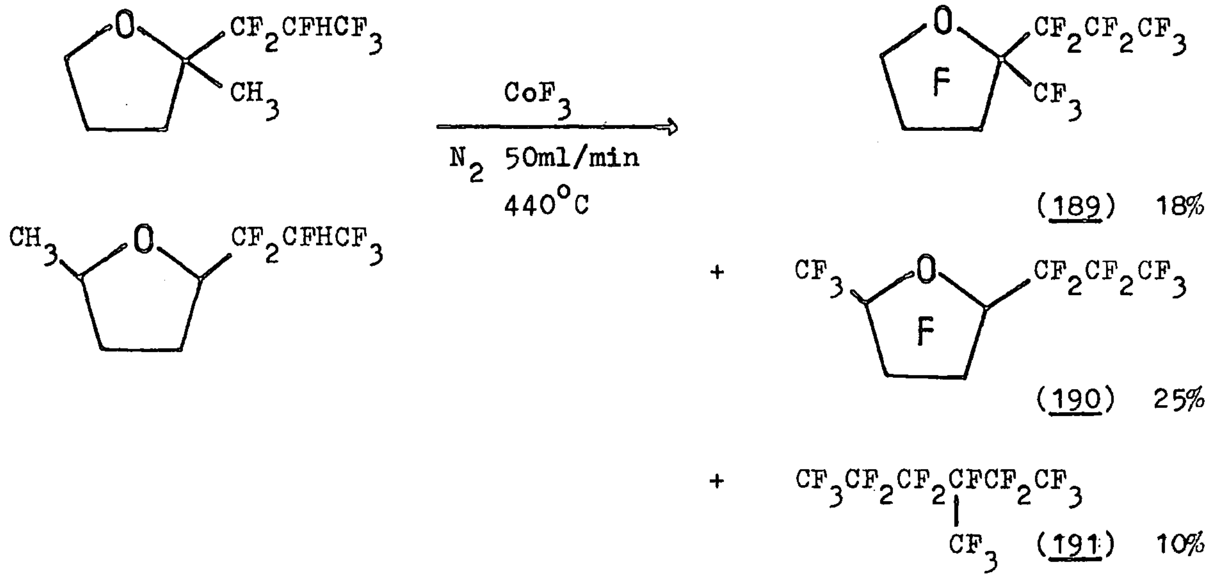
(188) 8%

+ $CF_3CF_2CF_2CF_2CF_3$ (169) 3%

+ $CF_3CF_2CF_2CF_2CF_2CF_3$ (158) 10%

Therefore ether adducts composed of five or six membered rings give the best yields of perfluoroethers.

To study the effect of substitution on an oxolane ring a mixture of 2-methyl- and 5-methyl-2-(1,1,2,3,3,3-hexafluoropropyl)oxolane was fluorinated. A mixture of the two perfluoroethers (189) and (190) were formed together with perfluoro-3-methylhexane (191) and other decomposition products. Therefore increased substitution on the carbon atoms alpha to the oxygen atom of the ether results in increased decomposition.

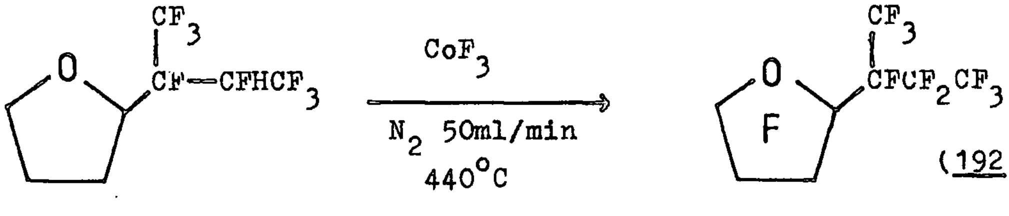


(189) 18%

(190) 25%

(191) 10%

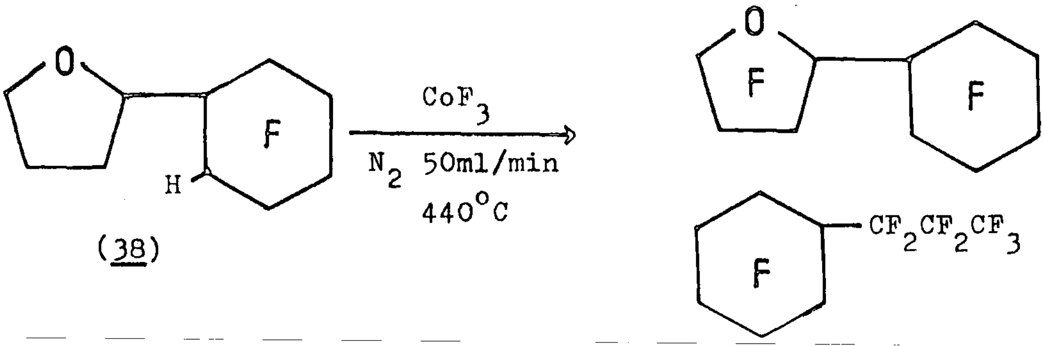
A series of reactions were attempted using ether adducts with various degrees of branching within the fluoroalkyl side chain. Fluorination of adduct (41) gave perfluoro-2-(1-methylpropyl)oxolane (192) in moderate yield, although not as high as the analogous reaction using the propyl side chain adduct.



(41)

(192) 53%

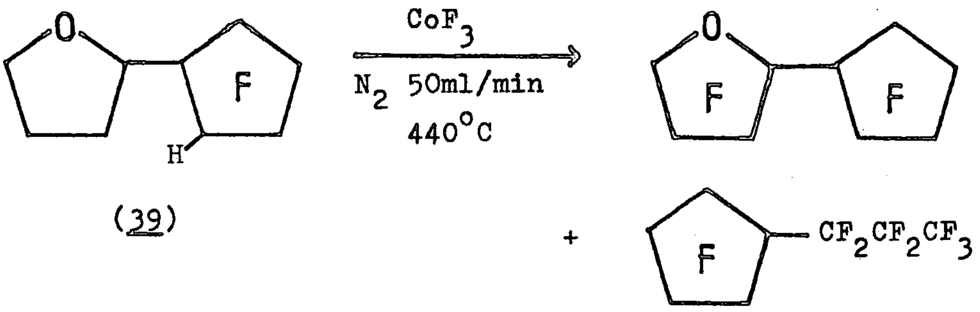
With polyfluorocycloalkyl side chains eg decafluorocyclohexyl (38), octafluorocyclopentyl (39), and hexafluorocyclobutyl (40) the yields of the perfluoroethers (193), (195), and (197) respectively were in the order of 60%. Carbon-oxygen bond cleavage to form perfluorocycloalkanes (194) and (196) was greater in these cases than with a propyl side chain.



(38)

(193) 51%

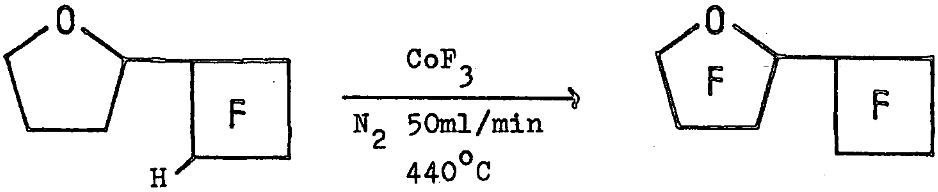
(194) 6%



(39)

(195) 65%

(196) 11%



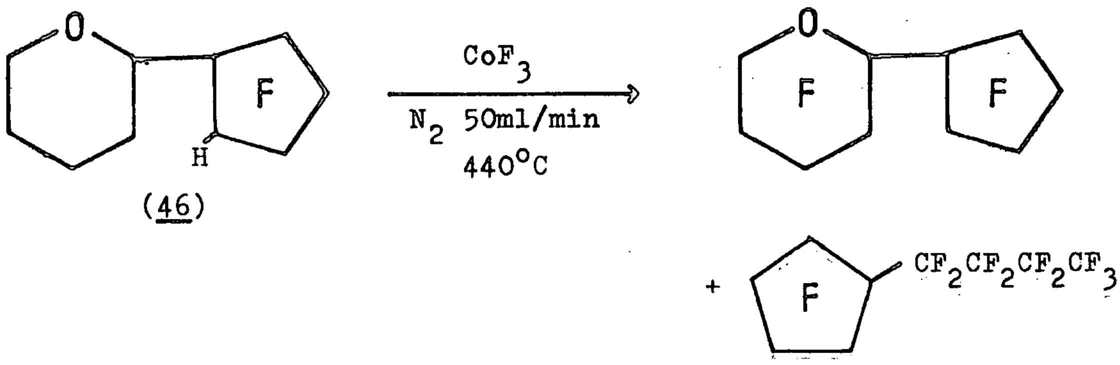
(40)

(197) 64%

+ Decomposition product 12%

In conclusion a large fluoroalkyl side chain in the ether adduct increases carbon-oxygen bond cleavage of the ether. However these are still very clean reactions and only small amounts of other decomposition products are present in the product mixtures.

The cleavage reaction may be observed within a series of fluorinations of cyclic ether perfluorocyclopentene adducts. The yields for these reactions were lower than for the corresponding hexafluoropropene adducts. The oxane adduct (46) gave the perfluoroether (198) and perfluorobutylcyclopentane (199)

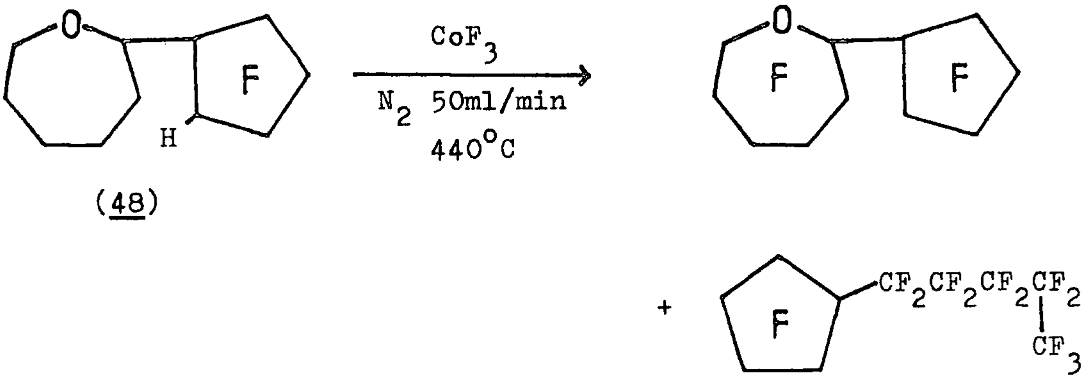


(46)

(198) 31%

(199) 20%

Similarly the oxepane adduct (48) gave the perfluoroether (200) and perfluoropentylcyclopentane (201).



(48)

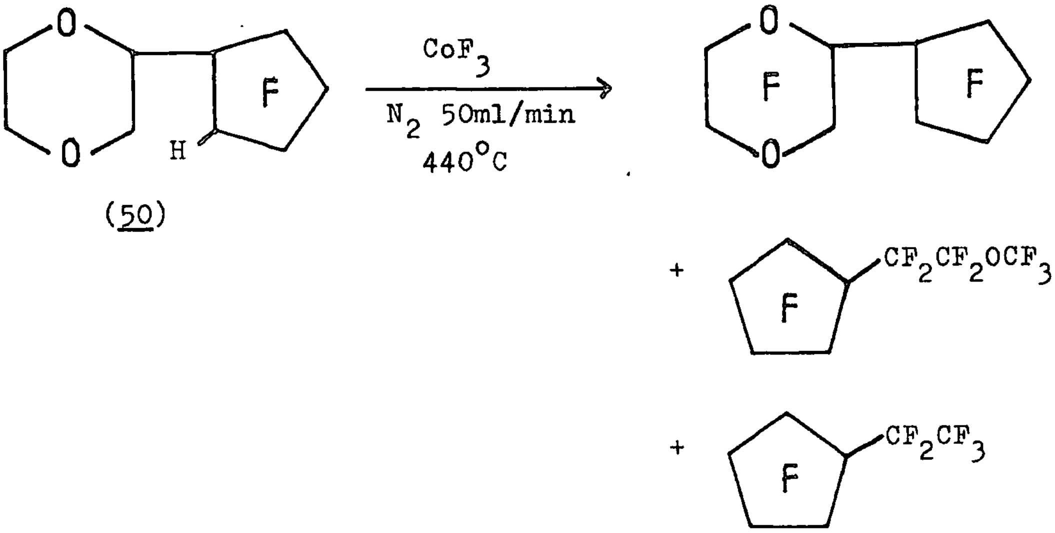
(200) 20%

(201) 22%

+ Decomposition products 32%

The cyclopentyl series shows that the larger the ether ring the greater the amount of carbon-oxygen bond fission occurs on fluorination, in agreement with the propyl series.

The dioxan adduct (50) gave the fully fluorinated ether (202) together with two products from successive carbon-oxygen bond cleavages, (203) and (204).



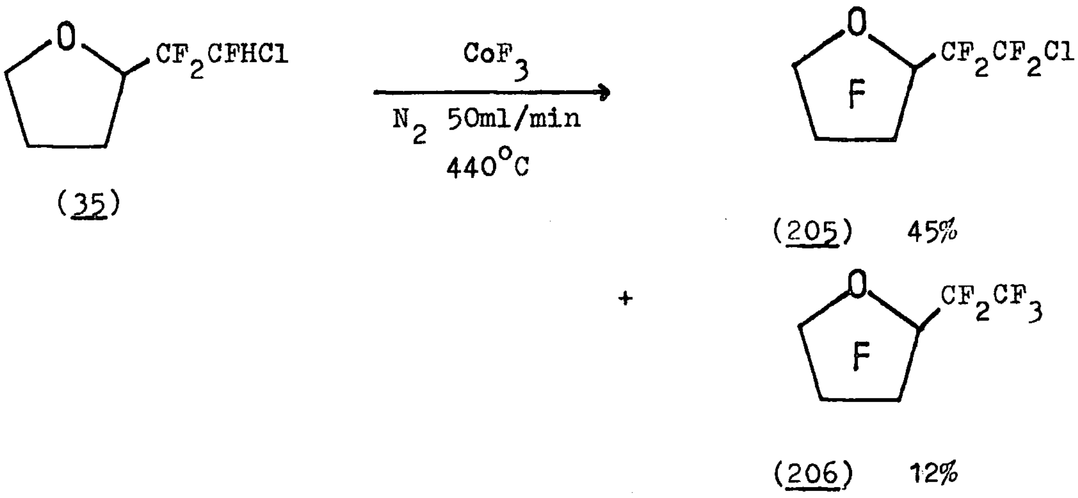
(50)

(202) 17%

(203) 8%

(204) 10%

A chlorine atom in the fluoroalkyl side chain is retained partially during fluorination. For example adduct (35) gave mainly perfluoro-2-(2-chloroethyl)oxolane (205), although there was a small amount of the dechlorinated product (206)

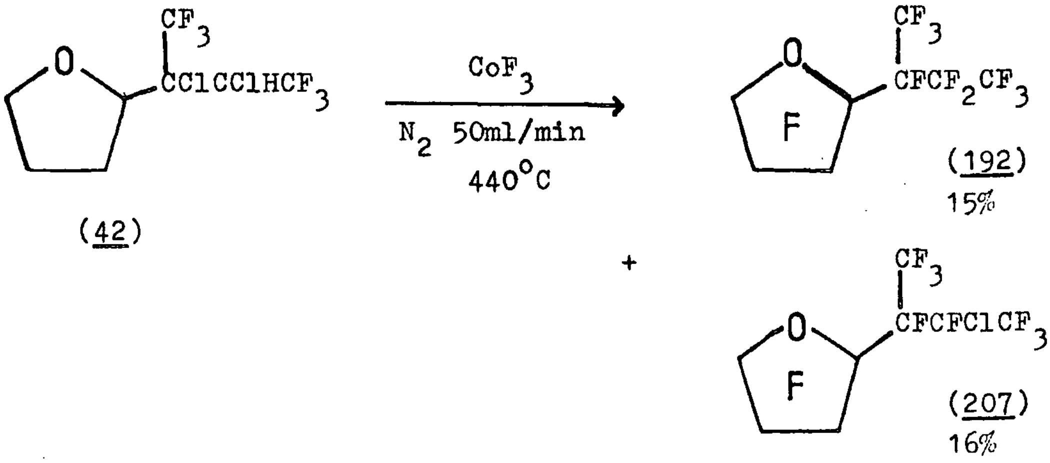


(35)

(205) 45%

(206) 12%

However with two adjacent chlorine atoms in the fluoroalkyl side chain the ether adduct is particularly susceptible to elimination reactions. A complex mixture of products was obtained from adduct (42) and only compounds (207) and (192) were isolated.

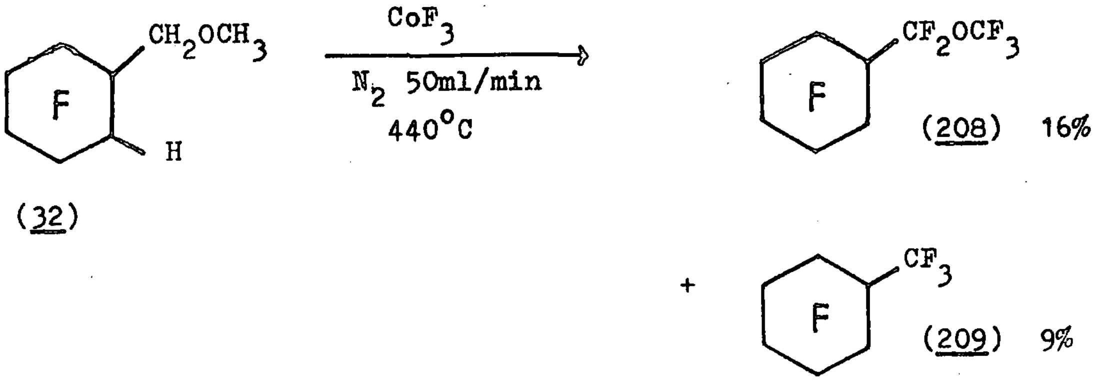


(42)

(192) 15%

(207) 16%

Ether adducts consisting of a cyclic fluoroalkyl group and a methyl ether group did not fluorinate very well. Fluorination of adduct (32) gave a low yield of the fully fluorinated ether (208) and the carbon-oxygen bond cleavage product, perfluoromethylcyclohexane (209).

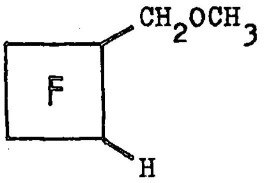


(32)

(208) 16%

(209) 9%

Similarly adduct (210) gave a very low yield of a complex mixture of products which were not investigated.



(210)

In view of the easy loss of methoxy groups on fluorination these results were not unexpected and analogous diethyl ether cycloalkene adducts would probably give better results.

F. CONCLUSION.

In summary, the high temperature cobalt trifluoride fluorination of ether adducts gives good yields of perfluoroethers, with little decomposition, if the following conditions apply.

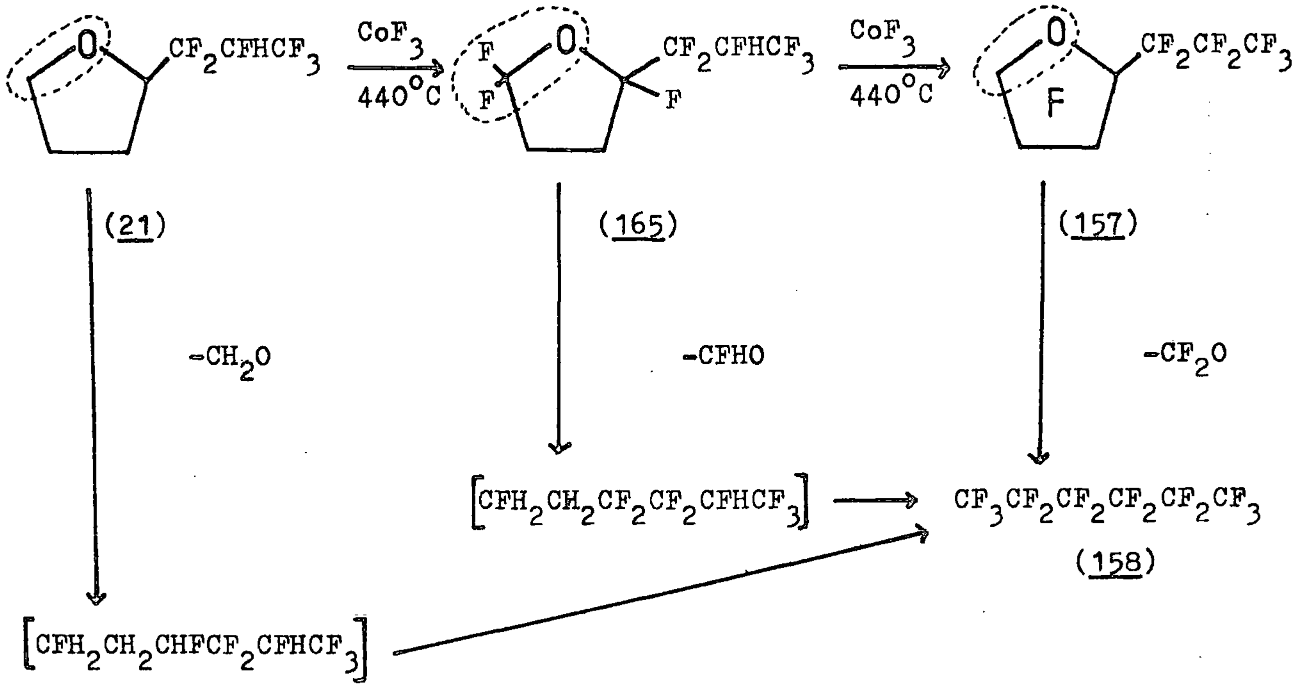
(a) Any alkoxy group must be either ethoxy or propoxy. A methoxy group is readily lost, while a butoxy group results in excessive decomposition.

(b) The hydrocarbon portion of the ether adduct is a ring system.

(c) Branching is avoided both in the hydrocarbon and the fluorocarbon portion of the adduct.

(d) Chlorine atoms are not in positions where elimination reactions may occur easily.

During fluorination the most probable decomposition pathway involves elimination of one of three possible fragments, $COF_{2-n}H_n$, n=0,1,2 . The remaining perfluorocarbon fragment was isolated, especially in the cyclic ether cases, as the only by-product with the perfluoroether. This process is illustrated in Scheme 4 .



Scheme 4 .

At present it is not clear at which stage the fragment is eliminated.

G. IDENTIFICATION OF PRODUCTS.

The molecular ions were not observed in the mass spectra of the perfluoroethers. The highest mass ions were due to either loss of fluorine or loss of perfluoroalkyl in the case of the higher molecular weight ethers, Scheme 5 .

The different fluorine atom environments of the perfluoroethers were identified from their fluorine-19 NMR chemical shift values which are summarized in Table 31 .

Scheme 5

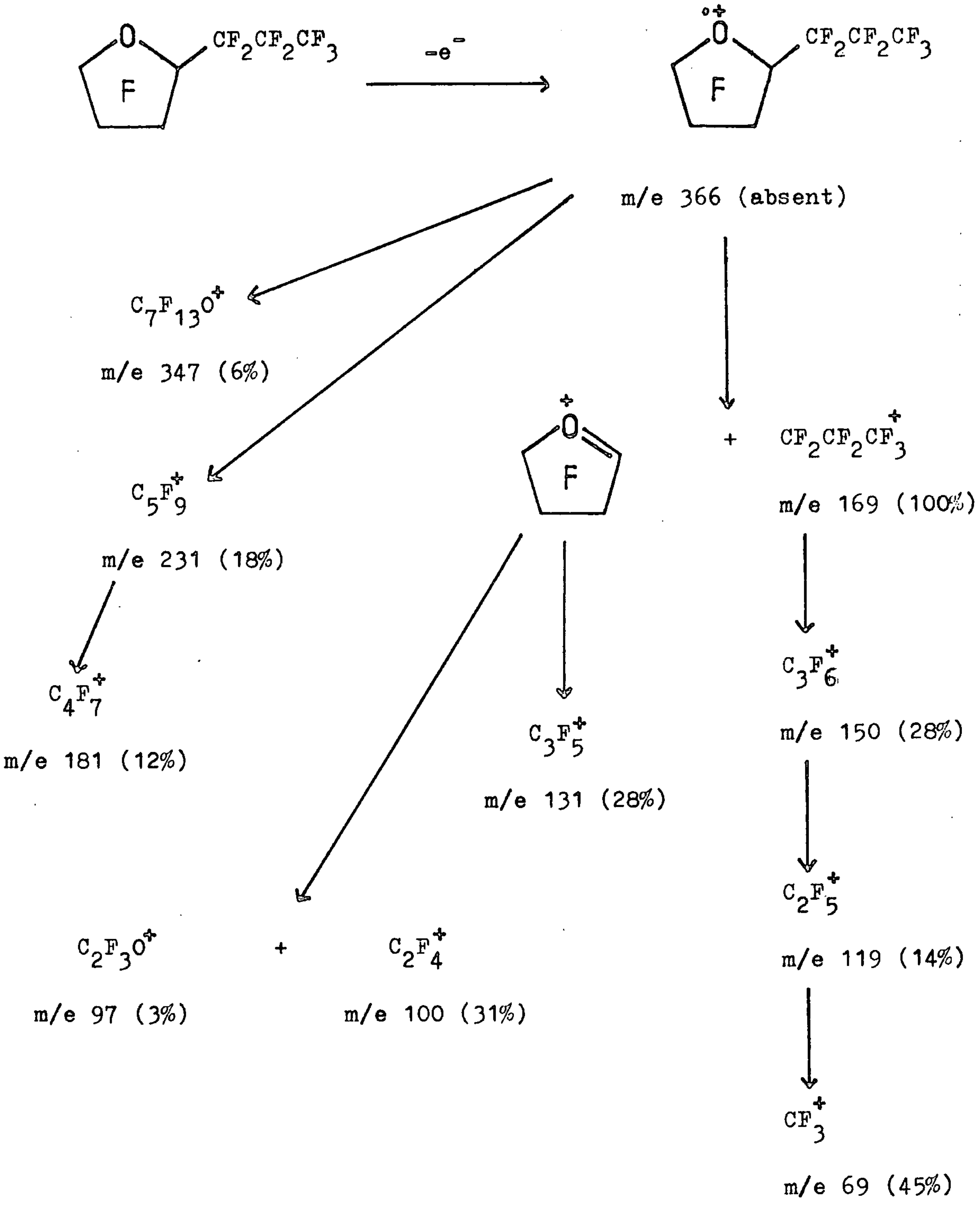
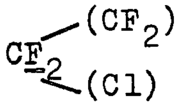
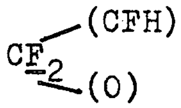
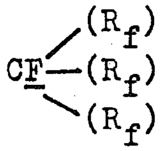
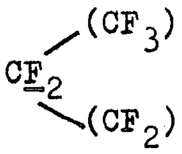
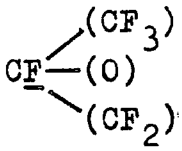
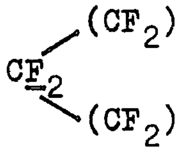
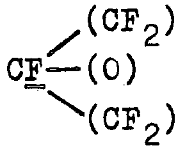
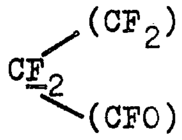
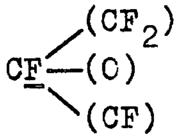
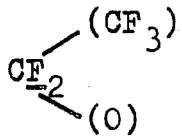
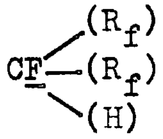
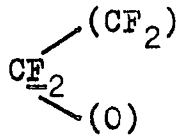
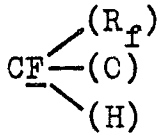
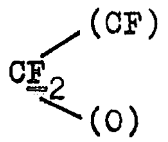

CF2CF2CF3
-e⁻
F
O
m/e 366 (absent)
C7F13O+
m/e 347 (6%)
C5F9+
m/e 231 (18%)
C4F7+
m/e 181 (12%)
+
CF2CF2CF3+
m/e 169 (100%)
C3F6+
m/e 150 (28%)
C2F5+
m/e 119 (14%)
CF3+
m/e 69 (45%)
C3F5+
m/e 131 (28%)
C2F3O+
+
C2F4+
m/e 97 (3%)
m/e 100 (31%)

Table 31

Fluorine-19 NMR Chemical Shift Values for Perfluoroethers

Environment	δ^a	Environment	δ^a
$C\underline{F}_3\text{-}(CF_2)^b$	83.5-85.4	 $C\underline{F}_2\left\langle\begin{matrix}(CF_2)\\(Cl)\end{matrix}\right.$	70.5
$C\underline{F}_3\text{-}(CFO)$	90.7		
$C\underline{F}_3\text{-}(CF)$	73.3-74.5	 $C\underline{F}_2\left\langle\begin{matrix}(CFH)\\(O)\end{matrix}\right.$	72.4-80.9
$C\underline{F}_3\text{-}(CFH)$	77.2-77.5		
$C\underline{F}_3\text{-}(O)$	58.7-58.8	 $C\underline{F}\left\langle\begin{matrix}(R_f)\\(R_f)\\(R_f)\end{matrix}\right.$	184.0-191.7
 $C\underline{F}_2\left\langle\begin{matrix}(CF_3)\\(CF_2)\end{matrix}\right.$	124.8	 $C\underline{F}\left\langle\begin{matrix}(CF_3)\\(O)\\(CF_2)\end{matrix}\right.$	136.8-142.8
 $C\underline{F}_2\left\langle\begin{matrix}(CF_2)\\(CF_2)\end{matrix}\right.$	113.7-147.7	 $C\underline{F}\left\langle\begin{matrix}(CF_2)\\(O)\\(CF_2)\end{matrix}\right.$	124.0-131.7
 $C\underline{F}_2\left\langle\begin{matrix}(CF_2)\\(CFO)\end{matrix}\right.$	127.4-130.3	 $C\underline{F}\left\langle\begin{matrix}(CF_2)\\(C)\\(CF)\end{matrix}\right.$	118.0-120.7
 $C\underline{F}_2\left\langle\begin{matrix}(CF_3)\\(O)\end{matrix}\right.$	89.3	 $C\underline{F}\left\langle\begin{matrix}(R_f)\\(R_f)\\(H)\end{matrix}\right.$	210.2-222.0
 $C\underline{F}_2\left\langle\begin{matrix}(CF_2)\\(O)\end{matrix}\right.$	79.4-93.5	 $C\underline{F}\left\langle\begin{matrix}(R_f)\\(C)\\(H)\end{matrix}\right.$	140.0-147.6
 $C\underline{F}_2\left\langle\begin{matrix}(CF)\\(O)\end{matrix}\right.$	73.0		

a)Chemical shifts δ relative to external $CFCl_3$, upfield shifts positive.

b)Adjacent groups in brackets.

EXPERIMENTAL

INSTRUMENTATION.

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

Quantitative gas liquid chromatographic (GLC) analyses were carried out on a Varian Aerograph Model 920 equiped with a gas density balance detector, using columns packed with 30% silicone gum rubber SE-30 on chromosorb P (column O), 20% di-isodecyl phthalate on chromosorb P (column A), 17% 2-cyanoethyl silicone on chromosorb P (column Z), and 'Krytox fluid' on chromosorb P (column K). Preparative scale gas liquid chromatography was carried out on a Varian Aerograph Model 920 instrument.

Melting points and boiling points were determined at atmospheric pressure unless otherwise stated and are uncorrected. Boiling points were recorded during fractional distillation or by the Siwoloboff method.

Carbon, hydrogen, and nitrogen analyses were obtained using a Perkin-Elmer 240 Elemental Analyser. Analyses for halogens were performed by the literature method.[158]

Ultra violet spectra were recorded using a Unicam SP8000 Spectrophotometer and using Spectrosol grade solvents.

Infra red spectra were recorded on a Perkin-Elmer 457 Grating Spectrophotometer using KBr plates, discs, and gas cells.

Proton (^{1}H) and fluorine (^{19}F) nuclear magnetic resonance spectra (NMR) were recorded on a Varian A56/60D spectrometer operating at 60 and 56.4MHz respectively or a Bruker HX90E spectrometer operating at 90 and 84.7MHz respectively. Chemical shifts are quoted in p.p.m. relative to external tetramethylsilane (TMS) and trichlorofluoromethane, upfield shifts positive. Carbon (^{13}C) NMR spectra were recorded on a Bruker HX90E spectrometer operating at 22MHz and chemical shifts are quoted in p.p.m. relative to internal TMS in deutereochloroform solvent.

Mass spectra were recorded on an A.E.I. MS9 spectrometer or on a V.G.Micromass 12B spectrometer fitted with a Pye 104 gas chromatograph.

CHAPTER 7

EXPERIMENTAL TO CHAPTER 2

A. GENERAL PROCEDURES.

1. PURIFICATION OF REAGENTS.

In general, hydrocarbon reagents were dried with anhydrous magnesium sulphate and distilled onto 4A molecular sieves. Oxolane and 1,4-dioxan were dried with potassium and diethyl ether with sodium. The hazards of ether peroxides are so great that it was important to establish that all ethersused gave a negative peroxide test. Trimethyl borate was used both with traces of methanol and after removal of methanol by treatment with lithium chloride.[149] Fluoroalkenes were used as received without further purification.

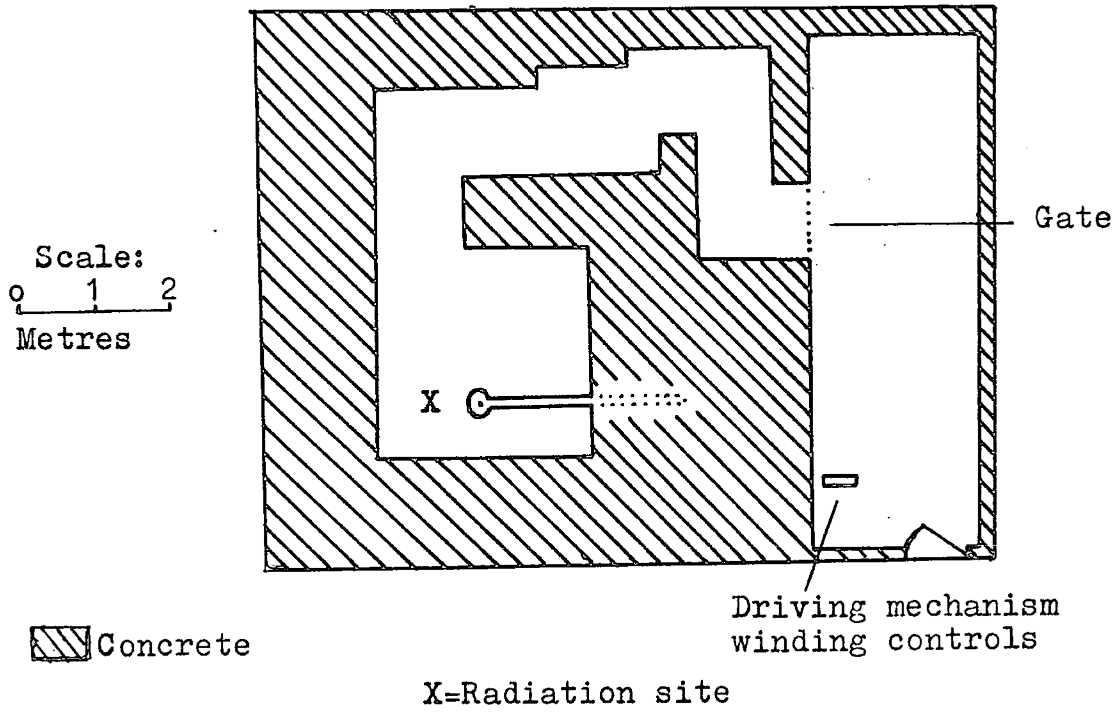
2. GAMMA RAY INITIATION.

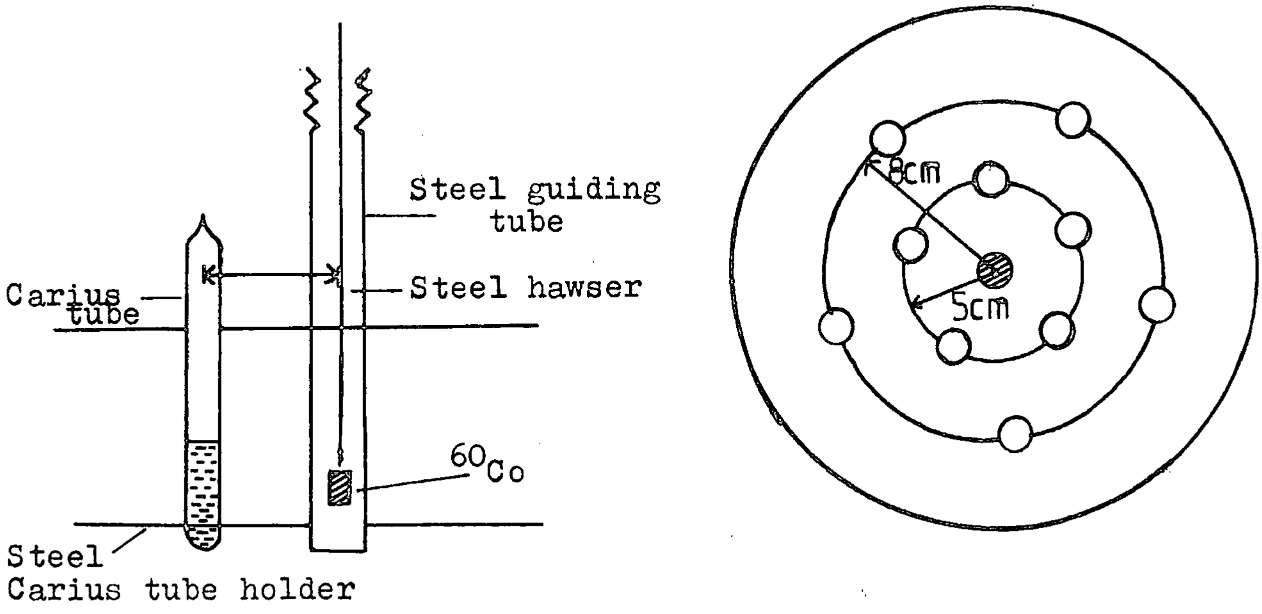
a. Cobalt-60 Gamma Ray Source.

All gamma ray initiated reactions were carried out using the Durham University cobalt-60 gamma ray facility. The source is housed in a purpose built irradiation chamber, shown in Figure 7 . Pellets of the source material are enclosed in a steel container which is located on the end of a steel hawser within the steel guiding tube . When not in use the source is located within a lead and concrete bunker. The source may be electrically, or mechanically driven from the bunker via the steel guide tube to the irradiation site by winding the hawser. A number of safety procedures are incorporated in the winding mechanism such that access to the irradiation chamber through the gate is not possible unless the source is in the bunker. Samples to be irradiated are placed in a metal holder which positions them a set distance from the source.

Figure 7

Durham University Cobalt-60 Gamma Ray Facility.


Lead and Concrete Bunker


X Vertical

X Horizontal

b. Measurements of Dose Rates.

i. Fricke Dosimeter.

The dose of radiation received by the samples was calculated using the Fricke dosimeter.[150] The method involves the oxidation of an acid solution of ferrous ions to ferric, in the presence of oxygen and under the influence of the radiation. The increase in ferric ion concentration was determined spectrophotometrically. The dosimeter solution was prepared by adding concentrated AR sulphuric acid (22ml) to distilled water (600ml) with continual stirring. When cool, AR ferrous ammonium sulphate (0.56g) and AR sodium chloride (0.06g) were dissolved and the volume made up to one litre using distilled water. The solution was irradiated with gamma rays using the same conditions as used for the reactions. An optimum dose of 15 to 20 krad is required for most accurate results because above a dose of 40 krad the dissolved oxygen becomes depleted in the dosimeter solution.

ii. Definitions.

RAD ; The unit of absorbed dose, corresponds to an energy absorption of 100 erg/g of material.

G Value ; The radiationchemical yield. The number of molecules of material changed or of product formed, for each 100 eV of radiation energy absorbed by the system.
G = 15.5 for ^{60}Co gamma rays in Fricke solution.

iii. Calculation.

A worked example is given below to show how the dose rate may be calculated using the Fricke dosimeter.

Fricke solution(20ml) was irradiated for 1.2 hours at 5 cm from the ^{60}Co gamma ray source. The absorbance of the irradiated solution was found to be 0.61 (at 304nm) when measured in a 1 cm cell at 24°C.

$$1 \text{ rad} = 100 \text{ erg/g}$$

$$\Rightarrow 1 \text{ rad} = 6{\circ}242 \times 10^{13} \text{ eV/g}$$

$$\therefore 1 \text{ rad will convert } 6{\circ}242 \times 10^{13} \times \frac{G}{100} \text{ molecules/g}$$

$$= 6{\circ}242 \times 10^{11} \times \frac{G}{N_a} \text{ mol/g}$$

where N_a = Avogadro number.

$$= 1{\circ}036 \times G \times 10^{-12} \text{ mol/g}$$

$$\therefore 1 \text{ Mrad will convert } 1{\circ}036 \times 10^{-3} \times G \times 1{\circ}024 \text{ mol/dm}^3 \text{—(1)}$$

where $1{\circ}024 g/cm^3$ is the density of the dosimeter solution.

The variation of the molar extinction coefficient with temperature is given by the expression,

$$\varepsilon_a = \varepsilon_1 \left[1 + 0{\circ}007(t_2 - t_1) \right]$$

As $\varepsilon_1 = 2193$ at $t_1 = 25^{\circ}C$ for Fe^{3+} at 304nm, then $\varepsilon_a = 2178$

$$\text{Concentration} = \frac{\text{Absorbance}}{\varepsilon_2} = \frac{0.61}{2178}$$

$$\Rightarrow \text{Concentration of } Fe^{3+} = 0{\circ}28 \times 10^{-3} \text{ mol/dm}^3$$

Therefore the dose produced a change of $0{\circ}28 \times 10^{-3}$ mol/dm^3 —(2)

$$(1) \wedge (2) \Rightarrow \text{Dose} = 1000 \times \frac{0{\circ}28}{15{\circ}5 \times 1{\circ}036 \times 1{\circ}024} \text{ krad}$$

$$\Rightarrow \text{Dose} = 17{\circ}0 \text{ krad.}$$

$$\therefore \text{Dose rate} = \frac{17{\circ}0}{1{\circ}2} \text{ krad/hr}$$

$$\Rightarrow \underline{\text{Dose rate} = 14{\circ}2 \text{ krad/hr}}.$$

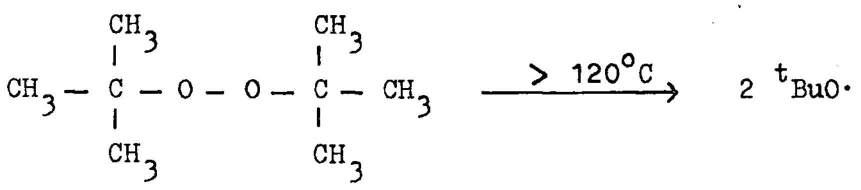
The value of the dose is within the optimum range for the dosimeter. The dose rate was determined periodically throughout the duration of this work. The half life of cobalt-60 is 5.26 years.

c. General Procedure.

The free radical addition reactions were carried out in sealed pyrex Carius tubes (ca 100ml). The liquid reagents were added to the tube and degassed and the gaseous reagents were vacuum transferred into the tube. Degassing was accomplished by three freeze thaw cycles. Normal vacuum line techniques were used for these procedures. The tube was sealed with the reactants frozen (liquid air) and under vacuum. The hydrocarbon substrate was used normally in a 2.5:1 excess over the fluoroalkene. Unless otherwise stated the tube was irradiated with gamma rays at a distance and for the calculated time to give a total dose of ca 10 Mrad, at a temperature of 18°C. The tube was opened while the contents were frozen (liquid air) and the gaseous components transferred under vacuum.

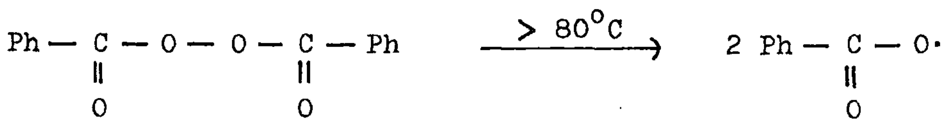
3. THERMAL INITIATION.

Two peroxide initiators have been used during this study. Di-t-butyl peroxide has a useful half life above 120°C,



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-O-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \xrightarrow{>120^{\circ}C} 2\ {}^{t}BuO\cdot$$

and benzoyl peroxide above 80°C.



$$Ph-\underset{O}{\underset{\|}{C}}-O-O-\underset{O}{\underset{\|}{C}}-Ph \xrightarrow{>80^{\circ}C} 2\ Ph-\underset{O}{\underset{\|}{C}}-O\cdot$$

They were added to the reactant mixture at 1 to 5% (wt:wt) concentration.

The same procedure was used to seal the reactant mixture in a Pyrex Carius tube as discussed for gamma ray initiation. The sealed tube was placed in a metal sleeve then into a thermostatically controlled furnace at the required temperature. The tube was cooled and the contents frozen (liquid air) before opening.

B. ADDITIONS OF ETHERS TO HEXAFLUOROPROPENE.

1. DIMETHYL ETHER.

A mixture of dimethyl ether (9.8g , 213mmol) and hexafluoropropene (13.8g , 92mmol) was irradiated with gamma rays. The excess ether was allowed to evaporate to leave a colourless liquid. Distillation gave 2,2,3,4,4,4-hexafluorobutyl methyl ether (9) (12.28g , 68%); b.p. 87-88°C; n_D^{25} 1.3050; (Found: C,30.9%; H,3.2%; Calc. for $C_5H_6F_6O$:[7] C,30.6%; H,3.1%); IR, NMR, mass spectra 1.

2. DIETHYL ETHER.

A mixture of diethyl ether (14.5g , 196mmol) and hexafluoropropene (10.8g , 70mmol) was irradiated with gamma rays. The product was distilled to give 1-methyl-2,2,3,4,4,4-hexafluorobutylethyl ethyl ether (10), (6.05g, 38%); b.p. 116-117°C; (Found: C, 38.2%; H, 5.0%; F, 47.7%. Calc.[94] for $C_7H_{10}F_6O$: C, 37.5; H,4.5; F,50.9%); IR , NMR , mass spectra 2. The residue was distilled in vacuo to give di-(1-methyl-2,2,3,4,4,4-hexafluorobutyl) ether (11), (5.84g , 43%); b.p. 60-61°C at 15mmHg; (Found: C, 32.4%; H, 2.5%; F, 57.2%. Calc. for $C_{10}H_{10}F_{12}O$[94] : C, 32.1%; H, 2.7%; F, 61.0%); IR , NMR , mass spectra 3.

3. DI-n-PROPYL ETHER.

A mixture of di-n-propyl ether (14.58g , 143mmol) and hexafluoropropene (9.5g , 63mmol) was irradiated with gamma rays. Hexafluoropropene was transferred under vacuum to leave a liquid (18.12g) which was distilled to remove excess ether (10.56g). The residue was distilled in vacuo to give 1-ethyl-2,2,3,4,4,4-hexafluorobutyl propyl ether (12), (12% by GLC, column K, 150°C); b.p. 46°C at 15mmHg; (Found: C, 43.0%; H, 6.0%; F, 45.9%. $C_9H_{14}F_6O$ requires: C, 42.9%; H, 5.6%; F, 45.2%); IR , NMR , mass spectra 4; and di-(1-ethyl-2,2,3,4,4,4-hexafluorobutyl) ether (13), (28% by GLC, column K, 150°C); b.p. 88-90°C at 15mmHg; (Found: C, 36.3%; H, 3.9%; F, 56.1%. $C_{12}H_{14}F_{12}O$ requires: C,35.8%; H, 3.5%; F, 56.7%); IR , NMR , mass spectra 5.

4. DI-n-BUTYL ETHER.

A mixture of di-n-butyl ether (15.72g , 121mmol) and hexafluoropropene (11.8g , 79mmol) was irradiated with gamma rays. Hexafluoropropene was transferred under vacuum to leave a liquid (23.91g). The liquid was distilled in vacuo to give three products, 1-propyl-2,2,3,4,4,4-hexafluorobutyl butyl ether (14), (16% by GLC, column K, 170°C); b.p. 88-90°C at 25mmHg; (Found: C, 46.8; H, 6.7%; F,44.6%. $C_{11}H_{18}F_6O$ requires: C, 47.1%; H, 6.4%; F, 40.7%); IR , NMR , mass spectra 6; di-(1-propyl-2,2,3,4,4,4-hexafluorobutyl) ether (15), (28% by GLC, column K, 170°C); b.p. 120-130°C at 25mmHg; (Found: C, 39.8%; H, 4.5%; F, 51.0%. $C_{14}H_{18}F_{12}O$ requires: C, 39.1%; H, 4.2%; F, 53.0%); IR , NMR , mass spectra 7; and 1-propyl-2,2,3,4,4,4-hexafluorobutyl 1-propyl-1-(1,1,2,3,3,3-hexafluoropropyl)-2,2,3,4,4,4-hexafluorobutyl ether (16), (26% by GLC, column K, 170°C); (Found: C, 38.3%; H, 4.1%; F, 59.4%. $C_{17}H_{18}F_{18}O$ requires: C, 35.2%; H, 3.1%; F, 59.0%); IR , NMR , mass spectra 8.

5. DI-iso-PROPYL ETHER.

A mixture of di-iso-propyl ether (9.85g , 97mmol) and hexafluoropropene (5.8g , 39mmol) was irradiated with gamma rays. The starting materials were recovered (GLC, column A, 112°C and IR).

6. ETHYLENE OXIDE.

A mixture of ethylene oxide (6.32g , 144mmol) and hexafluoropropene

(5.5g , 37mmol) was irradiated with gamma rays. A liquid remained (3.64g) after all the starting materials were allowed to evaporate. Preparative GLC (column Z, 110°C) of the liquid gave 1,4-dioxan, (16% by GLC), (identified by comparison of spectra with an authentic sample), 3,3,4,5,5,5-hexafluoropentan-2-one (0.8% by GLC), (identified by comparison of spectra with an authentic sample), and 2-(1,1,2,3,3,3-hexafluoropropyl)dioxan (5% by GLC), (identified by comparison of spectra with an authentic sample).

7. OXETANE.

A mixture of oxetane (3.99g , 69mmol) and hexafluoropropene (5.4g , 36mmol) was irradiated with gamma rays. Excess ether was allowed to evaporate to leave a liquid (9.24g). The liquid was distilled in vacuo to give 2-(1,1,2,3,3,3-hexafluoropropyl)oxetane (20), (7.06g , 65%) as a mixture of diasteriomers; b.p. 47-52°C at 45mmHg; (Found: C, 35.1%; H, 2.9%. $C_6H_6F_6O$ requires: C,34.6%; H, 2.9%); IR , NMR , mass spectra 9.

8. OXOLANE.

A mixture of oxolane (10.4g , 144mmol) and hexafluoropropene (5.5g , 37mmol) was irradiated with gamma rays. The liquid product was distilled to give 2-(1,1,2,3,3,3-hexafluoropropyl)oxolane (21), (8.10g , 95%); as a mixture of diasteriomers; b.p. 136-137°C; (Found: C, 37.7%; H, 4.0%; F, 50.9%. Calc. for $C_7H_8F_6O$[94] : C, 37.8%; H, 3.6%; F, 51.3%); IR , NMR, mass spectra 10.

9. OXANE.

A mixture of oxane (9.81g , 114mmol) and hexafluoropropene (10.7g , 71mmol) was irradiated with gamma rays. The liquid product was distilled in vacuo to give 2-(1,1,2,3,3,3-hexafluoropropyl)oxane (22),(12.33g, 61%), mixture of disteriomers; b.p. 86°C at 70mmHg; IR , NMR , mass spectra 11, and 2,5-di(1,1,2,3,3,3-hexafluoropropyl)oxane (23), as a mixture of diasteriomers, (3.8g , 35%); IR , NMR , mass spectra 12.

10. OXEPANE.

A mixture of oxepane (8.6g , 86mmol) and hexafluoropropene (4.3g , 29mmol) was irradiated with gamma rays. The liquid product was distilled in vacuo to give 2-(1,1,2,3,3,3-hexafluoropropyl)oxepane, (24), (5.0g , 70%); b.p. 79-81^{o}C at 24mmHg; (Found: C, 43.4%; H, 5.2%; F, 45.1%. $C_9H_{12}F_6O$ requires: C, 43.2%; H, 4.8%; F, 45.6%); IR , NMR , mass spectra 13.

11. 1,4-DIOXAN.

A mixture of 1,4-dioxan (9.36g , 106mmol) and hexafluoropropene (5.0g , 33mmol) was irradiated with gamma rays. The liquid product was distilled in vacuo to give 2-(1,1,2,3,3,3,-hexafluoropropyl)-1,4-dioxan, (25), (6.28g , 79%), as a mixture of diasteriomers; b.p. 80^{o}C at 46mmHg; (Found: C, 36.2%; H, 3.4%. Calc. for $C_7H_8F_6O_2$[94] : C,35.3%; H, 3.4%); IR , NMR , mass spectra 14.

12. 1,3,5-TRIOXAN.

a. Neat.

A mixture of 1,3,5-trioxan (2.78g , 31mmol) and hexafluoropropene (13.3g , 89mmol) was irradiated with gamma rays. Most of the alkene was recovered (9.64g), together with a white solid which was washed with acetone (50ml), dried, and identified as paraformaldehyde by comparison with an authentic sample (IR). The acetone washings were concentrated and transferred under vacuum to give a yellow liquid (0.91g) which was not investigated further.

b. Using di-iso-propyl ether as solvent.

A mixture of 1,3,5-trioxan (2.9g , 32mmol), hexafluoropropene (16.65g, 111mmol), and di-iso-propyl ether (30ml) were irradiated with gamma rays. The product was transferred under vacuum to leave a white solid (3,78g). Trioxan was sublimbed from the white solid to leave a yellow liquid (0.3g) which contained products (GLC, column A, 120°C) but not in sufficient quantity to isolate (5%).

13. 12-CROWN-4 POLYETHER.

A mixture of 12-crown-4 polyether (1.41g , 8mmol) and hexafluoropropene (0.73g , 4.9mmol) was irradiated with gamma rays. The two reactants were recovered by transfer under vacuum (GLC, column K, 160°C and IR).

14. 2,4,6-TRIMETHYL-1,3,5-TRIOXAN.

A mixture of 2,4,6-trimethyl-1,3,5-trioxan (3.08g , 23mmol) and hexafluoropropene (10.5g , 70mmol) was irradiated with gamma rays. The liquid product was transferred under vacuum to give hexafluoropropene (3.35g) and a liquid residue (10.13g). The residue was distilled to give 3,3,4,5,5,5-hexafluoropentan-2-one (19)[7] , (68%); b.p. 77°C; λ_{max} (ε_{max}) 295nm (28.5 dm^{3}mol^{-1}cm^{-1}), 289sh, 305sh, 317sh, 328sh; IR , NMR , mass spectra 15.

15. 2-METHYLOXOLANE.

a. At 18°C

A mixture of 2-methyloxolane (2.74g , 32mmol) and hexafluoropropene (3.07g , 20mmol) was irradiated with gamma rays. Preparative GLC (column Z, 90°C) of the liquid product (5.71g) gave 2-methyl-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane (27), (31% by GLC, column A , 120°C); b.p. 86°C at 100mmHg; IR , NMR , mass spectra 16, and 2-methyl-2-(1,1,2,3,3,3-hexafluoropropyl)oxolane (26), (64% by GLC, column A, 120°C); b.p. 88°C at 100mmHg; IR , NMR , mass spectra 17.

b. At 75°C.

A mixture of 2-methyloxolane (2,79g , 32mmol) and hexafluoropropene (1.81g , 12mmol) was irradiated with gamma rays at 75°C. The liquid product (4.65g) was shown by comparison of GLC (column A, 120°C) retension times to be adducts (27) (33%) and (26) (62%).

16. p-HYDROXYMETHYLANISOLE.

A mixture of p-hydroxymethylanisole (13.84g , 100mmol) and hexafluoropropene (6.6g , 44mmol) was irradiated with gamma rays. All the alkene was recovered by transfer under vacuum and the ether showed no new bands in the IR.

17. n-BUTYL PHENYL ETHER.

A mixture of n-butyl phenyl ether (14.91g , 99mmol) and hexafluoropropene (4.50g , 30mmol) was irradiated with gamma rays. The product was transferred under vacuum to give the two starting materials quantitatively.

18. DIBENZYL ETHER.

A mixture of dibenzyl ether (15.04g , 76mmol) and hexafluoropropene (4.56g , 30mmol) was irradiated with gamma rays. The product was transferred under vacuum to recover the starting materials.

19. DI-(2-CHLOROETHYL) ETHER.

A mixture of di-(2-chloroethyl) ether (15.38g , 108mmol) and hexafluoropropene (6.5g , 43mmol) was irradiated with gamma rays. The product was transferred under vacuum to recover the starting materials.

20. (1,2,3,3,4,4,5,5,6,6-DECAFLUOROCYCLOHEXYL)METHYL METHYL ETHER (32).

a. At 18°C.

A mixture of adduct (32) (0.54g , 1.7mmol) and hexafluoropropene (0.3g , 2mmol) was irradiated with gamma rays. The product was transferred under vacuum to recover the starting materials.

b. At 75°C.

A mixture of adduct (32) (3.18g , 10.3mmol) and hexafluoropropene (0.6g , 4mmol) was irradiated with gamma rays at 75°C. The product was transferred under vacuum to recover the starting materials.

21. n-BUTYL VINYL ETHER.

A mixture of n-butyl vinyl ether (10.30g , 103mmol) and hexafluoropropene (6.4g , 43mmol) was irradiated with gamma rays. A white rubbery solid was obtained that was boiled in toluene (50ml), washed with acetone (3 x 50ml), and dried in vacuo for 4 hours. The solid was insoluble in all common solvents and it was assigned as a co-polymer of the reactants, (33); m.p. $>300^{\circ}$C (decomp.); (Found: C, 50.8%; H, 8.1%; F, 31.2%. A copolymer of ether and alkene in the molar ratio 103:43 respectively requires: C, 53.5; H, 7.5%; F, 29.3%).

22. DIHYDROPYRAN.

a. With Fluoroalkene.

A mixture of dihydropyran (8.62g , 103mmol) and hexafluoropropene (5.14g , 34mmol) was irradiated with gamma rays. The product was transferred under vacuum to give mainly alkene (5.41g) and to leave a white solid(8.32g) The solid was re-crystallized (acetone) to give poly-dihydropyran, (34), soluble in ether, dioxan, CH_2Cl_2 , and CCl_4 ; sparingly soluble in water and acetone; ν_{max} 2940 and 2850(CH), 1463, 1450, 1438, 1375, 1352, 1345, 1300, 1280, 1263, 1235, 1205, 1135, 1085, 1050, 1030, 961, 870 cm^{-1}; δ_H 1.6(6H, s br,), and 3.5-3.83 (4H, br m); m/z 83 (22%), 85(100), 97(9), 168(7), 169(18), 250(4), 252(5), 253(7), 336(2), 337(1), 420(1), 421(0.4), 504(0.4).

b. Without Fluoroalkene.

Dihydropyran (4.37g) was irradiated with gamma rays to give no products.

C. ADDITION OF ETHERS TO CHLOROTRIFLUOROETHENE.

1. OXOLANE.

A mixture of oxolane (9.56g , 133mmol) and chlorotrifluoroethene (9.6g , 82mmol) was irradiated with gamma rays. The product (19.11g) was distilled in vacuo to give 2-(2-chloro-1,1,2-trifluoroethyl)oxolane (35), (8.94g , 78%); b.p. 66°C at 25mmHg; (Found: C, 38.3%; H, 4.4%; F, 28.0%; Cl, 18.0%. Calc. for $C_6H_8ClF_3O$[90] : C, 38.2; H, 4.2%; F, 30.2%; Cl, 18.8%); IR , NMR , mass spectra 18; and leave a residue of telomer adducts (3.24g , 20%) which were not separated.

D. ADDITION OF ETHERS TO HEXAFLUOROCYCLOBUTENE.

1. OXOLANE.

A mixture of oxolane (10.54g , 146mmol) and hexafluorocyclobutene (5.32g , 33mmol) was irradiated with gamma rays. The product (15.93g) was distilled to give 2-(1,2,3,3,4,4-hexafluorocyclobutyl)oxolane (40), mixture of isomers, (6.98g , 91%); b.p. 154-156°C; (Found: C, 41.9%; H, 2.8%; F, 48.6%. $C_8H_8F_6O$ requires : C, 41.0%; H, 3.4%; F, 48.7%); IR , NMR , mass spectra 19.

E. ADDITIONS OF ETHERS TO OCTAFLUOROCYCLOPENTENE.

1. OXOLANE.

A mixture of oxolane (7.46g , 104mmol) and octafluorocyclopentene (4.86g , 23mmol) was irradiated with gamma rays. The product (12.3g) was distilled in vacuo to give 2-(1,2,3,3,4,4,5,5-octafluorocyclopentyl) oxolane (39), mixture of isomers, (5.39g , 83%); b.p. 110°C at 70mmHg; (Found: C, 41.9%; H, 3.3%; F, 51.4. $C_9H_8F_8O$ requires: C, 38.0%; H, 2.8%; F, 53.5%), IR , NMR , mass spectra 20.

2. OXANE.

A mixture of oxane (7.81g , 91mmol) and octafluorocyclopentene (5.2g, 25mmol) was irradiated with gamma rays. The product (12.97g) was distilled in vacuo to give 2-(1,2,3,3,4,4,5,5,-octafluorocyclopentyl)oxane (46), mixture of isomers, (5.58g , 76%); b.p. 75°C at 15mmHg; (Found: C, 41.1%; H, 3.9%; F, 50.0%. $C_{10}H_{10}F_8O$ requires: C, 40.3%; H, 3.4%; F, 51.0%), IR , NMR , mass spectra 21.

3. OXEPANE.

A mixture of oxepane (7.75g , 77mmol) and octafluorocyclopentene (5.7g , 27mmol) was irradiated with gamma rays. The product was distilled in vacuo to give 2-(1,2,3,3,4,4,5,5-octafluorocyclopentyl)oxepane (48), mixture of isomers, (5.89g , 71%); b.p. 106°C at 23mmHg; (Found: C, 42.6%; H, 4.1%; F, 48.0%. $C_{11}H_{12}F_8O$ requires : C, 42.3%; H, 3.9%; F, 48.7%), IR, NMR , mass spectra 22.

4. 1,4-DIOXAN.

A mixture of 1,4-dioxan (11.92g , 135mmol) and octafluorocyclopentene (8.9g , 42mmol) was irradiated with gamma rays. The product was distilled in vacuo to give 2-(1,2,3,3,4,4,5,5-octafluorocyclopentyl)-1,4-dioxan, (50), mixture of isomers, (6.18g , 49%); b.p. 95-98°C at 15mmHg; (Found: C, 37.1%; H, 3.1%; F, 46.3%. $C_9H_8F_8O_2$ requires: C, 36.0%; H, 2.7%; F, 50.7%); IR , NMR , mass spectra 23.

F. ADDITION OF ETHERS TO DECAFLUOROCYCLOHEXENE.

1. OXOLANE.

A mixture of oxolane (9.05g , 126mmol) and decafluorocyclohexene (8.65g , 33mmol) was irradiated with gamma rays. The product (17.67g) was distilled in vacuo to give 2-(1,2,3,3,4,4,5,5,6,6-decafluorocyclohexyl) oxolane (38), mixture of isomers, (10.01g , 91%); b.p. 91-94°C at 25mmHg; (Found: C, 36.5%; H, 2.3%; F, 57.5%. $C_{10}H_8F_{10}O$ requires: C, 35.9%; H, 2.4%; F, 56.9%); IR , NMR , mass spectra 24.

G. ADDITION OF ETHERS TO OCTAFLUOROBUT-2-ENE.

1. OXOLANE.

A mixture of oxolane (5.83g , 81mmol) and octafluorobut-2-ene (4.16g, 21mmol) was irradiated with gamma rays. The product (9.92g) was distilled to give 2-(1-trifluoromethyl-1,2,3,3,3-pentafluoropropyl)oxolane (41), mixture of isomers, (5.05g , 89%); b.p. 149-150°C; (Found: C,36.2%; H, 3.2%; F, 55.0%. $C_8H_8F_8O$ requires: C, 35.3; H, 2.9%; F, 55.9%); IR , NMR , mass spectra 25.

2. OXANE.

A mixture of oxane (7.95g , 92mmol) and octafluorobut-2-ene (5.8g , 29mmol) was irradiated with gamma rays. The product was transferred under vacuum to give some alkene(2.57g) and a liquid (10.59g). The liquid was distilled in vacuo to give 2-(1-trifluoromethyl-1,2,3,3,3-pentafluoropropyl)oxane (47), (1.77g , 21%); b.p. 65°C at 20mmHg; (Found: C, 38.1%; H, 3.3%; F, 53.4%. $C_9H_{10}F_8O$ requires: C,37.8%; H, 3.5%; F, 53.2%); IR , NMR , mass spectra 26.

3. OXEPANE.

A mixture of oxepane (7.97g , 80mmol) and octafluoro but-2-ene (5.7g , 28mmol) was irradiated with gamma rays. The product was distilled in vacuo to give 2-(1-trifluoromethyl-1,2,3,3,3-pentafluoropropyl)oxepane, (49), (5.1g , 60%); b.p. 84-85°C at 24mmHg; (Found: C, 40.3%; H, 3.7%; F, 50.7%. $C_{10}H_{12}F_8O$ requires: C, 40.0%; H, 4.0%; F, 50.7%); IR , NMR , mass spectra 27.

4. 1,4-DIOXAN.

A mixture of 1,4-dioxan (11.84g , 135mmol) and octafluorobut-2-ene (8.2g , 41mmol) was irradiated with gamma rays. Excess alkene was removed by transfer under vacuum to leave a liquid (16.57g). The liquid was distilled in vacuo to give 2-(1-trifluoromethyl-1,2,3,3,3-pentafluoropropyl)-1,4-dioxan (51), (2.24g , 19%); b.p. 70°C at 15mmHg; (Analysis unsatisfactory); IR , NMR , mass spectra 28, and a mixture of unassigned di-adducts, (1.71g , 15%).

H. ADDITION OF ETHERS TO 2,3-DICHLOROHEXAFLUOROBUT-2-ENE.

1. OXOLANE.

A mixture of oxolane (8.81g , 122mmol) and 2,3-dichlorohexafluorobut-2-ene (8.67g , 37mmol) was irradiated with gamma rays. The product was distilled in vacuo to give 1-(1,2-dichloro-1-trifluoromethyl-3,3,3-trifluoropropyl)oxolane (42), (89% by GLC, column K, 175°C); b.p. 98-100°C at 25mmHg; (Found: C, 31.7%; H, 3.0%; F, 41.5; Cl, 25.0%. $C_8H_8Cl_2F_6O$ requires: C, 31.5%; H, 2.6%; F, 37.4; Cl, 23.3%); IR , NMR , mass spectra 29; and a product identified as probably the dehydrochlorinated mono-adduct, (Found: C, 37.8%; H, 4.1%; F, 42.5%; Cl, 13.9%. $C_8H_7ClF_6O$ requires: C, 35.8%; H, 2.6%; F, 42.5%; Cl, 13.2%), (9% by GLC).

I. ADDITION OF ETHERS TO PERFLUORO-3-METHYLPENT-2-ENE.

1. OXOLANE.

A mixture of oxolane (5.85g , 81mmol) and perfluoro-3-methylpent-2-ene (3.42g , 11mmol) was irradiated with gamma rays. The product was transferred under vacuum to give a volatile component (3.63g) and an involatile component (4.68g). Preparative GLC (column K, 150°C) of the volatile component gave 2-(1,2-di(trifluoromethyl)-1,3,3,4,4,4-hexafluorobutyl)oxolane (43), (70% by GLC, column K, 200°C), (Found: C, 32.5%; H, 1.8%. $C_{10}H_8F_{12}O$ requires: C, 32.3%; H, 2.1%); IR , NMR , mass spectra 30; Microdistillation in vacuo of the involatile component gave 2,5-di(1,2-di(trifluoromethyl)-1,3,3,4,4,4-hexafluorobutyl)oxolane (44), (22% by GLC, column K, 200°C); b.p. 232°C (Siwoloboff); (Found: C, 28.8%; H, 0.5%; F, 65.9%. $C_{16}H_8F_{24}O$ requires: C, 28.6%; H, 1.2%; F, 67.9%); IR , NMR , mass spectra 31.

J. ADDITION OF ETHERS TO PERFLUORO-3,4-DIMETHYL-4-ETHYLHEX-2-ENE.

1, OXOLANE.

A mixture of oxolane (9.7g , 135mmol) and perfluoro-3,4-dimethyl-4-ethylhex-2-ene (13.89g , 28mmol) was irradiated with gamma rays. The product consisted of two layers. The upper hydrocarbon layer was distilled in vacuo to give mainly oxolane and to leave a white sticky solid containing no fluorine. The lower fluorocarbon layer was micro-distilled in vacuo to give alkene and a small amount of product (0.5g). The product was identified by GLC/mass spectrum as 2-(1,2,3-tri(trifluoromethyl)-3-pentafluoroethyl-1,4,4,5,5,5-hexafluoropentyl)oxolane (45), (4%), mass spectrum 32.

K. ADDITION OF ETHERS TO PERFLUORO-3,4-DIMETHYLHEX-3-ENE.

1. OXOLANE.

A mixture of oxolane (8.73g , 121mmol) and perfluoro-3,4-dimethylhex-3-ene (11.48g , 29mmol) was irradiated with gamma rays. The product consisted of two layers, neither of which showed the presence of adducts by GLC (column K, 190°C). Distillation of the upper hydrocarbon layer gave mainly oxolane with a white sticky solid residue which did not contain fluorine and was assigned as oligomers of oxolane.

L. ADDITION OF ETHERS TO OCTAFLUOROCYCLOHEXA-1,3-DIENE.

1. OXOLANE.

A mixture of oxolane (9.89g , 137mmol) and octafluorocyclohexa-1,3-diene (4.52g , 20mmol) was irradiated with gamma rays. All the volatile materials were removed under high vacuum for 5 hours to leave a white (5.2g) rubbery solid which was not investigated further.

M. ADDITION OF ESTERS TO HEXAFLUOROPROPENE.

1. METHYL FORMATE.

a, At 18°C.

A mixture of methyl formate (9.7g , 162mmol) and hexafluoropropene (7.3g , 49mmol) was irradiated with gamma rays. The product was transferred under vacuum at 0°C to give starting materials(by GLC, column A, 120°C and IR).

b. At 120°C.

A mixture of methyl formate (6.56g , 109mmol), hexafluoropropene (4.85g , 32mmol), and di-t-butyl peroxide (0.46g , 3mmol) was heated at 120°C for 16 hours. The starting materials were transferred under vacuum to leave a liquid (3.04g). Preparative GLC (columns Z at 100°C and A at 130°C) of the liquid gave methyl-2,2,3,4,4,4-hexafluorobutanoate (54), impure sample, (4.5% by GLC, column A, 105°C); b.p. 116°C (Simoloboff); IR , NMR , mass spectra 33; 2,2,3,4,4,4-hexafluorobutyl formate (55), (11% by GLC, column A, 105°C; b.p. 119°C (Siwoloboff); (Found: C, 29.0%; H, 2.1%; F, 54.2%. $C_5H_4F_6O_2$ requires: C, 28.6%; H, 1.9%; F, 54.3%), IR , NMR , mass spectra 34 ;2,2,3,4,4,4-hexafluorobutan-1-ol (56),(21% by GLC, column A, 105°C); IR , NMR , mass spectra 35; and an unassigned compound, (8% by GLC, column A, 105°C.

2. METHYL ACETATE.

A mixture of methyl acetate (7.10g , 96mmol) , hexafluoropropene (5,4g , 36mmol), and di-t-butyl peroxide (0.33g , 2mmol) was heated at 120°C for 18 hours. The starting materials were transferred under vacuum to leave a liquid (4.24g). Preparative GLC (column A, 130°C) gave 2-trifluoromethyl-2,3,3,-trifluoropropyl acetate (59),(3% by GLC, column A, 130°C); b.p. 126°C (Siwoloboff); (Found: C, 32.4%; H, 2.8%; F, 51.6%. Calc. for $C_6H_6F_6O_2$ [124] : C, 32.1%; H, 2.7%; F, 50.9%), IR , NMR , mass spectra 36; 2,2,3,4,4,4-hexafluorobutyl acetate (57), (39% by GLC, column A, 130°C); b.p. 134°C (Siwoloboff); (Found: C, 34.3%; H, 3.2%; F, 49.7%. Calc. for $C_6H_6F_6O_2$[124] : C,32.1%; H, 2.7%; F, 50.9%); IR , NMR , mass spectra 37; methyl 3,3,4, 5,5,5-hexafluoropentanoate (58), (10% by GLC, column A, 130°C); b.p. 135°C (Siwoloboff); (Found: C, 32.2%; H, 2.7%; F, 50.8%. Calc. for $C_6H_6F_6O_2$[124] : C, 32.1%; H, 2.7%; F, 50.9%); IR , NMR , mass spectra 38 ; and 2,2,3,4,4,4-hexafluorobutan-1-ol (56), (2% by GLC, column A, 130°C).

3. METHYL BENZOATE.

a. At 18°C.

A mixture of methyl benzoate (13.69g , 100mmol) and hexafluoropropene (5.4g , 36mmol) was irradiated with gamma rays. The product was transferred under vacuum to give a quantitative recovery of starting materials, (GLC, column O, 212°C and IR and NMR).

b. AT 120°C.

A mixture of methyl benzoate (13.54g , 99mmol) , hexafluoropropene (5.1g , 34mmol), and di-t-butyl peroxide (0.28g , 2mmol) was heated at 120°C for 18 hours. The product was transferred under vacuum to give a 95% recovery of starting materials.

4. METHYL CHLOROFORMATE.

A mixture of methyl chloroformate (9.98g , 106mmol) , hexafluoropropene (4.6g , 31mmol), and di-t-butyl peroxide (0.48g , 3mmol) was heated at 120°C for 18 hours. The product was transferred under vacuum to give a good recovery of starting materials (GLC, column A, 120°C).

5. DIMETHYL MALONATE.

a. At 18°C.

A mixture of dimethyl malonate (12.20g , 92mmol) and hexafluoropropene

(4.35g , 29mmol) was irradiated with gamma rays. The product was transferred under vacuum to give a quantitative recovery of starting materials (by GLC, column K , 115°C).

b. At 120°C.

A mixture of dimethyl malonate (14.43g , 109mmol), hexafluoropropene (5,81g , 38mmol) , and di-t-butyl peroxide (0.29g , 1.8mmol) was heated at 120°C for 18 hours. The product was transferred under vacuum to give a 95% recovery of starting materials (by GLC, column K, 115°C).

6. DIETHYL OXALATE.

A mixture of diethyl oxalate (14.45g , 99mmol) and hexafluoropropene (5.2g , 35mmol) was irradiated with gamma rays. The product was transferred under vacuum to give starting materials.

7. DIMETHYL CARBONATE.

a. At 18°C.

A mixture of dimethyl carbonate (4.75g , 53mmol) and hexafluoropropene (5.0g , 33mmol) was irradiated with gamma rays. The product was transferred under vacuum and distilled to give a 95% recovery of starting materials.

b. At 120°C.

A mixture of dimethyl carbonate (8,86g , 98mmol) , hexafluoropropene (7.5g , 50mmol) , and di-t-butyl peroxide (0.3g , 2mmol) was heated at 120°C for 18 hours. The product was transferred under vacuum to give alkene (3.72g) and a liquid which was distilled to give 2,2,3,4,4,4-hexafluorobutyl methyl carbonate (60), (4.0g , 55%); b.p. 146°C; (Found: C, 30.4%; H, 2.8%; F, 48.5%. $C_6H_6F_6O_3$ requires: C, 30.0%; H, 2.5%; F, 47.5%); IR , NMR , mass spectra 39.

N. ADDITION OF FLUOROALKENES TO TRIMETHYL BORATE.

1. HEXAFLUOROPROPENE.

a. At 18°C

A mixture of trimethyl borate (16.5g , 158mmol) and hexafluoropropene (10.3g , 69mmol) was irradiated with gamma rays. The product (26.72g) was distilled in vacuo to give tri(2,2,3,4,4,4-hexafluorobutyl) borate (63), (8.2g , 65%); b.p. 62°C at 0.05mmHg; (Found: C, 26.1%; H, 1.8%; F, 61.5%; B, 3.1%. $C_{12}H_9BF_{18}O_3$ requires: C, 26.0%; H, 1.6%; F, 61.7%; B, 2.0%); IR , NMR , mass spectra 40.

b. At 80°C.

A mixture of trimethyl borate (7.40g , 71mmol), hexafluoropropene (4.94g , 33mmol), and benzoyl peroxide (0.1g , 0.5mmol) was heated at 80°C for 25 hours. The product (12.3g) was distilled in vacuo to give adduct (63), (1.5g , 25%).

2. CHLOROTRIFLUOROETHENE.

A mixture of trimethyl borate (9.11g , 88mmol) and chlorotrifluoroethene (6.0g , 52mmol) was irradiated with gamma rays. Theproduct (15.01g) was distilled in vacuo to remove excess borate and leave a sticky semi-solid residue (62) (5.5g) which was not investigated further.

3. HEXAFLUOROCYCLOBUTENE.

a. At 18°C.

A mixture of trimethyl borate (10.68g , 105mmol) and hexafluorocyclobutene (6.77g , 42mmol) was irradiated with gamma rays. The product (17.4g) was distilled in vacuo to give tri((1,2,3,3,4,4-hexafluorocyclobutyl)-methyl) borate (64), (3.94g , 49%); b.p. 72°C at 0.05mmHg; (Found: C, 31.2%; H, 1.5%; F, 58.0%; B, 3.5%. $C_{15}H_9BF_{18}O_3$ requires: C, 30.5%; H,1.5%; F, 58.0%; B, 1.9%); IR , nmr , mass spectra 41.

b. At 80°C.

A mixture of trimethyl borate (9.03g , 87mmol) , hexafluorocyclobutene (7.86g , 48mmol) , and benzoyl peroxide (0.19g , 0.8mmol) was heated at 80°C for 25 hours. The product (16.96g) was transferred under vacuum to give excess borate (7.42g) and a liquid (6.96g) which was distilled in vacuo to give adduct (64), (3.69g , 43%).

4. DECAFLUOROCYCLOHEXENE.

A mixture of trimethyl borate (9.19g , 88mmol) and decafluorocyclohexene (7.65g , 29mmol) was irradiated with gamma rays. The product (16.77g) was transferred under vacuum to leave a liquid (8.85g) which was distilled in vacuo to give tri((1,2,3,3,4,4,5,5,6,6-decafluorocyclohexyl)methyl) borate (65), (6.23g , 63%); b.p. 140°C at 3mmHg; (Found: C, 28.5%; H, 1.2%; F, 64.4%; B, 2.5%. $C_{21}H_9BF_{30}O_3$ requires: C, 28.3%; H, 1.0%; F, 64.0%; B, 1.2%); IR , NMR , mass spectra 42.

5. PERFLUORO-3,4-DIMETHYLHEX-3-ENE.

A mixture of trimethyl borate (7.99g , 77mmol) and perfluoro-3,4-dimethylhex-3-ene (11.5g , 77mmol) was irradiated with gamma rays. The product was transferred under vacuum to give excess borate (3.1g) and a liquid which was distilled in vacuo to give tri(2-pentafluoroethyl-4,4,5,5,5-pentafluoro-2,3-di(trifluoromethyl)pentyl) borate (66), (9.31g , 74%); b.p. 100°C at 2mmHg; (Found: C, 25.1%; H, 0.7%; F, 69.6%; B, 2.1%. $C_{27}H_9BF_{48}O_3$ requires: C, 24.9%; H, 0.7%; F, 69.9%; B, 0.8%); IR , NMR , mass spectra 43.

6. OCTAFLUOROCYCLOHEXA-1,3-DIENE.

a. At 18°C.

A mixture of trimethyl borate (12.34g , 119mmol) and octafluorocyclohexa-1,3-diene (7.39g , 33mmol) was irradiated with gamma rays. The product was transferred under vacuum to give a liquid composed of starting materials only (GLC, column K, 18°C) and no residue.

b. At 80°C.

A mixture of trimethyl borate (5.01g , 48mmol) , octafluorocyclohexa-1,3-diene (7.22g , 32mmol) , and benzoyl peroxide (0.44g) was heated at 80°C for 21 hours. The product was transferred under vacuum to give a liquid composed of starting materials only (GLC, column K, 18°C) and no residue.

7. OCTAFLUOROCYCLOHEXA-1,4-DIENE.

a. At 18°C.

A mixture of trimethyl borate (10.52g , 101mmol) and octafluorocyclohexa-1,4-diene (7.0g , 31mmol) was irradiated with gamma rays. The product was dissolved in acetone (20ml), filtered, the solvent removed in vacuo, and dried by heating in vacuo to give a white solid (67), (8.44g), m.p. (indeterminate); (Found: C, 31.3%; H, 3.3%); δ_H 3.4, 3.7, and 4.1 (2H, broad, $-OCH_2-$) , 4.97 (1H, broad D, -CFH-), δ_F 116.7, 120.3, 121.7, and123.3 (2F, $-CF_2-$), 183.0, 185.0, 189.7, and 192.3 (1F, -CFR-), 209.0, 216.0, 219.3, 223.3, 225.7, 233.0 (1F, -CFH-).

b. At 80°C.

A mixture of trimethyl borate (7.71g , 74mmol) , octafluorocyclohexa-1,4-diene (3.04g , 13mmol), and benzoyl peroxide (0.47g) was heated at 80°C for 21 hours. The product was transferred under vacuum to give a volatile component (5.12g) and a liquid which was heated in vacuo for 10 mins to give a white solid (67), (2.93g).

O. ADDITION OF TRI-n-BUTYL BORATE TO HEXAFLUOROPROPENE.

1. A mixture of tri-n-butyl borate (16.62g , 72mmol) and hexafluoropropene (6.6g , 44mmol) was irradiated with gamma rays. No alkene was recovered and the liquid product (22.8g) was distilled in vacuo to give an adduct (69); b.p. 65-67°C at 0.5mmHg; (Found: C, 36.3%; H, 3.6%); IR , NMR , mass spectra 128.

2. A mixture of tri-n-butyl borate (4.71g , 20mmol) and hexafluoropropene (10.5g , 70mmol) was irradiated with gamma rays. A small amount of alkene was recovered (1.0g) and the remaining liquid product was distilled in vacuo to give the adduct (69).

3. A mixture of tri-n-butyl borate (0.84g , 3.7mmol) and hexafluoropropene (5.4g , 36mmol) was irradiated with gamma rays. Some alkene was recovered (4.26g) and the remaining liquid was distilled in vacuo to give the adduct (69), (2.14g).

P. HYDROLYSIS OF TRI-n-BUTYL BORATE / HEXAFLUOROPROPENE ADDUCT. (69).

A sample of the adduct (69) was added to distilled water (20ml). The lower fluorocarbon layer was separated, dried ($MgSO_4$), and preparative GLC (column K, 180°C) gave 1,1,1,2,3,3-hexafluoroheptan-4-ol (70), (27%), IR , NMR , mass spectra 129, and 1,1,1,2,3,3-hexafluoro-4-(1,1,2,3,3,3-hexafluoropropyl)heptan-4-ol (71), (67%); (Found: C, 32.7%; H, 3.7%; F, 59.1%. $C_{10}H_{10}F_{12}O$ requires: C, 32.1%; H, 2.7%; F, 60.9%); IR , NMR , mass spectra 130, as the main products.

CHAPTER 8

EXPERIMENTAL TO CHAPTER 3.

A. PURIFICATION OF REAGENTS.

Amines and amides were distilled onto 4A molecular sieves before use. N,N-dimethylbenzamide was prepared from benzoyl chloride and dimethylamine and distilled in vacuo. N-Acetylpiperidine and N-acetylmorpholine were prepared by acetylation of piperidine and morpholine respectively.

B. ADDITION OF AMINES TO HEXAFLUOROPROPENE.

1. PIPERIDINE.

A mixture of piperidine (3.1g , 36mmol) and hexafluoropropene (1.85g, 12mmol) was irradiated with gamma rays. Diethyl ether was added, the solution filtered and the solvent removed in vacuo to leave a yellow brown oil. Sublimation gave crystals of N-(2,3,3,3-tetrafluoropropanoyl) piperidine (74), (1.0g , 40%); m.p. 42-44°C; (Found: C, 46.3%; H, 6.2%; N, 6.9%; F, 35.3%. Calc. for $C_8H_{11}F_4NO$[152] : C, 45.1%; H, 5.2%; N, 6.6%; F, 35.7%); IR , NMR , mass spectra 44.

2. N-METHYLPIPERIDINE.

A mixture of N-methylpiperidine (6.33g , 64mmol) and hexafluoropropene (2.99g , 20mmol) was irradiated with gamma rays. The product was transferred under vacuum to give a volatile component (6.91g) and leave a liquid (1.26g). Preparative GLC (column K, 120°C) of the liquid gave N-(2,2,3,4,4,4-hexafluorobutyl)piperidine (75), (1.7% by GLC, column K, 140°C); (insufficient for analysis); IR , NMR , mass spectra 45; N-methyl-2-(1,1,2,3,3,3-hexafluoropropyl)piperidine (76), (2.3% by GLC, column K, 140°C); (insufficient for analysis); IR , NMR , mass spectra 46; and N-(2,2,3,4,4,4-hexafluorobutyl)-2-(1,1,2,3,3,3-hexafluoropropyl)piperidine (77), (18% by GLC, column K, 140°C); b.p. 220°C (Siwoloboff); (Found: C, 36.6%; H, 2.9%; N, 3.2%; F, 53.2%. $C_{12}H_{13}F_{12}N$ requires: C, 36.1%; H, 3.3%; N, 3.5%;

F, 57.1%); IR , NMR , mass spectra 47.

3. N-METHYLMORPHOLINE.

A mixture of N-methylmorpholine (9.28g , 92mmol) and hexafluoropropene (6.4g , 43mmol) was irradiated with gamma rays. The product was transferred under vacuum to give a volatile component (4.01g) and to leave a liquid (11.65g). Distillation in vacuo of the liquid gave N-(2,2,3,4,4,4-hexafluorobutyl)morpholine (78), (0.2g , 0.6%); b.p. 74°C at 11mmHg; (Found: C, 38.2%; H, 4.6%; N, 5.1%; F, 45.2%. $C_8H_{11}F_6NO$ requires: C, 38.2%; H, 4.4%; N, 5.6%; F, 45.4%); IR , NMR , mass spectra 48, N-(2,2,3,4,4,4-hexafluorobutyl)-2-(1,1,2,3,3,3-hexafluoropropyl)morpholine (79), (3.3g, 28%); b.p. 114°C at 11mmHg; (Found: C, 33.2%; H, 2.9%; N, 4.2%; F, 54.2%. $C_{11}H_{11}F_{12}NO$ requires: C, 32.9%; H, 2.7%; N, 3.5%; F, 56.8%); IR , NMR , mass spectra 49.

4. N,N,N',N'-TETRAMETHYLDIAMINOMETHANE.

A mixture of N,N,N',N'-tetramethyldiaminomethane (5.07g , 50mmol) and hexafluoropropene (2.5g , 17mmol) was irradiated with gamma rays. The product was transferred under vacuum to leave a liquid residue (2.62g). Preparative GLC (column Z, 100°C) gave three unidentified products, (211), a mixture of two components(GLC, column K, 115°C); ν_{max} 2950, 1669, 1290, 1190, 1105; δ_H 2.15(3H, s), 2.57(3H, m), 4.5(1H, br m); m/z 238(0.76%), 206(3), 205(3), 175(7), 173(16), 156(10), 141(7), 106(7), 72(100), 60(13), 44(22), 43(7), 42(31), 31(11), 28(23); (212), ν_{max} 2950, 2860, 2832, 2791, 1655, 1400, 1294, 1198, 1125, 1075, 1042, 992; δ_H 2.00(2H, s), 2.77(3H, m), δ_F 77.3(3F, d), 173.3(1F, dm); m/z 230(0.5%), 210(1), 166(4), 72(8), 58(100), 44(5), 42(6), 28(11); and (213), (Found: F, 60.8%); ν_{max} 2950, 1666, 1340, 1324, 1263, 1250, 1198, 1118, 993, 897, 821, 748; δ_H 2.65(br s), δ_F 52.5(5.5F, m), 57.8(2.3F, m), 63.3(1F, m), 82.8(6.3F, t), 103.3(3.3F, m), 125.7 (4F, m); m/z 326(2%), 325(22), 306(23), 206(100), 156(12), 154(12), 72(20), 60(11), 44(14), 42(18), 31(15).

5. N,N-DIMETHYLANILINE.

a. At 18°C.

A mixture of N,N-dimethylaniline (12.91g , 107mmol) and hexafluoropropene (6.0g , 40mmol) was irradiated with gamma rays. The product was transferred under vacuum to give a 95% recovery of starting materials.

b. At 120°C.

A mixture of N,N-dimethylaniline (10.84g , 90mmol), hexafluoropropene (5.39g , 36mmol), and di-t-butyl peroxide (0.27g) was heated at 120°C for 19 hours. The product was transferred under vacuum to give a volatile mixture of hexafluoropropene oligomers (2.7g) (by GLC/mass spectra, column K, 75°C) and a residue (14.16g). The residue was filtered to give a red liquid (mainly N,N-dimethylaniline by IR) and a solid which was recrystallized (methanol/acetone), dried in vacuo, to give an unidentified fluoride salt (4.06 g), (by IR , NMR), (Found: F, 28.55%).

C. ADDITION OF AMIDES TO HEXAFLUOROPROPENE.

1. N,N-DIMETHYLFORMAMIDE.

A mixture of N,N-dimethylformamide (20.33g , 278mmol) and hexafluoropropene (17.1g , 114mmol) was irradiated with gamma rays. The product was distilled in vacuo to give N-(2,2,3,4,4,4-hexafluorobutyl)-N-methylformamide (81), (50% by GLC, column K, 115°C); b.p. 38°C at 1mmHg); (Found: C, 32.3%; H, 3.5%; N, 6.5%; F, 51.1%. $C_6H_8F_6NO$ requires: C, 32.1%; H, 3.6%; N, 6.3%; F, 50.9%); IR , NMR , mass spectra 50; N,N-dimethyl-2,2,3,4,4,4-hexafluorobutanamide (82), (23% by GLC, column K, 115°C); b.p. 161°C (Siwoloboff); (Found: C, 32.6%; H, 3.3%; N, 6.6%; F, 50.4%. $C_6H_7F_6NO$ requires: C, 32.3%; H, 3.1%; N, 6.3%; F, 51.1%); IR , NMR , mass spectra 51 ; and N-(2,2,3,4,4,4-hexafluorobutyl)-N-methyl-2,2,3,4,4,4-hexafluorobutanamide (83), (7% by GLC, column K, 115°C); b.p. 196°C (Swoloboff); (Found: C, 29.8%; H, 2.3%; N, 4.3%; F, 60.8%. $C_9H_7F_{12}NO$

requires: C, 29.0%; H, 1.9%; N, 3.8%; f, 61.1%); IR , NMR , mass spectra 52.

2. N,N-DIMETHYLACETAMIDE.

A mixture of N,N-dimethylacetamide (10.34g , 119mmol) and hexafluoropropene (5.6g , 37mmol) was irradiated with gamma rays. The product was distilled in vacuo to give N-(2,2,3,4,4,4-hexafluorobutyl)-N-methylacetamide (84), (7.24g , 82%); b.p. 42°C at 1mmHg; (Found: C, 36.9%; H, 4.3%; N, 6.2%; F, 50.0%. $C_7H_9F_6NO$ requires: C, 35.4%; H, 3.8%; N, 5.9%; F, 48.1%); IR , NMR , mass spectra 53.

3. N,N,N',N'-TETRAMETHYLUREA.

a. Excess Amide.

A mixture of N,N,N', N'-tetramethylurea (7.54g , 65mmol) and hexafluoropropene (6.6g , 44mmol) was irradiated with gamma rays. The product was distilled in vacuum to give N-(2,2,3,4,4,4-hexafluorobutyl)-N,N',N'-trimethylurea (85), (6.93g , 55%); b.p. 72°C at 1mmHg; m.p. 36-38°C; (Found: C, 36.1%; H, 4.3%; N, 10.4%; F, 41.3%. $C_8H_{12}F_6N_2O$ requires: C, 36.1%; H, 4.5%; N, 10.5%; F, 42.9%); IR , NMR , mass spectra 54.

b. Excess Alkene.

i. At 18°C.

A mixture of N,N,N',N'-tetramethylurea (2.85g , 24.6mmol) and hexafluoropropene (13.9g , 92.7mmol) was irradiated with gamma rays. The product was transferred under vacuum to give alkene (5.71g) and a liquid (11.08g). The liquid was distilled in vacuo to give adduct (85), (10% by GLC, column K, 195°C); N,N'-di(2,2,3,4,4,4-hexafluorobutyl)-N,N'-dimethylurea (87), (53% by GLC); b.p. 101°C at 5mmHg; (Found: C, 32.0%; H, 2.7%; N, 6.3%; F, 54.0%. $C_{11}H_{12}F_{12}N_2O$ requires: C, 31.7%; H, 2.9%; N, 6.7%; F, 54.8%); IR , NMR , mass spectra 55; N,N-di(2,2,3,4,4,4-hexafluorobutyl)-N',N'-dimethylurea (86), (9% by GLC), mass spectrum 56; N,N,N'-tri(2,2,3,4,4,4-hexafluorobutyl)-N'-methylurea (88), (24% by GLC), IR,NMR,mass spectra 57; and N,N,N',N'-tetra(2,2,3,4,4,4-hexafluorobutyl)urea (89), (3% by GLC), mass spectrum 58.

ii. At 120°C.

A mixture of N,N,N',N'-tetramethylurea(0.9g , 7.8mmol) and hexafluoropropene (6.9g , 46mmol) and di-t-butyl peroxide (0.27g) was heated at 120°C for 65 hours to give adducts (85),(4% by GLC, column K, 195°C), (86),(5%), (87),(27%), (88),(40%), and(89),(24%).

4. N-(2,2,3,4,4,4-HEXAFLUOROBUTYL)-N,N',N'-TRIMETHYLUREA.

A mixture of N-(2,2,3,4,4,4-hexafluorobutyl)-N,N',N'-trimethylurea (0.43g , 1.6mmol) and hexafluoropropene (4.3g , 29mmol) was irradiated with gamma rays. The product was transferred under vacuum to give alkene (3.79g) and a liquid(0.91g) composed of adducts (85),(2% by GLC, column K, 195°C), (86),(2%), (87),(56%), (88), (32%), and (89),(8%).

5. N,N-DIMETHYLBENZAMIDE.

a. At 60°C.

A mixture of N,N-dimethylbenzamide (2.10g , 14mmol) and hexafluoropropene (2.5g , 17mmol) was irradiated with gamma rays at 60°C. The product was transferred under vacuum to give a 95% recovery of materials.

b. At 120°C.

A mixture of N,N-dimethylbenzamide (2.02g , 13.5mmol), hexafluoropropene (2.27g , 15mmol), and di-t-butyl peroxide (0.22g , 1.4mmol) was heated at 120°C for 18 hours. The product was transferred under vacuum to give alkene (1.6g) and a liquid (2.81g). The liquid was distilled in vacuo to give N-(2,2,3,4,4,4-hexafluorobutyl)-N-methylbenzamide (90), (30%); m.p. 60-62°C; (Found: C, 49.0%; H, 4.0%; N, 4.3%; F, 37.0%. $C_{12}H_{11}F_6NO$ requires: C, 48.2%; H, 3.7%; N, 4.7%; F, 38.1%); IR , NMR , mass spectra 59.

6. N-METHYLPYRROLIDIN-2-ONE.

A mixture of N-methylpyrrolidin-2-one (10.1g , 102mmol) and hexafluoropropene (5,1g , 34mmol) was irradiated with gamma rays. The product was distilled in vacuo to give N-methyl-5-(1,1,2,3,3,3-hexafluoropropyl) pyrrolidin-2-one (91), (5.1g , 60%); b.p. 83-85°C at 1mmHg; (Found: C, 39.1%; H, 3.9%; N, 5.5%; F, 43.8%. $C_8H_9F_6NO$ requires: C, 38.6%; H,3.6%; N, 5.6%; F, 45.8%); IR , NMR , mass spectra 60.

7. N-ACETYLPIPERIDINE.

A mixture of N-acetylpiperidine (5.9g , 46mmol) and hexafluoropropene (4.3g , 29mmol) was irradiated with gamma rays. The product was transferred under vacuum to give alkene (1.84g) and leave a liquid(8.31g). The liquid was distilled in vacuo to give N-acetyl-2-(1,1,2,3,3,3-hexafluoropropyl)piperidine (92), (40% by GLC, column K, 200°C); b.p. 43°C at 0.1mmHg; (Found: C, 44.1%; H, 5.0%; N, 5.0%; F, 39.8%. $C_{10}H_{13}F_6NO$ requires: C, 43.3%; H, 4.7%; N, 5.0%; F, 41.2%); IR , NMR , mass spectra 61; and a mixture of di-adducts (17% by GLC/mass spectra , column K, 200°C).

8. N-ACETYLMORPHOLINE.

A mixture of N-acetylmorpholine (5.9g , 46mmol) and hexafluoropropene (3.5g , 23mmol) was irradiated with gamma rays. The product was transferred under vacuum to give alkene(2.26g) and leave a liquid (7.15g). The liquid was composed of adduct products (35% by GLC/mass spectra, columnK, 195°C), but they were not separated.

D. ADDITION OF AMIDES TO CHLOROTRIFLUOROETHENE.

1. N,N,-DIMETHYLACETAMIDE.

A mixture of N,N-dimethylacetamide (7.6g , 87mmol) and chlorotrifluoroethene (3.2g , 27mmol) was irradiated with gamma rays. The product (10.72g) was distilled in vacuo to remove starting materials then micro-distilled in vacuo to give N-methyl-N-(3-chloro-2,2,3-trifluoropropyl)acetamide (93), (76% by GLC, column K, 190°C); b.p. 225°C (Siwoloboff); (Found: C, 35.1%; H, 4.8%; N, 6.8%; F, 27.6%; Cl, 17.9%. $C_6H_9ClF_3NO$ requires: C, 35.4%; H, 4.4%; N,6.9%; F, 28.0%; Cl, 17.4%); IR , NMR , mass spectra 62; and leave a residue of a mixture of telomer adducts (22% by GLC/mass spectra, column K, 190°C).

2. N-METHYLPYRROLIDIN-2-ONE.

A mixture of N-methylpyrrolidin-2-one (8.9g , 90mmol) and chlorotrifluoroethene (6.1g , 52mmol) was irradiated with gamma rays. The product (14.46g) was distilled in vacuo to give N-methyl-5-(2-chloro-1,1,2-trifluoroethyl)pyrrolidin-2-one (97), (75% by GLC, column K, 190°C) b.p. 50-53°C at 5mmHg; (Found: C, 39.1%; H, 4.5%; N, 6.2%; F, 25.1%; Cl, 17.0%. $C_7H_9ClF_3NO$ requires: C, 39.0%; H, 4.2%; N, 6.5%; F, 26.4%; Cl, 16.5%); IR , NMR , mass spectra 63; and a mixture of telomer adducts (24% by GLC/mass spectra, column K, 190°C).

E. ADDITION OF AMIDES TO HEXAFLUOROCYCLOBUTENE.

1. N,N-DIMETHYLACETAMIDE.

A mixture of N,N-dimethylacetamide (8.52g , 97mmol) and hexafluorocyclobutene (5,1g , 31mmol) was irradiated with gamma rays. The product was transferred under vacuum to give alkene (3.63g) and leave a liquid (9.73g). Water (50ml) was added to the liquid, the lower layer separated, and micro-distilled in vacuo to give N-(1,2,3,3,4,4-hexafluorocyclobutyl)-methyl-N-methylacetamide (96), (29%); b.p. >230°C (decomp) (Siwoloboff); (Found: C, 38.6%; H, 3.9%; N, 5.3%; F, 49.7%. $C_8H_9F_6NO$ requires: C, 38.6%; H, 3.6%; N, 5.6%; F, 45.8%); IR , NMR , mass spectra 64.

F. ADDITION OF AMIDES TO OCTAFLUOROCYCLOPENTENE.

1. N,N-DIMETHYLACETAMIDE.

A mixture of N,N-dimethylacetamide (7.5g , 86mmol) and octafluorocyclopentene (6.8g , 32mmol) was irradiated with gamma rays. The product was transferred under vacuum to give alkene (4.86g) and leave a liquid (9.18g). Water (25ml) was added to the liquid, the lower layer separated, washed twice with water (2 x 25ml), and distilled in vacuo to give N-(1,2,3,3,4,4,5,5-octafluorocyclopentyl)methyl-N-methylacetamide (95), (28%); b.p. 54°C at 0.1mmHg; (Found: C, 36.7%; H, 2.6%; N, 1.2%; F, 49.9%. $C_9H_9F_8NO$ requires: C, 36.1%; H, 3.0%; N, 4.7%; F, 50.8%); IR , NMR , mass spectra 65.

G. ADDITION OF AMIDES TO DECAFLUOROCYCLOHEXENE.

1. N,N-DIMETHYLACETAMIDE.

A mixture of N,N-dimethylacetamide (0.96g , 11mmol) and decafluorocyclohexene (1.42g , 5mmol) was irradiated with gamma rays. The product was dissolved in the minimum amount of acetone, excess water added, and ether extracted (3 x 50ml). The etherial solution was washed with water (3 x 20ml) and the solvent removed in vacuo.The remaining solid was re-crystallized (acetone) to give cis-N-(1,2,3,3,4,4,5,5,6,6-decafluorocyclohexyl)methyl-N-methylacetamide (94), (90%); m.p. 95-98°C; (Found: C, 34.4%; H, 2.9%; N, 4.0%; F, 57.6%. $C_{10}H_9F_{10}NO$ requires: C, 34.4%; H, 2.6%; N, 4.0%; F, 54.4%); IR , NMR , mass spectra 66.

2. N-METHYLPYRROLIDIN-2-ONE.

A mixture of N-methylpyrrolidin-2-one (7.1g , 78mmol) and decafluorocyclohexene (6.5g , 25mmol) was irradiated with gamma rays. The product was washed three times with water to leave a lower layer which was heated in vacuo. The remaining viscous liquid (4.28g) was composed of at least three components (GLC, column K, 180°C) which could not be separated by distillation, sublimation, or thin layer chromatography.

H. ADDITION OF AMIDES TO OCTAFLUOROBUT-2-ENE.

1. N,N-DIMETHYLACETAMIDE.

A mixture of N,N-methylacetamide (5.2g , 60mmol) and octafluorobut-2-ene (6.5g , 33mmol) was irradiated with gamma rays. The product was transferred under vacuum to give alkene(4.43g) and leave a liquid(7.02g). The liquid contained at least two adduct products (GLC/mass spectra, column K, 195°C) which could not be separated.

I. ADDITION OF AMIDES TO PERFLUORO-3,4-DIMETHYL-4-ETHYLHEX-2-ENE.

1. N,N-DIMETHYLACETAMIDE.

A mixture of N,N-dimethylacetamide (0.83g , 9.5mmol) and perfluoro-3,4-dimethyl-4-ethylhex-2-ene (2.37g , 4.7mmol) was irradiated with gamma rays. The product consisted of two layers that were separated and shown to be starting materials (GLC, column k, various temperatures).

J. ADDITION OF AMIDES TO PERFLUORO-2,3-DIMETHYLHEX-3-ENE.

1. N,N-DIMETHYLACETAMIDE.

A mixture of N,N-dimethylacetamide (0.93g , 10.7mmol) and perfluoro-2,3-dimethylhex-3-ene (2.05g , 5.1mmol) was irradiated with gamma rays. The product consisted of two layers that were separated and shown to be starting materials (GLC, column K, various temperatures).

2. N-METHYLPYRROLIDIN-2-ONE.

A mixture of N-methylpyrrolidin-2-one (4.1g , 41mmol) and perfluoro-3,4-dimethylhex-3-ene (5.6g , 14mmol) was irradiated with gamma rays. The product consisted of two layers that were separated and shown to be starting materials (GLC, column K, various temperatures).

K. MISCELLANEOUS ADDITIONS TO HEXAFLUOROPROPENE.

1. N,N,N',N'-TETRAMETHYLTHIOUREA.

A mixture of N,N,N',N'-tetramethylthiourea (5.86g , 44mmol) and hexafluoropropene (4.2g , 29mmol) was irradiated with gamma rays at 90°C. The product was transferred under vacuum to give a volatile component (3.93g) and leave a residue (5.85g). The residue was dissolved in acetone (20ml) , precipitated by water(50ml), the liquid decanted off, re-dissolved in acetone (20ml), re-precipitated by water (50ml), and filtered. Methanol (20ml) was added, the solid filtered, washed with methanol (3x20ml), and dried in vacuo to give a polymeric solid (100), (1.79g).

2. TETRAMETHYLGUANIDINE.

A mixture of tetramethylguanidine (9.7g , 84mmol) and hexafluoropropene (5.6g , 37mmol) was irradiated with gamma rays. The product was transferred under vacuum to give a volatile component (2.24g) and leave a liquid (11.99g). Acetone (20ml) was added to the liquid, the crystals (2.97g) filtered and recrystallized (acetone) to give an unassigned fluoride salt (101); m.p. 91-92°C; (Found; F, 17.6%); δ_F 119.0(s).

3. POLYVINYLPYRROLIDINONE.

A mixture of polyvinylpyrrolidinone (2.84g) and hexafluoropropene (12.3g 82mmol) was irradiated with gamma rays to a high dose (100Mrad). Excess alkene (9.51g) was transferred under vacuum to leave a solid (5.08g). The solid was refluxed with water for 1 hour, washed with water, and dried in vacuo to give compound (99), (Found: C, 33.2%; H, 1.2%; N, 3.4%; F, 52.1%).

L. MISCELLANEOUS ADDITIONS.

1. N,N,N',N',-TETRAMETHYLUREA TO PERFLUOROCYCLOHEXA-1,4-DIENE.

A mixture of N,N,N',N'-tetramethylurea (2.43g , 21mmol) and perfluorocyclohexa-1,4-diene (3.97g , 17mmol) was irradiated with gamma rays. The solid product was powdered, dissolved in acetone (20ml), precipitated with water (50ml), filtered, re-dissolved in acetone (20ml), and re-precipitated with water (50ml). The solid was washed with water, then petroleum ether, and dried in vacuo (P_2O_5) to give a polymer (98), m.p. >75°C (decomp.); (Found: C, 40.0%; H, 4.1%; N, 9.2%; F, 38.9%); IR , NMR , mass spectra 67.

CHAPTER 9

EXPERIMENTAL TO CHAPTER 4.

A. PURIFICATION OF REAGENTS.

Di -t-butyl peroxide was purified on an alumina column to remove traces of t-butyl hydroperoxide.

B. COMPETITION EXPERIMENTS WITH HEXAFLUOROPROPENE.

1. OXOLANE AND DIOXAN.

A mixture of oxolane (3.2g , 44mmol), dioxan (3.9g , 44mmol), and hexafluoropropene (2.4g , 16mmol) was irradiated with gamma rays. The product mixture was shown by comparison of GLC retention times (column K, 100°C) to consist of 2-(1,1,2,3,3,3-hexafluoropropyl)oxolane (21) only.

2. OXOLANE AND OXANE.

A mixture of oxolane (0.45g , 6.2mmol), oxane (0.53g , 6.2mmol), and hexafluoropropene (0.28g , 1.9mmol) was irradiated with gamma rays. The product mixture was shown by comparison of GLC retention times (column K, 95°C) to consist of 2-(1,1,2,3,3,3-hexafluoropropyl)oxolane (21) only.

3. DIOXAN AND 1,3,5-TRIOXAN.

A mixture of dioxan (6.04g , 69mmol), trioxan (6.18g , 69mmol), and hexafluoropropene (3.3g , 22mmol) was irradiated with gamma rays. The product mixture was shown by comparison of GLC retention times (column K, 95°C) to consist of 2-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dioxan (25) only.

C. ACETONE / t-BUTANOL RATIOS.

A mixture of di-t-butyl peroxide (approx. 0.1g) and substrate (10:1 molar excess) contained in a pyrex Carius tube (approx. 7ml) was degassed, sealed in vacuo, and heated at 120°C for 8hours. The product was analysed by GLC (column A, 85°C) using a gas density balanced detector and the proportion of acetone and t-butanol determined from the area of their respective peaks.

This procedure was used to determine the acetone/t-butanol ratios for all the substrates in Table 20 .

D. MECHANISM OF BORATE ADDITION TO FLUOROALKENES.

1. EXCHANGE OF TRIMETHYL BORATE WITH (1,2,3,3,4,4,5,5,6,6-DECAFLUOROCYCLOHEXYL)METHANOL (68).

A mixture of trimethyl borate (0.52g , 5.0mmol) and alcohol (68) (1.58g , 5.4mmol) was kept in a sealed Carius tube for 10 days. The tube was opened and the product distilled in vacuo to give tri((1,2,3,3,4,4,5,5-6,6-decafluorocyclohexyl)methyl) borate (65), (1.26g , 71%).

2. REACTION OF TRIMETHYL BORATE AND HEXAFLUOROPROPENE IN THE DARK.

A mixture of trimethyl borate (1.6g , 15mmol) and hexafluoropropene (1.4g , 9mmol) was kept in a sealed Carius tube in the dark for 7 days. The tube was opened and the starting materials were recovered.

3. ADDITION OF METHANOL TO HEXAFLUOROPROPENE.

A mixture of methanol (1.28g , 40mmol) and hexafluoropropene (2.6g , 17mmol) was irradiated with gamma rays to a dose of 1 Mrad. GLC (column K, 100°C) showed that the product contained an appreciable amount of 2,2,3,4,4,4-hexafluorobutan-1-ol (56),(retention time = 1.3mins)

4. ADDITION OF TRIMETHYL BORATE TO HEXAFLUOROPROPENE.

A mixture of trimethyl borate (5.57g , 54mmol) and hexafluoropropene (4.2g , 28mmol) was irradiated with gamma rays to a dose of 1 Mrad. The product was analysed by GLC. Using conditions of column K at 100°C no alcohol adduct (56) was present but there was a broad peak starting with a retention time of 2.6mins. Using conditions of column K at 155°C there was two peaks with retention times of 0.65min and 1.0mins but none of the borate tri-adduct (63) (retention time = 2.05mins).

5. ADDITION OF METHANOL AND TRIMETHYL BORATE TO HEXAFLUOROPROPENE.

A mixture of methanol (0.43g , 13mmol), trimethyl borate (4.86g , 47mmol) and hexafluoropropene (3.2g , 21mmol) was irradiated with gamma rays to a dose of 1 Mrad. The product was analysed by GLC. Using conditions of column K at100°C no alcohol adduct (56) was present but there was a broad peak starting with a retention time of 2.5mins. Using conditions of column K at 155°C there was two peaks with retention times of 0.6 and 0.95mins and none of the borate tri-adduct (63) (retention time= 2mins).

6. ADDITION OF METHANOL AND TRI-n-BUTYL BORATE TO HEXAFLUOROPROPENE.

A mixture of methanol (1.09g , 34mmol), tri-n-butyl borate (2.56g , 11mmol), and hexafluoropropene (5g , 33mmol) was irradiated with gamma rays to a dose of 10 Mrad. The product (8.58g) was added to water (20ml) and the lower fluorocarbon layer separated and analysed by GLC, column K at 140°C and 205°C. The product was composed of 2,2,3,4,4,4-hexafluorobutan-1-ol (56) (10%) , 1,1,1,2,3,3-hexafluoroheptan-4-ol (70) (38%), 1,1,1,2,3,3-hexafluoro-4-(1,1,2,3,3,3-hexafluoropropyl)heptan-4-ol (71) (16%), and unidentified products (35%).

CHAPTER 10

EXPERIMENTAL TO CHAPTER 5

A. PURIFICATION OF REAGENTS.

Chlorine was transferred under vacuum direct from a cylinder and was used without further purification.

B. HALOGENATION OF 2,2,3,4,4,4-HEXAFLUOROBUTYL METHYL ETHER (9).

1. CHLORINATION.

a. Neat.

Compound (9) (1.95g , 9.9mmol) contained in a Pyrex tube with rotoflo tap was degassed and chlorine (1.16g , 16mmol) introduced by vacuum transfer. The mixture was left in sunlight until the chlorine colour disappeared (30mins). The tap was opened with the contents frozen in liquid air and on warming, white fumes were given off to leave a colourless liquid (2.49g). Preparative GLC (column Z, 105°C) gave 1-chloro-2,2,3,4,4,4-hexafluorobutyl methyl ether (126), (6.8%); IR , NMR , mass spectra 68; 2,2,3,4,4,4-hexafluorobutyl chloromethyl ether (127), (45.5%); b.p. 133°C (Siwoloboff); (Found: C, 26.4%; H, 2.3%; F, 48.5%; Cl, 15.7%. $C_5H_5ClF_6O$ requires: C, 26.0%; H, 2.2%; F, 49.5%; Cl, 15.4%); IR , NMR , mass spectra 69; and a mixture of di-chlorinated species (128), (47.7%); (Found: C, 23.0%; H, 1.8%; F, 41.1%; Cl, 26.9%. $C_5H_4Cl_2F_6O$ requires: C, 22.6%; H, 1.5%; F, 43.0%; Cl, 26.8%); δ_H 4.37(m , $CF_2C\underline{H}_2O$) and 5.10(dm , $CF\underline{H}$) (3.76H), 5.70(0.6H , s , $OC\underline{H}_2Cl$), 7.48 (1H, s , $OC\underline{H}Cl_2$).

Repeat experiments gave (126)(12.7%),(127)(39.9%),(128)(47.4%) and (126)(13.5%),(127)(50.4%),(128)(36.1%) respectively.

b. Carbon Tetrachloride Solvent.

A mixture of compound (9) (0.99g , 5.0mmol), chlorine (0.51g , 7mmol), and carbon tetrachloride (3.11g , 20mmol) was left in sunlight for 1 hour.

The gaseous by-products were allowed to evaporate leaving a liquid. Comparison of GLC retention times(column A, 120°C) gave the chlorinated products (126)(4.8%) , (127)(49.5%) , and (128)(45.7%).

c. Perfluoromethyldecalin solvent.

A mixture of compound (9) (0.56g , 2.9mmol) , chlorine (0.1g , 1.4mmol), and perfluoromethyldecalin (4.59g , 9mmol) was left in sunlight for 30 mins. The gaseous by-products were allowed to evaporate leaving a liquid. Comparison of GLC retention times (column A, 120°C) gave the chlorinated products (126)(17.6%) , (127)(67.0%) , and (128)(15.4%).

d. Carbon Disulphide Solvent.

A mixture of compound (9) (1.04g , 5,3mmol) , chlorine (0.45g , 6.3mmol), and carbon disulphide (2.81g , 37mmol) was left in sunlight for one hour. The gaseous by-products were allowed to evaporate leaving a liquid. Comparison of GLC retention times (column A, 120°C) gave the chlorinated products (126)(16%) , (127)(76.5%) , and (128)(7.5%).

A repeat experiment using compound (9) (0.56g , 2.9mmol) , chlorine (0.07g , 1mmol) and carbon disulphide (2.14g , 28mmol) gave the chlorinated products (126)(19.9%) and (127)(80.1%) only.

e. Competitive Chlorination with 1,2,3,3,4,4,5,5-Octafluorocyclopentylmethoxymethane (122).

A mixture of compound (122) (0.55g , 2.8mmol) , compound (9) (0.72g, 2.8mmol) , and chlorine (0.1g , 1.4mmol) was left in sunlight for 15mins. The gaseous by-products were allowed to evaporate leaving a liquid. Comparison of GLC retention times (column A , 120°C) with authentic samples gave the composition of the product as (122)(55%) , (9)(31%) , (127)(9%) , and (128)(5%),(molar percentage composition).

2. CHLORINATION WITH IODINE MONOCHLORIDE.

A mixture of compound (9) (1.99g , 10mmol) and iodine monochloride (3.46g , 21mmol) contained in a rotoflo tube was left in sunlight for 36 hours, opened, and gaseous by-products allowed to evaporate. Water (10ml) was added to give a precipitate that dissolved in potassium iodide solution. The iodine was removed with sodium thiosulphate solution to leave a yellow solution. The aqueous solution was extracted with ether (3 x 50ml), dried ($MgSO_4$), and the ether removed in vacuo to leave a yellow oil. Comparison of GLC retention times (column A, 120°C) gave the chlorinated products (126) (1.6%) , (127) (49%) , (128) (10%) and an unknown compound (129) (39%) (possibly a dimer of (9) from GLC/mass spectrum).

3. BROMINATION.

a. Neat.

A mixture of (9) (1.94g , 9.9mmol) and bromine (2.04g , 12.8mmol) contained in a rotoflo tube was degassed and left in sunlight for 3 days. The tube was opened and gaseous by-products were allowed to evaporate to leave a yellow liquid (1.7g). Preparative GLC (column Z , 100°C) gave 1-bromo-2,2,3,4,4,4-hexafluorobutyl methyl ether (130), (12%); b.p. 134°C (Siwoloboff); (Found: C, 22.1%; H, 1.8%. $C_5H_5BrF_6O$ requires: C, 21.8%; H, 1.8%); IR , NMR , mass spectra 70; 2,2,3,4,4,4-hexafluorobutan-1-ol (56), (38%); and two unassigned dimers of (9), (131) (27%); (Found: C, 27.6%; H, 1.9%; Br, 0%; F, 58.8%. $C_{10}H_{10}F_{12}O_2$ requires: C, 30.8%; H, 2.6%; F, 58.5%); ν_{max} 2950, 2900, 2850, 1455, 1380, 1365, 1350, 1285, 1245, 1185, 1095, 1050, 998, 950, 890, 885, 839, 820, 796, 722, 708, 700, 688, 600, 530, 485 cm^{-1} ; δ_H 3.60(3H, s), 4.07(3H , m), 4.77(2H , m), 5.43(1H , m) and 5.60(1H , s); m/z 51 (39%), 61(75), 63(15), 69(32), 77(24), 81(10), 83(16), 95(54), 113(7), 145(11), 165(6) , 195(91), 225(100), 275(1), 337(1), 345(2), 357(1); and (132) (23%); (Found: C, 28.5%; H, 1.8%;

Br, 0%; F, 58.8%. $C_{10}H_{10}F_{12}O_2$ requires: C, 30.8%; H, 2.6%; F, 58.5%); ν_{max} 2955, 2905, 1480, 1460, 1418, 1400, 1379, 1365, 1286, 1230, 1185, 1165, 1130, 1100, 1053, 978, 950, 885, 840, 725, 689, 620, 605, 555, 530, 487 cm^{-1}; δ_H 3.87(2H , m), 4.77(1H , s), 5.00(1H , dm , J= 44 and 7), δ_F 76.7(3F , dq , J= 9 and 11), 120.4,122.4,117.3, and 125.7(2F , m), 216.6(1F, dm , J= 44); m/z 51(12%), 61(4), 69(9), 77(11), 83(6), 95(24), 123(7), 142(19), 165(2), 175(3), 195(100).

b. Carbon Disulphide Solvent.

A mixture of adduct (9) (0.3g , 1,5mmol), bromine (0.12g , 0.75mmol), and carbon disulphide (2.78g , 36.6mmol) contained in a rotoflo flask was degassed and left in sunlight for 72hours. The flask was opened and the gaseous products allowed to evaporate to leave a liquid. Comparison of GLC retention times (column A , 120°C) gave the products as 2,2,3,4,4,4-hexafluorobutan-1-ol (56) (9%), 1-bromo-2,2,3,4,4,4-hexafluorobutyl methyl ether (130) (81%), and the dimer (131) (9%).

c. Using Thermal Initiation.

A mixture of adduct (9) (0.79g , 4.6mmol) and bromine (0.39g , 2.4mmol), contained in a pyrex Carius tube was degassed and sealed in vacuo. The tube was heated at 220°C for 19 hours , opened, and the gaseous products allowed to evaporate to leave a liquid. Comparison of GLC retention times (column A, 120°C) gave the products as 2,2,3,4,4,4-hexafluorobutan-1-ol (56) (8%), 1-bromo-2,2,3,4,4,4-hexafluorobutyl methyl ether (130), (57%), and the dimer (131) (34%).

4. FLUORINATION.

A mixture of adduct (9) (2.46g , 12.5mmol) and Arcton 113 (55.05g) was placed in a flask assembled with a reflux condenser and an inlet bubbler of 'Fomblin' fluid connected to a nitrogen cylinder and an electrolytic fluorine cell. The apparatus had been previously flushed with nitrogen (100ml/min) for 30 mins, fluorine for 30mins, then nitrogen again for 10mins. The solution at room temperature was purged with nitrogen for 10mins then fluorine (2 Amp = 1.3g F_2/hr; used 22mins to give 0.48g, 12.5mmol). Nitrogen was passed for a further 10mins. No starting material remained (GLC, column a, 80°C) and preparative GLC (column Z, 80°C and 130°C) gave 2,2,3,4,4,4-hexa-fluorobutyl difluoromethyl ether (133) (18%), spectra identical to an authentic sample[7] ; 2,2,3,4,4,4-hexafluorobutyl fluoromethyl ether (134) (44%), IR , NMR , mass spectra 71 ; 2,2,3,4,4,4-hexafluorobutyl formate (55) (20%); and 2,2,3,4,4,4-hexafluorobutan-1-ol (56) (7%).

C. OXIDATIVE CHLORINATION.

1. TRI(2,2,3,4,4,4-HEXAFLUOROBUTYL) BORATE (63).

a. With Sunlight.

A mixture of borate (63) (0.57g , 1mmol) and chlorine (6.11g , 86mmol) contained in a rotoflo tube, was sealed in vacuo, and left in sunlight for 4 hours. The gaseous by-products were allowed to evaporate leaving a liquid (0.57g). The liquid was transferred under vacuum with heating to leave a white solid. The volatile product was further transferred under vacuum at 0°C to give 2,2,3,4,4,4-hexafluorobutanoyl chloride (138), (25%); (Found: C, 22.4%; H, 0.7%; Cl, 16.1%; F, 49.8%. C_4HClF_6O requires: C, 22.4%; H, 0.5%; Cl, 16.5%; F, 53.1%); IR , NMR , mass spectra 72.

b. With Ultra Violet Light.

A mixture of borate (63) (0.97g , 1.8mmol) and chlorine (6.61g , 93mmol) contained in a rotoflo tube was degassed and sealed in vacuo. The tube was irradiated with a high pressure ultra violet lamp for 1 hour and then opened to allow gaseous components to evaporate leaving a liquid residue. This liquid was transferred under vacuum at 18°C to give mainly 2,2,3,4,4,4-hexafluorobutanoyl chloride (138), (0.85g , 75%).

2. TRI((1,2,3,3,4,4,5,5,6,6-DECAFLUOROCYCLOHEXYL)METHYL) BORATE (65).

a. With Sunlight.

A mixture of borate (65) (0.46g , 0.5mmol) and chlorine (6.77g , 95mmol) contained in a rotoflo tube was sealed in vacuo. The tube was left in sunlight for 30 mins, opened, and the gaseous components allowed to evaporate leaving a liquid. The liquid was transferred under vacuum at 18°C to give 1,2,3,3,4,4,5,5,6,6-decafluorocyclohexylmethanoyl chloride (139) (mixture of isomers) (0.43g , 85%); (Found: C, 25.9%; H, 0%; Cl, 13.4%; F, 59.4%. $C_7HClF_{10}O$ requires: C, 25.7%; H, 0.3%; Cl, 10.9%; F, 58.2%); IR , NMR , mass spectra 73 ; and leave a white residue (0.05g).

b. With Ultra Violet Light.

A mixture of borate (65) (0.68g , 0.8mmol) and chlorine (6.06g , 85mmol) contained in a rotoflo tube was irradiated with a high pressure ultra violet lamp for 2 hours, opened, and the gaseous components allowed to evaporate. The remaining liquid was transferred under vacuum at 18°C to give acid chloride (139) (0.62g , 83%) (mixture of isomers).

3. TRI((1,2,3,3,4,4,-HEXAFLUOROCYCLOBUTYL)METHYL) BORATE (64).

a. With Sunlight.

A mixture of borate (64) (1.07g , 1.8mmol) and chlorine (6.93g , 98mmol) contained in a rotoflo tube was sealed in vacuo and left in sunlight for 20mins. The tube was opened and gaseous components allowed to evaporate leaving a liquid (1.14g). The liquid was transferred under vacuum to give nothing at 18°C but with heating gave a small amount of 1,2,3,3,4,4-hexafluorocyclobutyl methanoyl chloride (140), (0.2g , 16%); (Found: C, 26.8%; H, 0.7%; Cl, 14.6%; F, 50.8%. C_5HClF_6O requires: C, 26.5%; H, 0.4%; Cl, 15.7%; F, 50.3%); IR , NMR , mass spectra 74 ; and a viscous residue.

b. With Ultra Violet Light.

A mixture of borate (64) (0.75g , 1.3mmol) and chlorine (10.34g , 146mmol) contained in a rotoflo tube was sealed in vacuo and irradiated with a high pressure ultra violet lamp for 1 hour. The tube was opened and the gaseous components allowed to evaporate leaving a liquid. The liquid was transferred under vacuum at 18°C to give a volatile component (0,73g). Preparative GLC (column K, 18°C) gave 3-chloro-hexafluorocyclobutyl methanoyl chloride (141) (63%); (Found: C, 22.3%; Cl, 24.7%; F, 44.4%; $C_5Cl_2F_6O$ requires: C, 23.0%; Cl, 27.2%; F, 43.7%); IR , NMR , mass spectra 75.

4. TRI(2-PENTAFLUOROETHYL-4,4,5,5,5-PENTAFLUORO-2,3-DI(TRIFLUOROMETHYL)-PENTYL) BORATE (66).

a. With Sunlight.

A mixture of borate (66) (0.75g , 0.6mmol) and chlorine (3.9g , 55mmol) contained in a rotoflo tube was sealed in vacuo and left in sunlight for 3 hours. The tube was opened and the gaseous components allowed to evaporate leaving a liquid. The liquid was transferred under vacuum and preparative GLC (column K, 75°C) gave a small amount of 3-chloro-3,4-di-(trifluoromethyl)-1,1,1,2,2,5,5,6,6,6-decafluorohexane (142), (1%); b.p. 127°C (Siwoloboff); (Found: C, 21.6%; H, 0%; Cl, 10.2%; F, 68.2%. C_8HClF_{16} requires: C, 22.0%; H, 0.2%; Cl, 8.1%; F, 69.6%); IR , NMR , mass spectra 76.

b. With Ultra Violet Light.

A mixture of borate (66) (0.92g , 0.7mmol) and chlorine (5.12g , 72mmol) contained in a rotoflo tube was sealed in vacuo and irradiated with a high pressure ultra violet lamp for 2 hours . The tube was opened and the gaseous components allowed to evaporate leaving a liquid. The liquid was transferred under vacuum to give a volatile component (0.89g) and preparative GLC (column K, 75°C) gave compound (142), (87%).

5. 1,2,3,3,4,4,5,5,6,6-DECAFLUOROCYCLOHEXYLMETHANOL. (68).

A mixture of alcohol (68) (1.51g , 5.1mmol) and chlorine (8.59g , 121mmol) contained in a rotoflo tube was sealed in vacuo and irradiated with a high pressure ultra violet lamp for 1 hour. The tube was opened and the gaseous components allowed to evaporate leaving a liquid. The liquid was transferred under vacuum at 18°C to give a volatile component (1.48g) and leave a residue (0.13g). The volatile component was shown by comparison of GLC retention times (column K, 75°C) to be mainly 1,2,3,3,4,4,5,5,6,6-decafluorocyclohexylmethanoyl chloride (139), (86%), isomer mixture.

6. 1,2,3,3,4,4-HEXAFLUOROCYCLOBUTYLMETHANOL (72).

A mixture of alcohol (72) (1.23g , 6.3mmol) and chlorine (9.04g , 127mmol) contained in a rotoflo tube was sealed in vacuo and irradiated with a high pressure ultra violet lamp for 1 hour. The tube was opened and the gaseous components allowed to evaporate leaving a liquid. The liquid was transferred under vacuum to give a volatile component (0.72g) and a residue (0.74g). Preparative GLC (column K, 18°C) of the volatile component gave 1,2,3,3,4,4-hexafluorocyclobutyl methanoyl chloride (140) (17%) and 2-chlorohexafluorocyclobutyl methanoyl chloride (141),(26%).

7. 1,1,3-TRIHYDROTETRAFLUOROPROPAN-1-OL (143).

A mixture of alcohol (143) (2.92g , 22mmol) and chlorine (11.1g , 156mmol) contained in a rotoflo tube was sealed in vacuo and irradiated with a high pressure ultra violet lamp for 3 hours. The tube was opened and the gaseous components allowed to evaporate leaving a liquid. The liquid was transferred under vacuum at 18°C to give 3-chlorotetrafluoropropanoyl chloride (144), (2.22g , 50%); (Found: C, 17.9%; Cl, 36.0%; F, 37.6%. Calc. for $C_3Cl_2F_4O$[153] : C, 18.1%; Cl, 35.7%; F, 38.2%); IR , NMR , mass spectra 77, a less volatile mixed fraction (0.94g), and a residue (0.38g).

8. 1,1,11-TRIHYDROEICOSAFLUOROUNDECAN-1-OL (145).

A mixture of alcohol (145) (10.33g , 19.4mmol) and chlorine (14.06g , 198mmol) contained in a rotoflo flask was sealed in vacuo and irradiated with a high pressure ultra violet lamp for 2.5 hours. The flask was opened and the gaseous components allowed to evaporate leaving a white solid. The solid was powdered and volatile impurities removed in vacuo to give 11-chloroeicosafluoroundecanoyl chloride (146), (11.49g); (Found: C, 21.8%; Cl, 11.3%; F, 62.8%. Calc. for $C_{11}Cl_2F_{20}O$ [154] :C, 22.0%; Cl, 11.8%; F, 63.4%); IR , NMR , mass spectra 78 . The purity of compound (146) was determined by two volumetric methods.

(i) Compound (146) (0.3974g) was added to distilled water (50ml) and left for 2 hours with occasional stirring. The solution was titrated with sodium hydroxide solution (0.115M , 9.9cm^3) using methyl red indicator. Therefore 1.138mmol of acid have been produced from a possible 1.327mmol, giving a purity of 86%.

(ii) Compound (146) (0.3974g) was added to sodium hydroxide solution (15ml , 0.115M) and distilled water (25ml) and left with occasional stirring until the solid had dissolved. The solution was titrated with hydrochloric acid (0.2050M , 2.65ml) using phenolphthalein indicator. Therefore compound (146) has 89% of available acid chloride groups.

9. 1,1,5-TRIHYDROOCTAFLUOROPENTAN-1-OL (147).

A mixture of alcohol (147) (1.81g , 7.8mmol) and chlorine (7.89g , 111mmol) contained in a rotoflo tube was sealed in vacuo and irradiated with a high pressure ultra violet lamp for 3.5 hours. The tube was opened and the gaseous components allowed to evaporate . The remaining liquid was transferred under vacuum with heating to give a mixture of products (GLC, column K, 70°C) which was not investigated further.

D. DEHYDRODIMERISATION.

1. 2,2,3,4,4,4-HEXAFLUOROBUTYL METHYL ETHER (9).

a. Using Di-t-butyl peroxide.

i. At 120°C.

A mixture of adduct (9) (0.48g , 2.5mmol) and di-t-butyl peroxide (0.41g , 2.8mmol) contained in a Carius tube was degassed and sealed in vacuo. The tube was heated at 120°C for 24 hours after which the product was transferred under vacuum to give a volatile component (0.64g) and a residue (0.22g). The residue was a mixture with an indication of some dimer products (GLC/mass spectra, column K, 115°C); m/z 239(4%), 209(5), 195(25).

ii. At 160°C.

A mixture of adduct (9) (1.1g , 5.6mmol) and di-t-butyl peroxide (0.1g , 1.4mmol) contained in a Carius tube was degassed, sealed in vacuo, and heated at 160°C for 22 hours. The liquid product (0.96g) consisted of adduct (9) and no indication of any dimer products (GLC, column A, 120°C).

b. USing Benzoyl Peroxide.

A mixture of adduct (9) (1.07g , 5.5mmol) and benzoyl peroxide (0.05g) contained in a Carius tube was degassed, sealed in vacuo, and heated at 80°C for 22 hours. The liquid product consisted mainly of adduct (9) by GLC (column A, 115°C).

2. 2-(1,1,2,3,3,3-HEXAFLUOROPROPYL)-1,4-DIOXAN (25).

A mixture of adduct (25) (0.91g , 3.8mmol) and di-t-butyl peroxide (0.12g , 0.8mmol) contained in a carius tube was degassed, sealed in vacuo, and heated at 120°C for 7 hours. The liquid product (0.94g) consisted only of adduct (25) by GLC (column K, 115°C).

3. 1,4-DIOXAN.

A mixture of 1,4-dioxan (10.02g , 114mmol) and di-t-butyl peroxide (4.39g , 30mmol) contained in a Carius tube was degassed, sealed in vacuo, and heated at 120°C for 8 hours. The product was filtered and washed (acetone) to give crystals of 2,2'-Di(1,4-dioxanyl) , (156), (2.5g , 25%); m/z 175 (2%, M^+-H), 87(100%).

4. DI-(1-METHYL-2,2,3,4,4,4-HEXAFLUOROBUTYL) ETHER (11).

A mixture of adduct (11) (2.5g , 17mmol) and di-t-butyl peroxide (1.45g , 10mmol) contained in a Carius tube was degassed, sealed in vacuo, and heated at 160°C for 55 hours. The liquid product (3.94g) consisted of adduct (11) and no indication of dimers by GLC (column K, 140°C).

CHAPTER 11

EXPERIMENTAL TO CHAPTER 6

A. FLUORINATION USING COBALT TRIFLUORIDE.

1. GENERAL PROCEDURE.

Tha apparatus for cobalt trifluoride fluorination is illustrated in Figure 8. A mixture of cobalt trifluoride (150g) and calcium difluoride (150g) was used in the reactor and the general procedure involved heating the reactor to the required temperature with continual stirring of the paddles. Dry nitrogen (50ml/min) was passed through the reactor for 10mins prior to use. The collection trap was cooled with liquid air and the reactant dropped into the reactor at a rate of 1ml/10mins and with a nitrogen flow (50ml/min). After all the reactant had been added the reactor was flushed out with nitrogen for 10mins, then the collection trap removed and left to warm up in an efficient fume cupboard. Anhydrous sodium carbonate or sodium fluoride was added to remove hydrogen fluoride and the product pipetted out or transferred under vacuum.

2. REGENERATING THE REACTOR.

The cobalt trifluoride must be regenerated from cobalt difluoride after fluorination. This was achieved by passing fluorine gas from a fluorine cell via a copper pipe through the heated reactor ($>300^{\circ}C$) until detected at the reactor outlet using starch/iodide paper (white to blue).

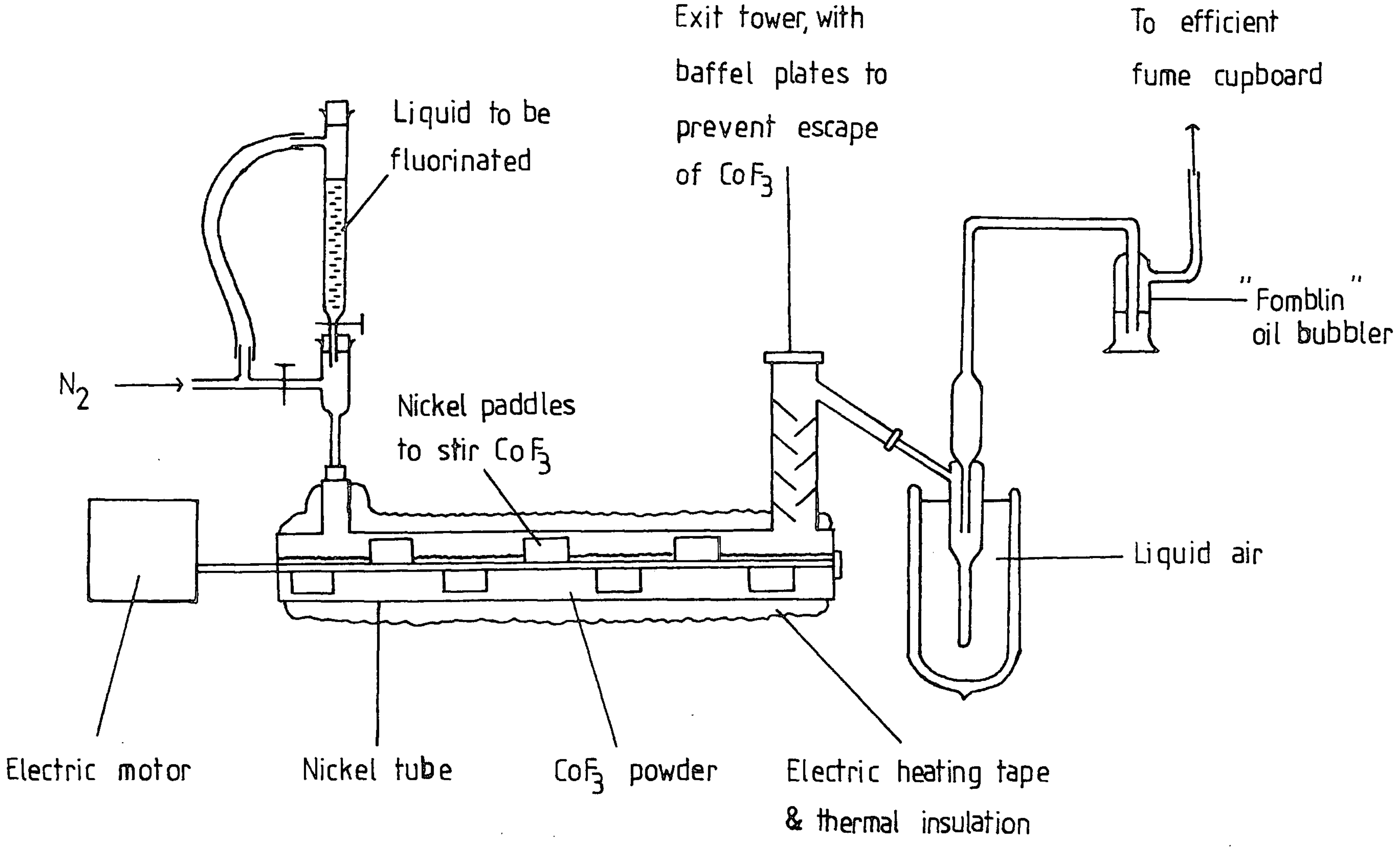
B. FLUORINATION OF 2-(1,1,2,3,3,3-HEXAFLUOROPROPYL)OXANE (22).

1. AT 190°C.

Adduct (22) (5.97g, 25mmol) was passed over the fully charged cobalt trifluoride bed at 190°C. The product (214) consisted of a complex mixture of polyfluorinated oxanes (GLC/Mass spectra, column A, 120 °C) which

FIGURE 8

A COBALT TRIFLUORIDE FLUORINATOR



were not separated.

The experiment was repeated with mixture (214) using a re-charged cobalt trifluoride bed. The product (215) consisted of a similar complex mixture of polyfluorinated oxanes (GLC/mass spectra , column A, 120°C) as mixture (214).

2. AT 250°C.

Mixture (215) was passed over a fully charged cobalt trifluoride bed at 250°C. The product (216) consisted of a complex mixture of polyfluorinated oxanes (GLC/mass spectra , column A, 120°C) but with a higher degree of fluorination than mixture (215).

3. AT > 300°C.

Mixture (216) was passed over a fully charged cobalt trifluoride bed at > 300°C. The product (217) (3.70g) consisted of one main component (GLC/mass spectra , column A, 120°C).

4. AT 380°C.

Adduct (22) was passed over a fully charged cobalt trifluoride bed at 380°C. Preparative GLC (column A, 80°C) of the product (1.96g) gave a pure sample of the main component, perfluoro-2-propyloxane (156), (60%); (Found: C, 20.1%; F, 73.4%. Calc. for $C_8F_{16}O$[16]: C, 23.1%; F, 73.1%); IR , NMR , mass spectra 79.

C. FLUORINATION OF 2-(1,1,2,3,3,3-HEXAFLUOROPROPYL)OXOLANE (21).

1. AT 440°C.

Adduct (21) (1.93g , 8.7mmol) was passed over cobalt trifluoride at 440°C. Preparative GLC (column A, 20°C) of the product (2.27g) gave perfluoro-2-propyloxolane (157) (70%); b.p. 79°C; (Found: C, 22.8%; F, 72.5%. Calc. for $C_7F_{14}O$[16] : C, 22.9%; F, 72.7%); IR , NMR , mass spectra 80; and perfluorohexane (158), (3%); b.p. 60°C (lit.,[4] 57°C); (Found: C, 21.4%. Calc. for C_6F_{14} : C, 21.3%); IR, NMR, mass spectra 81, as the two main products.

2. AT 355°C.

Adduct (21) (2.82g , 13mmol) was passed over cobalt trifluoride at 355°C. Preparative GLC (column A, 100°C) of the product (3.24g) gave the perfluoroether (157) (23.1%) , a mixture of 2-(1,1,2,3,3,3-hexafluoropropyl)heptafluorooxolane and 2-heptafluoropropylhexafluoro-oxolane (159), (17.9%) (Found: 23.4%, H,0%; F, 69.2%. $C_7F_{13}HO$ requires: C, 24.1%; H, 0.3%; F, 71.0%); m/z 329(7%, M^+-F), 197(30, $C_4F_7O^+$), 179(26, $C_4F_6HO^+$); δ_F 216.2 and 213.3 (1F , m , $C\underline{F}H$), 81.7 (m, $C\underline{F}_3CF_2$) , 74.2 (m , $C\underline{F}_3CFH$), a mixture of two isomers of 2,5,5-trifluoro-2-(heptafluoropropyl)trifluorooxolane (160), (8.5%); (Found: C, 24.3%; H, 0%; F, 67.3%. $C_7F_{13}HO$ requires: C, 24.1%; H, 0.3%; F, 71.0%); m/z 329(0.8%, M^+-F), and 2,3,3,4,5,5-hexafluoro-2-(heptafluoropropyl)oxolane (161) (5.7%); (Found: C, 24.4%; H, 0%; F, 71.2%. $C_7F_{13}HO$ requires: C, 24.1%; H, 0.3%;F, 71.0%); IR , NMR , mass spectra 82, as the major components. The minor components were assigned by GLC/mass spectra as shown in Table 28 .

3. AT 270°C.

Adduct (21) (3.55g , 16mmol) was passed over cobalt trifluoride at 270°C to give a liquid product (3.69g , 70%). GLC/mass spectra (column A, 110°C)were used to determine the extent of fluorination and the yield of each component of the product mixture as shown in Table 28 .

4. AT 240°C.

Adduct (21) (5.1g , 23mmol) was passed over cobalt trifluoride at 240°C to give a liquid product (5.67g , 79%). GLC/mass spectra (column A , 110°C) were used to analyse the product mixture as shown in Table 28 .

5. AT 180°C.

Adduct (21) (2.40g , 10.8mmol) was passed over cobalt trifluoride at 180°C to give a liquid product (1.66g , 49%). GLC/ mass spectra (column A, 110°C) were used to analyse the product mixture as shown in Table 28 .

6. AT 110°C.

Adduct (21) (1.75g , 7.9mmol) was passed over cobalt trifluoride at 110°C to give a liquid product (0.7g , 30%). Preparative GLC (column A, 125°C) gave 2,5,5-trifluoro-2-(1,1,2,3,3,3-hexafluoropropyl)oxol-3-en (162), mixture of isomers, (10.4%); IR , NMR , mass spectra 83, 2,3,4,5-tetrafluoro-2-(1,1,2,3,3,3-hexafluoropropyl)oxolane (163), (3.4%); IR , NMR , mass spectra 84, a mixture of isomers of trifluoro-2-(1,1,2,3,3,3-hexafluoropropyl)oxolanes (164), (2.2%); m/z 257(1.3%, M^+-F), 125 (23, $C_4F_3H_4O^+$), 77(100); IR , NMR , mass spectra 85, and a mixture of isomers of difluoro-2-(1,1,2,3,3,3-hexafluoropropyl)oxolanes (165), (4.1%); m/z 239(0.9%, M^+-F), 107(46, $C_4F_2H_5O^+$), 59(100); IR , NMR , mass spectra 86, as the major components. GLC/mass spectra were used to analyse the minor components as shown in Table 28 .

D. FLUORINATION OF 2,2,3,4,4,4-HEXAFLUORO-1-METHYLBUTYL ETHYL ETHER (10).

1. AT 440°C.

Adduct (10) (0.56g , 2.6mmol) was passed over cobalt trifluoride at 440°C. Preparative GLC (column A , 18°C) of the product (0.56g) gave the major component as perfluoro-1-methylbutyl ethyl ether (168), (43%); b.p. 78°C (Siwoloboff); (Found: C, 20.0%; F, 74.5%. $C_7F_{16}O$ requires: C, 20.8%; F, 75.2%); IR , NMR , mass spectra 87 and the minor component as perfluoropentane (169) (10%).

2. AT 410°C.

Adduct (10) (3.02g , 13.5mmol) was passed over cobalt trifluoride at 410°C. No components were isolated from the product mixture (2.07g) but GLC/mass spectra (column A, 110°C) were used to determine the degree of fluorination and yield of each component as shown in Table 29 .

3. AT 320°C.

Adduct (10) (2.47g , 11mmol) was passed over cobalt trifluoride at 320°C to give a liquid product (1.95g). GLC/mass spectra were used to determine the extent of fluorination and yield of each component of the product mixture as shown in Table 29 .

4. AT 240°C.

Adduct (10) (1.55g , 6,9mmol) was passed over cobalt trifluoride at 240°C. The product mixture (1.4g) was analysed by GLC/mass spectra as shown in Table 29 .

E. FLUORINATION OF 2-(1,1,2,3,3,3-HEXAFLUOROPROPYL)-1,4-DIOXAN (25).

1. AT 440°C.

Adduct (25) (2.17g , 9mmol) was passed over cobalt trifluoride at 440°C. Preparative GLC (column A , 18°C) of the product (2.55g) gave perfluoropropyl-1,4-dioxan (170), (68%); b.p. 90°C (Siwoloboff); (Found: C, 21.6%; F, 66.9%. $C_7F_{14}O_2$ requires: C, 22.0%; F, 69.6%); IR , NMR , mass spectra 88, as the major product.

2. AT 370°C.

Adduct (25) (3.71g , 16mmol) was passed over cobalt trifluoride at 370°C. Preparative GLC (column A , 100°C) of the product (3.97g) gave the two main components as the perfluoroether (170) (36%) and 1,1,2,3,3,3-hexafluoropropylheptafluoro-1,4-dioxan (171), (21%); b.p. 101°C (Siwoloboff); (Found: C, 23.5; F, 64.4%; H, 0%. $C_7F_{13}HO_2$ requires: C, 23.1%; H, 0.3%; F, 67.9%); IR , NMR , mass spectra 89. GLC/mass spectra were used to assign the degree of fluorination and yield of the minor components as shown in Table 30 .

3. AT 240°C.

Adduct (25) (3.37g , 14mmol) was passed over cobalt trifluoride at 240°C. Preparative GLC (column A , 130°C) of the product (3.62g) gave the major components as the perfluoroether (170) (4.7%), compound (171) (20.1%), 2,3,5,5,6,6-hexafluoro-2-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dioxan (172), (isomer A) (8.5%); b.p. 106°C (Siwoloboff); (Found: C, 23.8%; H, 0.4%; F, 65.6%. $C_7F_{12}H_2O_2$ requires: C, 24.3%; H, 0.6%; F, 65.9%); IR, NMR, mass spectra 90, 2,3,5,5,6,6-hexafluoro-2-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dioxan (173), (isomer B) (6.1%); b.p. 113°C (Siwoloboff); (Found: C, 24.3%; H, 0.8%; F, 66.1%. $C_7F_{12}H_2O_2$ requires: C, 24.3%; H, 0.6%; F, 65.9%); IR, NMR, mass spectra 91, 2,3,5,5,6,6-hexafluoro-2-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dioxan (174), (isomer C) (5.2%); b.p. 116°C (Siwoloboff); (Found: C, 21.1%; H, 0.6%. $C_7F_{12}H_2O_2$ requires: C, 24.3%; H, 0.6%), 2,3,3-trifluoro-2-(1,1,2,3,3,3-hexafluoropropyl)-trifluoro-1,4-dioxan (175), (isomer A) (3.7%); IR, NMR, mass spectra 93, 2,3,3-trifluoro-2-(1,1,2,3,3,3-hexafluoropropyl)trifluoro-1,4-dioxan, (176), (isomer B) (6.8%); IR, NMR, mass spectra 94, and 2,3,3-trifluoro-2-(1,1,2,3,3,3-hexafluoropropyl)trifluoro-1,4-dioxan (177) (isomer C), (2.4%); IR, NMR, mass spectra 95. GLC/mass spectra (column A, 110°C) were used to assign the degree of fluorination and yield of the minor components as shown in Table 30.

4. AT 130°C.

Adduct (25) (2.89g, 12mmol) was passed over cobalt trifluoride at 130°C. The product (1.58g) was a complex mixture of components and GLC/mass spectra (column A, 110°C) were used to assign the degree of fluorination and yield of each component as shown in Table 30.

F. FLUORINATION OF ACYCLIC ETHER ADDUCTS AT 440°C.

1. 2,2,3,4,4,4-HEXAFLUOROBUTYL METHYL ETHER (9).

Adduct (9) (2.04g, 10.4mmol) was passed over cobalt trifluoride at 440°C. Anhydrous sodium fluoride (5g) was put into the trap which was kept at liquid air temperature. The trap was warmed to -40°C (dry ice/acetone bath) for one hour and the products (2.57g) transferred under vacuum into a flask (one litre, containing a rubber septum). GLC/mass spectra (column A, -10°C) of the gaseous product gave perfluoro butyl methyl ether (178) (36%); mass spectrum 96 , and perfluorobutane (179), (44%); mass spectrum 97.

2. 1-ETHYL-2,2,3,4,4,4-HEXAFLUOROBUTYL PROPYL ETHER (12).

Adduct (12) (0.33g , 1.3mmol) was passed over cobalt trifluoride at 440°C. Preparative GLC (column A, 20°C) of the product (0.24g) gave perfluoro-1-ethylbutyl propyl ether (180), (32%); b.p. 137°C (Siwoloboff); (Found: C, 20.8%; F, 75.3%. $C_9F_{20}O$ requires: C, 21.4%; F, 75.4%); IR , NMR , mass spectra 98 , and a more volatile compound (8%) (insufficient for analysis).

3. 1-PROPYL-2,2,3,4,4,4-HEXAFLUOROBUTYL BUTYL ETHER (14).

Adduct (14) (0.56g , 2mmol) was passed over cobalt trifluoride at 440°C. Preparative GLC (column A, 70°C) of the product (0.35g) gave perfluoro-1-propylbutyl butyl ether (182), (18%); b.p. 149°C (Siwoloboff); (Found: C, 21.1%; F, 75.9%. $C_{11}F_{24}O$ requires: C, 21.8%; F, 75.5%); IR , NMR , mass spectra 99, and perfluoroheptane (181) (10%); IR , NMR , mass spectra 100.

4. DI-(1-METHYL-2,2,3,4,4,4-HEXAFLUOROBUTYL) ETHER (11).

Adduct (11) (2.07g , 5.5mmol) was passed over cobalt trifluoride at 440°C. Preparative GLC (column K, 90°C) of the product (1.68g) gave perfluoro-di(1-methylbutyl) ether (183), (41%); b.p. 136°C (Siwoloboff); (Found: C, 22.0%; F, 72.5%. $C_{10}F_{22}O$ requires: C, 21.7%; F, 75.4%); IR , NMR , mass spectra 101, and perfluoropentane (169) (9%); IR , NMR , mass spectra 102.

5. DI-(1-ETHYL-2,2,3,4,4,4-HEXAFLUOROBUTYL) ETHER (13).

Adduct (13) (1.77g , 4.4mmol) was passed over cobalt trifluoride at 440°C. Preparative GLC (column A, 120°C) of the product (1.15g) gave perfluoro-di(1-ethylbutyl) ether (184), (12%); b.p. 162°C (Siwoloboff); (Found: C, 21.9%; F, 74.0%. $C_{12}F_{26}O$ requires: C, 22.0%; F, 75.5%); IR , NMR , mass spectra 103, and perfluorohexane (158) (30%).

6. DI(1-PROPYL-2,2,3,4,4,4-HEXAFLUOROBUTYL) ETHER (15).

Adduct (15) (1.93g , 4.5mmol) was passed over cobalt trifluoride at 440°C. The product (1.3g) was a mixture of components and the major one was isolated by preparative GLC (column A, 60°C) and identified as perfluoroheptane (181) (32%).

7. 1-PROPYL-2,2,3,4,4,4-HEXAFLUOROBUTYL 1-PROPYL-1-(1,1,2,3,3,3-HEXAFLUOROPROPYL)-2,2,3,4,4,4-HEXAFLUOROBUTYL ETHER (16).

Adduct (16) (1.68g , 2.9mmol) was passed over cobalt trifluoride at 440°C. Preparative GLC (column A, 18°C) of the product (1.21g) gave perfluoroheptane (181) (26%) as the main component.

8. 2-METHOXY-3,3,4,5,5,5-HEXAFLUOROPROPYL METHYL ETHER (185).

Adduct (185) (2.08g , 8.7mmol) was passed over cobalt trifluoride at 440°C. Most of the product evaporated from the trap on warming,however a liquid (0.33g) remained which was composed of a mixture of compounds (GLC, column A, 20°C) that were not separated.

G. FLUORINATION OF CYCLIC ETHER ADDUCTS AT 440°C.

1. 2-(1,1,2,3,3,3-HEXAFLUOROPROPYL)OXEPANE (24).

Adduct (24) (1.63g , 6.5mmol) was passed over cobalt trifluoride at 440°C. Preparative GLC (column A, 65°C) of the product (1.98g) gave perfluoro-2-propyloxepane (186), (45%); b.p. 124°C (Siwoloboff); (Found: C, 22.6%; F, 76.9%. $C_9F_{18}O$ requires: C, 23.2%; F, 73.4%); IR , NMR , mass spectra 104, and perfluoro-octane (187), (12%); b.p. 103°C (Siwoloboff); (Found: C, 20.9 %; F, 78.5%. Calc. for C_8F_{18} : C, 21.9%; F, 78.1%); IR , NMR , mass spectra 105.

2. 2-(1,1,2,3,3,3-HEXAFLUOROPROPYL)OXETANE (20).

Adduct (20) (2.22g , 10.7mmol) was passed over cobalt trifluoride at 440°C. GLC/mass spectra (column A, 18°C) of the volatile product (0.71g) gave perfluoropentane (169) (3%) , perfluorohexane (158) (10%) , and perfluoro-2-propyloxetane (188) (8.5%); mass spectrum 106.

3. 2- and 5-METHYL-2-(1,1,2,3,3,3-HEXAFLUOROPROPYL)OXOLANE.

a) A mixture of 2- and 5-methyl-2-(1,1,2,3,3,3-hexafluoropropyl)oxolane (54% and 48% respectively) (1.63g , 6.9mmol) was passed over cobalt trifluoride at 440°C. Preparative GLC (column A, 20°C) of the product (1.9g) gave perfluoro-2-methyl-5-propyloxolane (190), (25%); b.p. 94°C (Siwoloboff); (Found: C, 22.5%. Calc. for $C_8F_{16}O$[155]: C, 23.1%); IR , NMR , mass spectra 107, perfluoro-2-methyl-2-propyloxolane (189), (18%); b.p. 101°C (Siwoloboff); (Found: C, 22.8%. $C_8F_{16}O$ requires: C, 23.1%); IR , NMR , mass spectra 108, and perfluoro-3-methylhexane (191), (10%), IR , NMR , mass spectra 109, as the main components.

b) A mixture of 2- and 5-methyl-2-(1,1,2,3,3,3-hexafluoropropyl)oxolane (90% and 10% respectively) (1.41g , 6mmol) was passed over cobalt trifluoride at 440°C. The products (1.15g) were identified by comparison of spectra as (190) (5%) , (189) (15%) , and (191) (11%).

4. 2-(1-TRIFLUOROMETHYL-1,2,3,3,3-PENTAFLUOROPROPYL)OXOLANE (41).

Adduct (41) (2.03g , 7.5mmol) was passed over cobalt trifluoride at 440°C. Preparative GLC (column A, 100°C) of the product (1.96g) gave perfluoro-2-(1-methylpropyl)oxolane (192), (53%); b.p. 101°C (Siwoloboff); (Found: C, 23.3%; F, 76.0%. $C_8F_{16}O$ requires: C, 23.1%; F, 73.1%); IR , NMR , mass spectra 110.

5. 2-(1,2,3,3,4,4,5,5,6,6-DECAFLUOROCYCLOHEXYL)OXOLANE (38).

Adduct (38) (2.42g , 7.2mmol) was passed over cobalt trifluoride at 440°C. Preparative GLC (column A, 65°C) of the product (2.73g) gave perfluoro-2-cyclohexyloxolane (193), (51%); b.p. 136°C (Siwoloboff); (Found: C, 24.9%; F, 71.9%. $C_{10}F_{18}O$ requires: C, 25.1%; F, 71.6%); IR , NMR , mass spectra 111, and perfluoropropylcyclohexane (194), (6%); IR , NMR , mass spectra 112.

6. 2-(1,2,3,3,4,4,5,5-OCTAFLUOROCYCLOPENTYL)OXOLANE (39).

Adduct (39) (1.87g , 6.6mmol) was passed over cobalt trifluoride at 440°C. Preparative GLC (column A, 80°C) of the product (2.22g) gave perfluoro-2-cyclopentyloxolane (195), (65%); b.p. 117°C (Siwoloboff); (Found: C, 24.7%; F, 76.0%. $C_9F_{16}O$ requires: C, 25.2%; F, 71.0%); IR , NMR , mass spectra 113, and perfluoropropylcyclopentane (196) (11%); IR , NMR , mass spectra 114.

7. 2-(1,2,3,3,4,4-HEXAFLUOROCYCLOBUTYL)OXOLANE (40).

Adduct (40) (2.32g , 9.9mmol) was passed over cobalt trifluoride at 440°C. Preparative GLC (column A , 70°C) of the product (2.98g) gave perfluoro-2-cyclobutyloxolane (197), (64%); (Found: C, 23.9%; F, 73.3%. $C_8F_{14}O$ requires: C, 25.4%; F, 70.4%); IR , NMR , mass spectra 115, and a decomposition product (12%) (insufficient for analysis).

8. 2-(1,2,3,3,4,4,5,5-OCTAFLUOROCYCLOPENTYL)OXANE (46).

Adduct (46) (3.06g , 10.3mmol) was passed over cobalt trifluoride at 440°C. Preparative GLC (column A, 80°C) of the product mixture (3.59g) gave perfluoro-2-cyclopentyloxane (198), (31%); b.p. 134°C (Siwoloboff); (Found: C, 23.1%; F, 72.1%. $C_{10}F_{18}O$ requires: C, 25.1%; F, 71.6%); IR , NMR , mass spectra 116, perfluorobutylcyclopentane (199), (20%); b.p. 127°C (Siwoloboff); (Found: C, 22.5%; F, 76.2%. C_9F_{18} requires: C, 24.0%; F, 76.0%); IR , NMR , mass spectra 117, and other unidentified decomposition products (17%).

9. 2-(1,2,3,3,4,4,5,5-OCTAFLUOROCYCLOPENTYL)OXEPANE (48).

Adduct (48) (1.81g , 5.8mmol) was passed over cobalt trifluoride at 440°C. Preparative GLC (column A, 80°C) of the product mixture (2.25g) gave perfluoro-2-cyclopentyloxepane (200), (20%); b.p. 158°C (Siwoloboff); (Found: C, 24.3%. $C_{11}F_{20}O$ requires C, 25.0%); IR , NMR , mass spectra 118, perfluoropentylcyclopentane (201), (22%); b.p. 139°C (Siwoloboff); (Found: C, 22.6%; F, 75.9%. $C_{10}F_{20}$ requires: C, 24.0%; F, 76.0%); IR , NMR , mass spectra 119, and other decomposition products (32%).

10. 2-(1,2,3,3,4,4,5,5-OCTAFLUOROCYCLOPENTYL)-1,4-DIOXAN (50).

Adduct (50) (2.80g , 9.3mmol) was passed over cobalt trifluoride at 440°C. Preparative GLC (column A, 80°C) of the product mixture (1.82g) gave perfluoro-2-cyclopentyl-1,4-dioxan (202), (17%); b.p. 125°C (Siwoloboff); (Found: C, 23.9%; F, 67.7%. $C_9F_{16}O_2$ requires: C, 24.3%; F, 68.5%); IR , NMR , mass spectra 120, perfluoro-2-cyclopentylethyl methyl ether (203), (8%); b.p. 101°C (Siwoloboff); IR , NMR , mass spectra 121, perfluoroethylcyclopentane (204) (10%); IR , NMR , mass spectra 122, and other decomposition products (10%).

11. 2-(2-CHLORO-1,1,2-TRIFLUOROETHYL)OXOLANE (35).

Adduct (35) (1,68g , 8.9mmol) was passed over cobalt trifluoride at 440°C. Preparative GLC (column A , 65°C) of the product (2.11g) gave perfluoro-2-(2-chloroethyl)oxolane (205), (45%); b.p. 82°C (Siwoloboff); (Found: C, 22.4%; F, 62.5%; Cl, 11.6%. $C_6ClF_{11}O$ requires: C, 21.7%; F, 62.9%; Cl, 10.7%); IR , NMR , mass spectra 123, and perfluoro-2-ethyloxolane (206) (12%); b.p. 54°C (Siwoloboff); IR , NMR , mass spectra 124.

12. 2-(1,2-DICHLORO-1-TRIFLUOROMETHYL-3,3,3-TRIFLUOROPROPYL)OXOLANE (42).

Adduct (42) (2.78g , 9.1mmol) was passed over cobalt trifluoride at 440°C. The frozen product had a yellow colouration which faded on warming to room temperature. Preparative GLC (column A, 20 °C and 70°C) of the product gave perfluoro-2-(2-chloro-1-methylpropyl)oxolane (207), (16%); IR , NMR , mass spectra 125, perfluoro-2-(1-methylpropyl)oxolane (192), (15%), and many unidentified compounds (18%).

13. 1,2,3,3,4,4,5,5,6,6-DECAFLUORO-1-METHOXYMETHYLCYCLOHEXANE (32).

Adduct (32) (1.87g , 6.1mmol) was passed over cobalt trifluoride at 440°C. Preparative GLC (column A, 70°C) of the product (1.05g) gave perfluoromethoxymethylcyclohexane (208), (16%); IR , NMR , mass spectra 126, perfluoromethylhexane (209), (9%); IR , NMR , mass spectra 127, and other unidentified decomposition products (21%).

14. 1,2,3,3,4,4-HEXAFLUORO-1-METHOXYMETHYLCYCLOBUTANE (210).

Adduct (210) (1.96g , 9.4mmol) was passed over cobalt trifluoride at 440°C. The product (0.78g) was very volatile and composed of many components (GLC, columnA, 20°C) that were not investigated.

APPENDIX

INDEX OF SPECTRA

1. 2,2,3,4,4,4-Hexafluorobutyl methyl ether (9).
2. 1-Methyl-2,2,3,4,4,4-hexafluorobutyl ethyl ether (10).
3. Di(1-methyl-2,2,3,4,4,4-hexafluorobutyl) ether (11).
4. 1-Ethyl-2,2,3,4,4,4-hexafluorobutyl propyl ether (12).
5. Di(1-ethyl-2,2,3,4,4,4-hexafluorobutyl) ether (13).
6. 1-Propyl-2,2,3,4,4,4-hexafluorobutyl butyl ether (14).
7. Di(1-propyl-2,2,3,4,4,4-hexafluorobutyl) ether (15).
8. 1-Propyl-2,2,3,4,4,4-hexafluorobutyl 1-propyl-1-(1,1,2,3,3,3-hexafluoropropyl)-2,2,3,4,4,4-hexafluorobutyl ether (16).
9. 2-(1,1,2,3,3,3-Hexafluoropropyl)oxetane (20).
10. 2-(1,1,2,3,3,3-Hexafluoropropyl)oxolane (21).
11. 2-(1,1,2,3,3,3-Hexafluoropropyl)oxane (22).
12. 2,5-Di(1,1,2,3,3,3-hexafluoropropyl)oxane (23).
13. 2-(1,1,2,3,3,3-Hexafluoropropyl)oxepane (24).
14. 2-(1,1,2,3,3,3-Hexafluoropropyl)-1,4-dioxan (25).
15. 3,3,4,5,5,5-Hexafluoropentan-2-one (19).
16. 2-Methyl-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane (27).
17. 2-Methyl-2-(1,1,2,3,3,3-hexafluoropropyl)oxolane (26).
18. 2-(2-Chloro-1,1,2-trifluoroethyl)oxolane (35).
19. 2-(1,2,3,3,4,4-Hexafluorocyclobutyl)oxolane (40).
20. 2-(1,2,3,3,4,4,5,5-Octafluorocyclopentyl)oxolane (39).
21. 2-(1,2,3,3,4,4,5,5-Octafluorocyclopentyl)oxane (46).
22. 2-(1,2,3,3,4,4,5,5-Octafluorocyclopentyl)oxepane (48).
23. 2-(1,2,3,3,4,4,5,5-Octafluorocyclopentyl)-1,4-dioxan (50).
24. 2-(1,2,3,3,4,4,5,5,6,6-Decafluorocyclohexyl)oxolane (38).

25. 2-(1-Trifluoromethyl-1,2,3,3,3-pentafluoropropyl)oxolane (41).

26. 2-(1-Trifluoromethyl-1,2,3,3,3-pentafluoropropyl)oxane (47).

27. 2-(1-Trifluoromethyl-1,2,3,3,3-pentafluoropropyl)oxepane (49).

28. 2-(1-Trifluoromethyl-1,2,3,3,3-pentafluoropropyl)-1,4-dioxan (51).

29. 1-(1,2-Dichloro-1-trifluoromethyl-3,3,3-trifluoropropyl)oxolane (42).

30. 2-(1,2-Di(trifluoromethyl)-1,3,3,4,4,4-hexafluorobutyl)oxolane (43).

31. 2,5-Di(1,2-di(trifluoromethyl)-1,3,3,4,4,4-hexafluorobutyl)-oxolane (44).

32. 2-(1,2,3-Tri(trifluoromethyl)-3-pentafluoroethyl-1,4,4,5,5,5-hexafluoropentyl)oxolane (45).

33. Methyl 2,2,3,4,4,4-hexafluorobutanoate (54).

34. 2,2,3,4,4,4-Hexafluorobutyl formate (55).

35. 2,2,3,4,4,4-Hexafluorobutan-1-ol (56).

36. 2-Trifluoromethyl-2,3,3-trifluoropropyl acetate (59).

37. 2,2,3,4,4,4-Hexafluorobutyl acetate (57).

38. Methyl 3,3,4,5,5,5-hexafluoropentanoate (58).

39. 2,2,3,4,4,4-Hexafluorobutyl methyl carbonate (60).

40. Tri(2,2,3,4,4,4-hexafluorobutyl) borate (63).

41. Tri((1,2,3,3,4,4-hexafluorocyclobutyl)methyl) borate (64).

42. Tri((1,2,3,3,4,4,5,5,6,6-decafluorocyclohexyl)methyl) borate (65).

43. Tri(2-pentafluoroethyl-4,4,5,5,5-pentafluoro-2,3-di(trifluoromethyl)-pentyl) borate (66).

44. N-(2,3,3,3-Tetrafluoropropanoyl)piperidine (74).

45. N-(2,2,3,4,4,4-Hexafluorobutyl)piperidine (75).

46. N-Methyl-2-(1,1,2,3,3,3-hexafluoropropyl)piperidine (76).

47. N-(2,2,3,4,4,4-Hexafluorobutyl)-2-(1,1,2,3,3,3-hexafluoropropyl)-piperidine (77).

48. N-(2,2,3,4,4,4-Hexafluorobutyl)morpholine (78).

49. N-(2,2,3,4,4,4-Hexafluorobutyl)-2-(1,1,2,3,3,3-hexafluoropropyl)-morpholine (79).

50. N-(2,2,3,4,4,4-Hexafluorobutyl)-N-methylformamide (81).
51. N,N-Dimethyl-2,2,3,4,4,4-hexafluorobutanamide (82).
52. N-(2,2,3,4,4,4-Hexafluorobutyl)-N-methyl-2,2,3,4,4,4-hexafluorobutanamide (83).
53. N-(2,2,3,4,4,4-Hexafluorobutyl)-N-methylacetamide (84).
54. N-(2,2,3,4,4,4-Hexafluorobutyl)-N,N',N'-trimethylurea (85).
55. N,N'-Di(2,2,3,4,4,4-hexafluorobutyl)-N,N'-dimethylurea (87).
56. N,N-Di(2,2,3,4,4,4-hexafluorobutyl)-N',N'-dimethylurea (86).
57. N,N,N'-Tri(2,2,3,4,4,4-hexafluorobutyl)-N'-methylurea (88).
58. N,N,N',N'-Tetra(2,2,3,4,4,4-hexafluorobutyl)urea (89).
59. N-(2,2,3,4,4,4-Hexafluorobutyl)-N-methylbenzamide (90).
60. N-Methyl-5-(1,1,2,3,3,3-hexafluoropropyl)pyrrolidin-2-one (91).
61. N-Acetyl-2-(1,1,2,3,3,3-hexafluoropropyl)piperidine (92).
62. N-Methyl-N-(3-chloro-2,2,3-trifluoropropyl)acetamide (93).
63. N-Methyl-5-(2-chloro-1,1,2-trifluoroethyl)pyrrolidin-2-one (97).
64. N-(1,2,3,3,4,4-Hexafluorocyclobutyl)methyl-N-methylacetamide (96).
65. N-(1,2,3,3,4,4,5,5-Octafluorocyclopentyl)methyl-N-methylacetamide (95).
66. N-(1,2,3,3,4,4,5,5,6,6-Decafluorocyclohexyl)methyl-N-methylacetamide (94).
67. N,N,N',N'-Tetramethylurea / Perfluorocyclohexa-1,4-diene polymer (98).
68. 1-Chloro-2,2,3,4,4,4-hexafluorobutyl methyl ether (126).
69. 2,2,3,4,4,4-Hexafluorobutyl chloromethyl ether (127).
70. 1-Bromo-2,2,3,4,4,4-hexafluorobutyl methyl ether (130).
71. 2,2,3,4,4,4-Hexafluorobutyl fluoromethyl ether (134).
72. 2,2,3,4,4,4-Hexafluorobutanoyl chloride (138).
73. 1,2,3,3,4,4,5,5,6,6-Decafluorocyclohexylmethanoyl chloride (139).
74. 1,2,3,3,4,4-Hexafluorocyclobutylmethanoyl chloride (140).
75. 3-Chlorohexafluorocyclobutylmethanoyl chloride (141).

76. 3-Chloro-3,4-di(trifluoromethyl)-1,1,1,2,2,5,5,6,6,6-decafluorohexane (142).
77. 3-Chlorotetrafluoropropanoyl chloride (144).
78. 11-Chloroeicosafluoroundecanoyl chloride (146).
79. Perfluoro-2-propyloxane (156).
80. Perfluoro-2-propyloxolane (157).
81. Perfluorohexane (158).
82. 2,3,3,4,5,5-Hexafluoro-2-(heptafluoropropyl)oxolane (161).
83. 2,5,5-Trifluoro-2-(1,1,2,3,3,3-hexafluoropropyl)oxol-3-en (162).
84. 2,3,4,5-Tetrafluoro-2-(1,1,2,3,3,3-hexafluoropropyl)oxolane (163).
85. Trifluoro-2-(1,1,2,3,3,3-hexafluoropropyl)oxolane , isomer mixture (164).
86. Difluoro-2-(1,1,2,3,3,3-hexafluoropropyl)oxolane , isomer mixture (165).
87. Perfluoro-1-methylbutyl ethyl ether (168).
88. Perfluoro-2-propyl-1,4-dioxan (170).
89. Heptafluoro-2-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dioxan (171).
90. 2,3,5,5,6,6-Hexafluoro-2-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dioxan, isomer A (172).
91. 2,3,5,5,6,6-Hexafluoro-2-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dioxan, isomer B (173).
92. 2,3,5,5,6,6-Hexafluoro-2-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dioxan, isomer C (174).
93. 2,3,3-Trifluoro-2-(1,1,2,3,3,3-hexafluoropropyl)trifluoro-1,4-dioxan, isomer A (175).
94. 2,3,3-Trifluoro-2-(1,1,2,3,3,3-hexafluoropropyl)trifluoro-1,4-dioxan , isomer B (176).
95. 2,3,3-Trifluoro-2-(1,1,2,3,3,3-hexafluoropropyl)trifluoro-1,4-dioxan , isomer C (177).

96. Perfluoro butyl methyl ether (178).

97. Perfluorobutane (179).

98. Perfluoro 1-ethylbutyl propyl ether (180).

99. Perfluoro 1-propylbutyl butyl ether (182).

100. Perfluoroheptane (181).

101. Perfluoro di(1-methylbutyl) ether (183).

102. Perfluoropentane (169).

103. Perfluoro di(1-ethylbutyl) ether (184).

104. Perfluoro 2-propyloxepane (186).

105. Perfluoro-octane (187).

106. Perfluoro 2-propyloxetane (188).

107. Perfluoro 2-methyl-5-propyloxolane (190).

108. Perfluoro 2-methyl-2-propyloxolane (189).

109. Perfluoro 3-methylhexane (109).

110. Perfluoro 2-(1-methylpropyl)oxolane (192).

111. Perfluoro 2-cyclohexyloxolane (193).

112. Perfluoropropylcyclohexane (194).

113. Perfluoro 2-cyclopentyloxolane (195).

114. Perfluoropropylcyclopentane (196).

115. Perfluoro 2-cyclobutyloxolane (197).

116. Perfluoro 2-cyclopentyloxane (198).

117. Perfluorobutylcyclopentane (199).

118. Perfluoro 2-cyclopentyloxepane (200).

119. Perfluoropentylcyclopentane (201).

120. Perfluoro 2-cyclopentyl-1,4-dioxan (202).

121. Perfluoro 2-cyclopentylethyl methyl ether (203).

122. Perfluoroethylcyclopentane (204).

123. Perfluoro 2-(2-chloroethyl)oxolane (205).

124. Perfluoro 2-ethyloxolane (206).

125. Perfluoro 2-(2-chloro-1-methylpropyl)oxolane (207).

126. Perfluoromethoxymethylcyclohexane (208).

127. Perfluoromethylhexane (209).

128. Adduct of tributyl borate and hexafluoropropene (69).

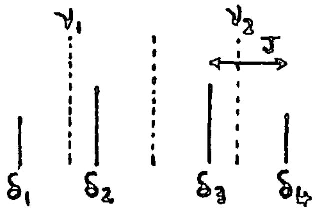
129. 1,1,1,2,3,3-Hexafluoroheptan-4-ol (70).

130. 1,1,1,2,3,3-Hexafluoro-4-(1,1,2,3,3,3-hexafluoropropyl)-heptan-4-ol (71).

ABBREVIATIONS.

The following abbreviations are used for the splitting patterns of the NMR resonances;

S = singlet
D = doublet
T = triplet
Q = quartet
AB = AB quartet



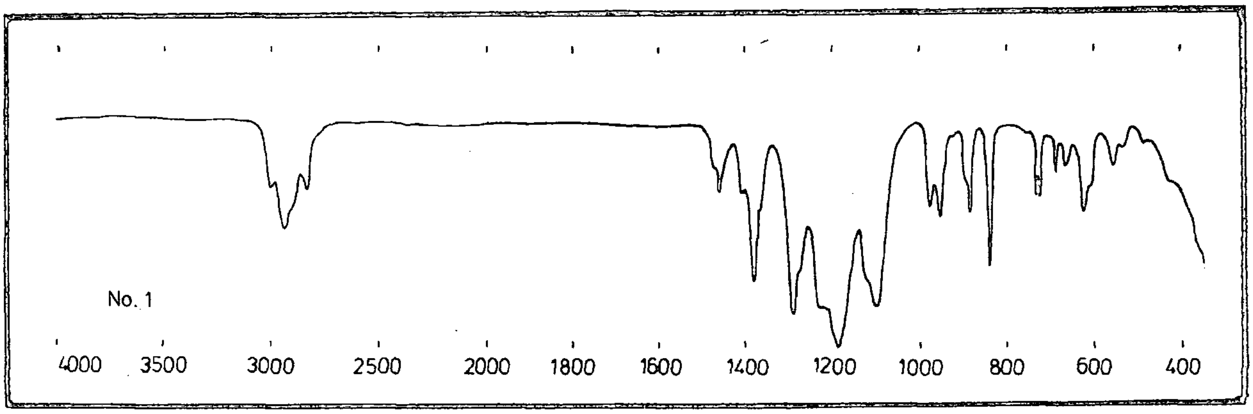
Chemical shifts quoted as 'centre of gravity' or $\pm\Delta\nu/2$ from the mid point of the pattern, calculated from $(\delta_1-\delta_3) = (\delta_2-\delta_4) = \sqrt{(\Delta\nu)^2 + J^2}$

P = pentet
Sx = sextet
Sp = septet
Oc = octet
M = multiplet.

No. 1

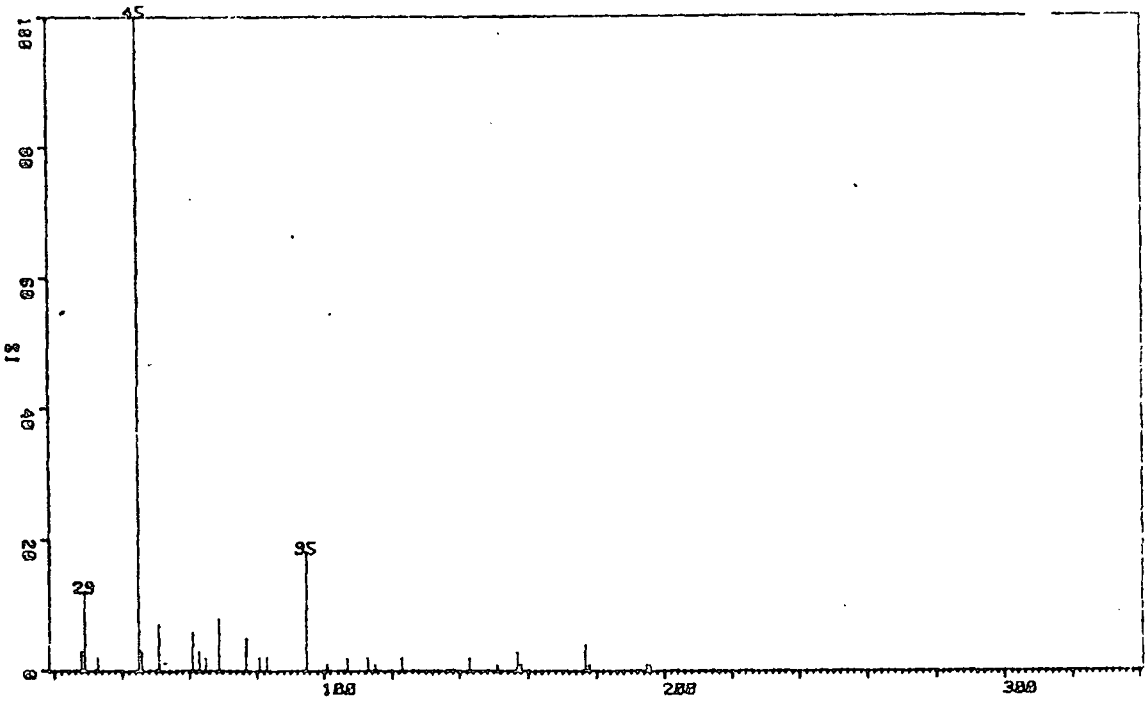
$\overset{a}{CF_3}\,\overset{b}{CFH}\,\overset{c}{CF_2}\,\overset{d}{CH_2}O\,\overset{e}{CH_3}$

2,2,3,4,4,4-Hexafluorobutyl methyl ether (9).



SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
76.3	M, J=6	3	a
120.1, 121.8	AB, J_{FF}=260	2	c
216.7	D of M, J_{HF}=43	1	b
^{1}H			
3.47	S	3	e
3.7	M(broad)	2	d
5.08	D of M, J_{HF}=43	1	b

M.Wt. 196 No.1



PEAK NO.	MASS	%HT. BASE
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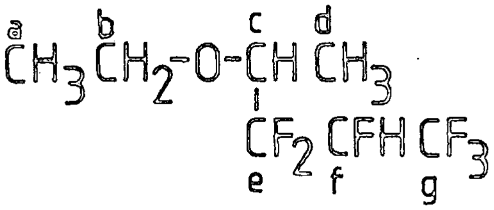
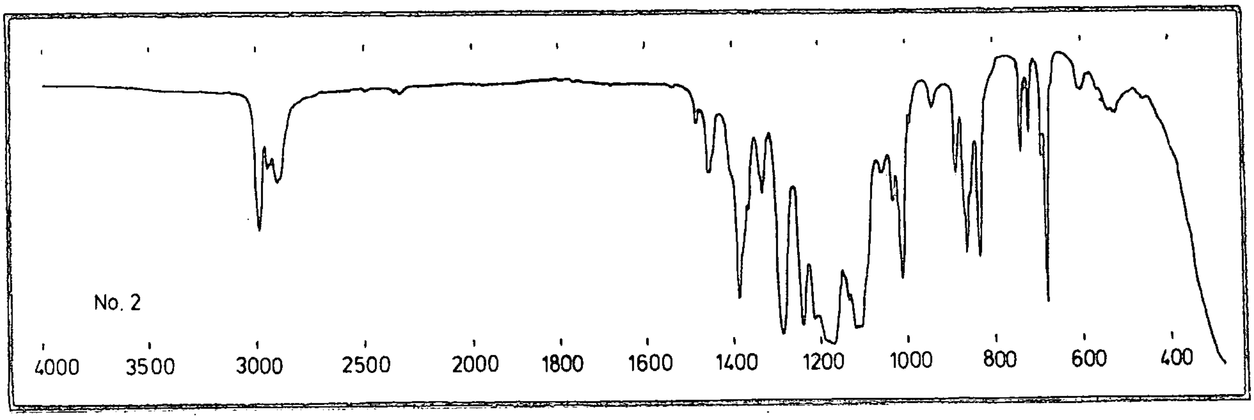
2	29.00	12.00*
3	33.00	2.00*
4	45.00	100.00*
5	46.00	3.00*
6	51.00	7.00*
7	61.00	6.00*
8	63.00	3.00*
9	65.00	2.00*
10	69.00	8.00*
11	77.00	5.00*
12	81.00	2.00*
13	83.00	2.00*
14	95.00	18.00*
15	101.00	1.00*
16	107.00	2.00*
17	113.00	2.00*
18	115.00	1.00*
19	123.00	2.00*
20	143.00	2.00*
21	151.00	1.00*
22	157.00	3.00*
23	158.00	1.00*
24	177.00	4.00*
25	178.00	1.00*
26	195.00	1.00*
27	196.00	1.00*

No. 2



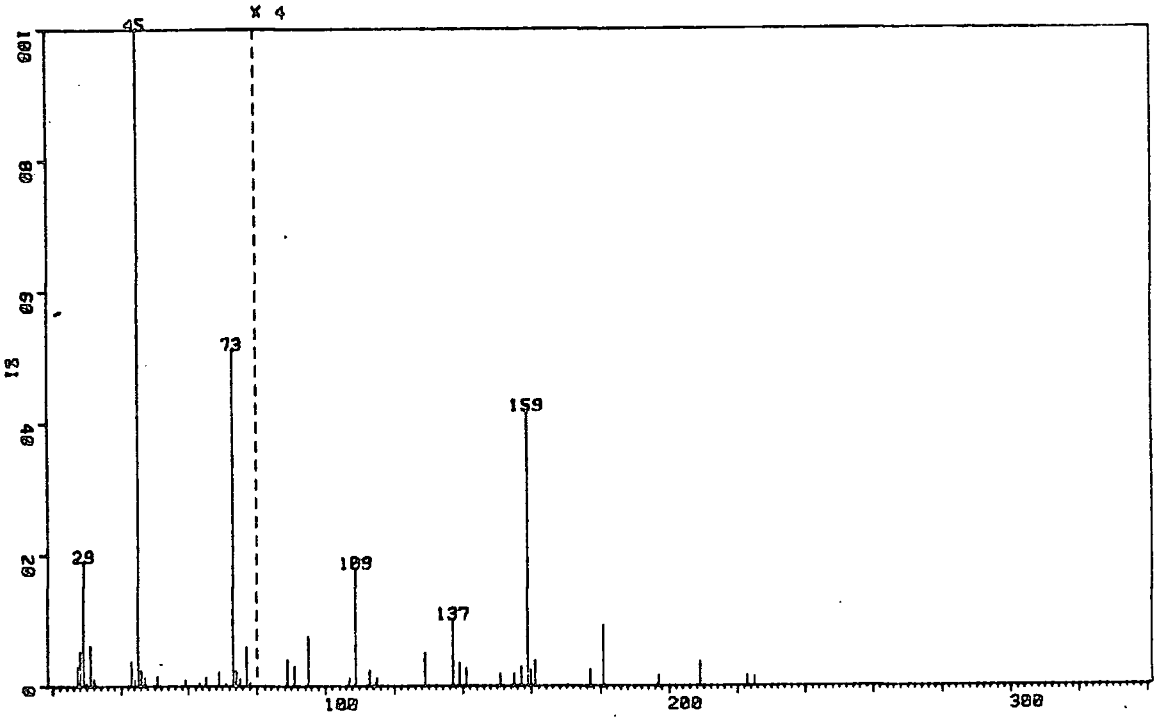
$$\overset{a}{C}H_3\overset{b}{C}H_2\text{-O-}\overset{c}{C}H\overset{d}{C}H_3$$
$$\underset{e}{C}F_2\underset{f}{C}FH\underset{g}{C}F_3$$

1-Methyl-2,2,3,4,4,4-hexafluorobutyl ethyl ether (10).

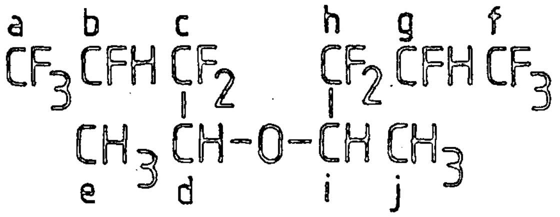


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
0.87	T, J_{a-b}= 8	3	a
0.95	D, J_{d-c}= 7	3	d
3.25	M, J = 7	3	b
3.53	M		c
4.80	D of M, J_{H-F}= 44	1	f
^{19}F			
76.7	M	3	g
77.2	M		
121.3, 126.2	AB, J_{F-F}=273	2	e
127.0, 131.4	AB, J_{F-F}=273		
215.7	D of M, J_{F-H}=38	1	f
218.5	D of M, J_{F-H}=42, J_{F-F}=10		

M.Wt. 224 No. 2

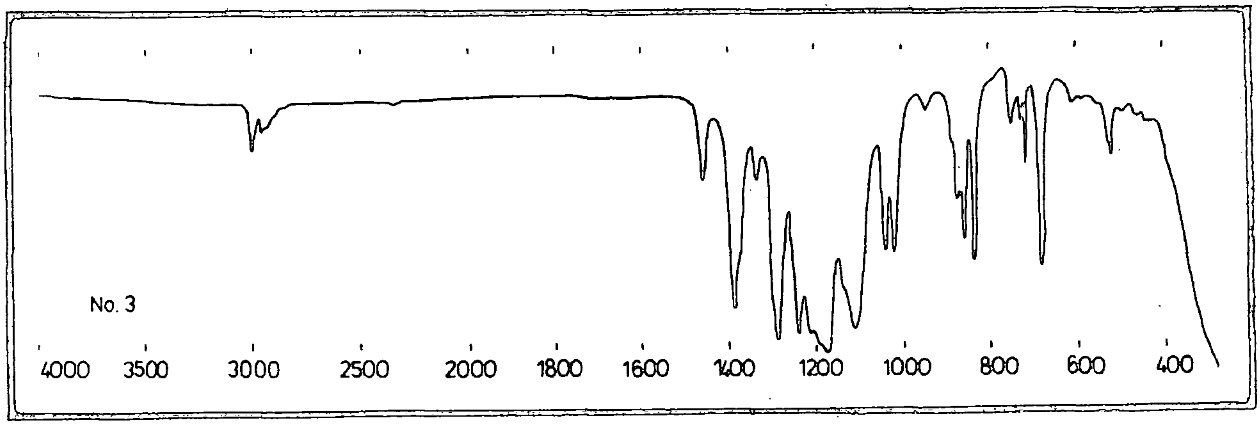


PEAK NO.	MASS	%HT. BASE
1	27.25	2.89
2	28.13	5.21
3	29.02	18.95
4	29.86	0.37
5	30.93	6.11
6	32.02	1.01
7	43.11	3.73
8	44.15	0.95
9	45.17	100.00
10	46.17	2.33
11	47.13	1.30
12	50.95	1.46
13	59.01	0.93
14	63.09	0.37
15	65.12	1.35
16	68.95	2.20
17	70.78	0.34
18	73.09	51.24
19	74.12	2.22
20	75.05	1.16
21	77.01	5.96
22	77.99	0.53
23	88.94	1.01
24	90.95	0.77
25	95.01	1.91
26	106.99	0.32
27	108.91	4.50
28	112.96	0.61
29	115.00	0.32
30	128.92	1.24
31	136.96	2.57
32	138.95	0.87
33	140.91	0.69
34	150.90	0.45
35	154.97	0.45
36	156.99	0.71
37	158.90	10.46
38	159.89	0.61
39	160.94	0.98
40	177.03	0.61
41	180.96	2.30
42	196.99	0.40
43	208.97	0.93
44	223.02	0.40
45	225.06	0.34



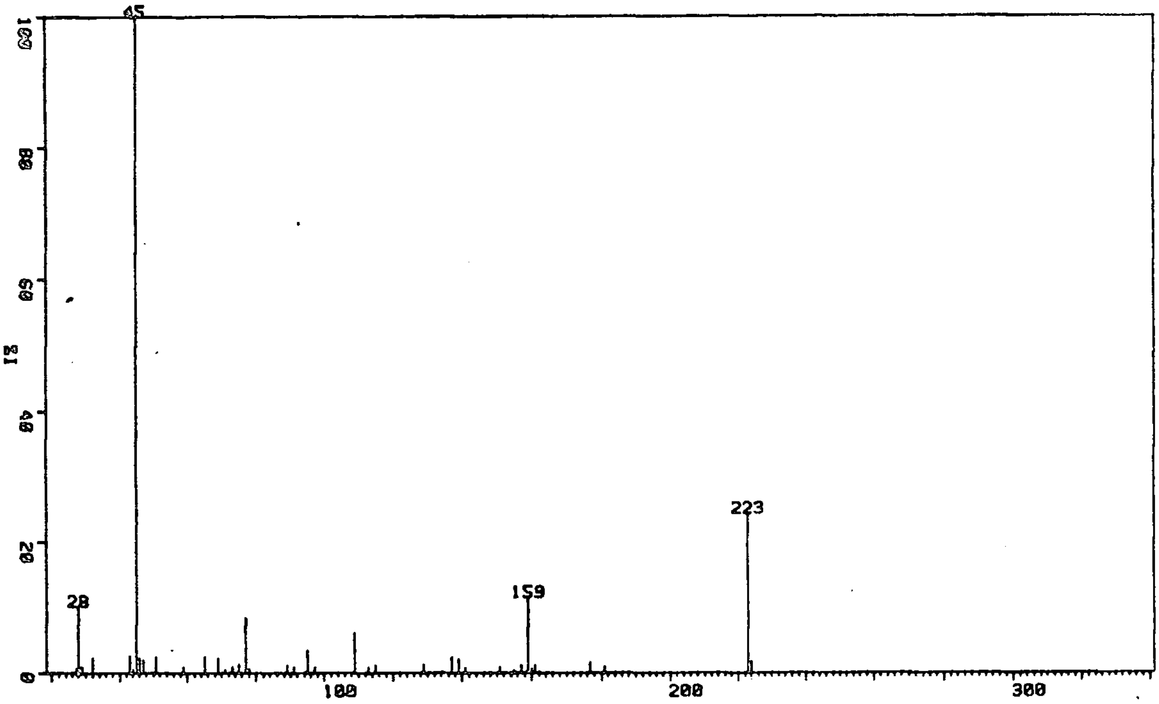
No. 3

Di(1-methyl-2,2,3,4,4,4-hexafluorobutyl) ether (11).



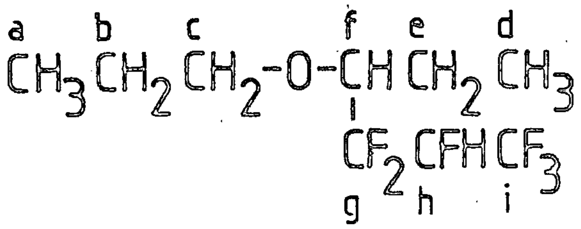
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
1.07	S	3	a, f
1.17	S	3	
3.77	M(broad)	2	d, i
4.78	D of M(broad), J_{HF}=44	2	b, g
^{19}F			
76.3	M	3	a, f
117.0, 121.7, 122.0, 123.2, 124.2, 126.3, 127.3, 128.8, 129.7, 132.2, 133.7, 134.7.	Overlapping AB's	2	c, h
213.5, 214.3, 215.2, 216.5.	M(broad)	1	b, g

M.Wt. 374 No. 3



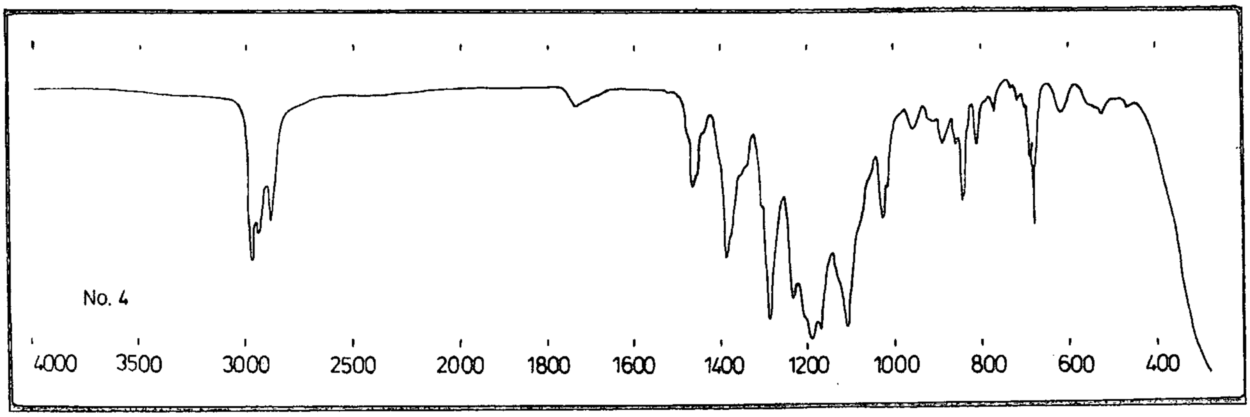
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.25	0.68	36	177.00	1.54
2	28.13	10.21	37	190.96	0.98
3	29.00	0.90	38	223.99	24.47
4	32.02	2.22	39	224.00	1.77
5	43.11	2.64			
6	44.15	0.53			
7	45.18	100.00			
8	46.17	2.22			
9	47.13	2.00			
10	50.94	2.37			
11	59.01	0.87			
12	65.13	2.45			
13	68.95	2.15			
14	70.98	0.45			
15	73.09	0.98			
16	75.08	1.32			
17	77.05	8.40			
18	78.01	0.57			
19	88.96	1.17			
20	90.96	0.87			
21	95.04	3.43			
22	97.03	0.87			
23	108.96	6.14			
24	112.99	0.87			
25	115.02	1.21			
26	128.94	1.28			
27	137.01	2.37			
28	138.95	2.15			
29	140.96	0.72			
30	150.95	0.90			
31	154.99	0.49			
32	156.99	1.17			
33	158.93	11.57			
34	159.91	0.64			
35	160.91	1.13			

No. 4



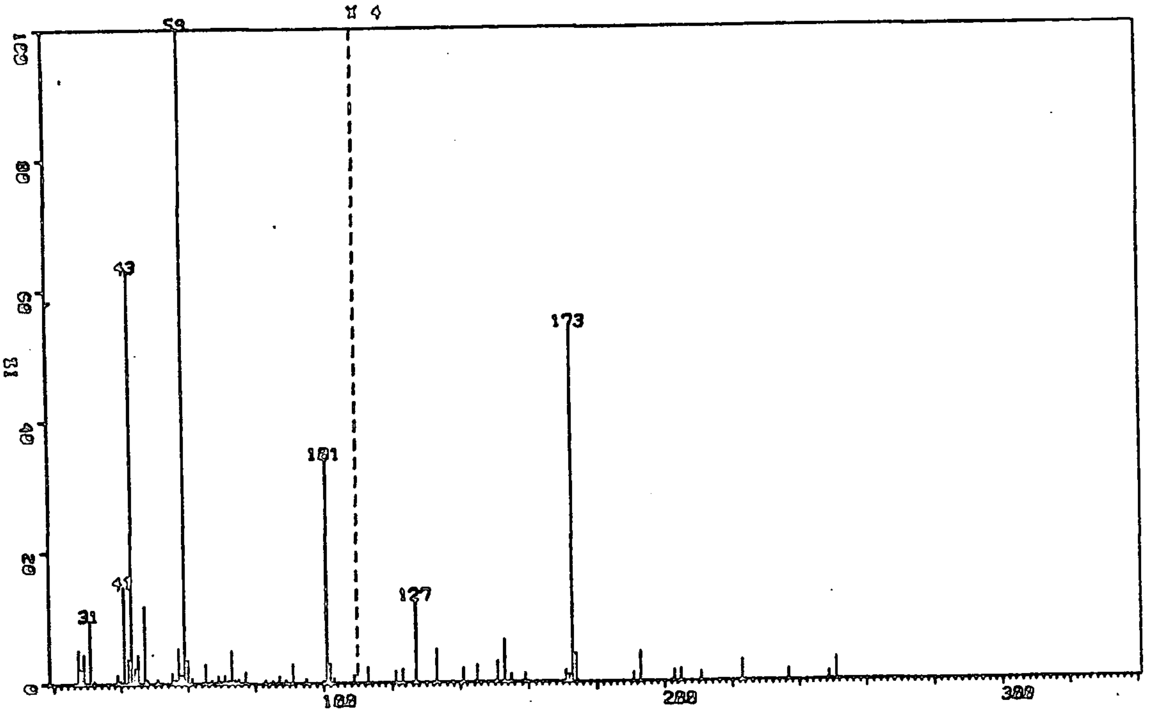
$CH_3CH_2CH_2\text{-}O\text{-}CH(CF_2CFHCF_3)CH_2CH_3$

1-Ethyl-2,2,3,4,4,4-hexafluorobutyl propyl ether (12).

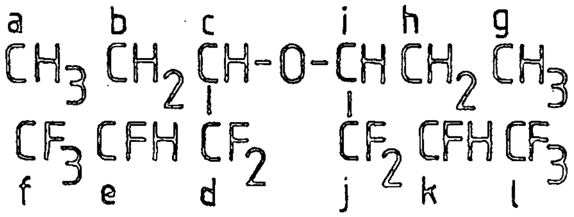


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
1.04	M	6	a , d
1.67	M	4	b , e
3.57	M	4	c
4.00	M(broad)		f
5.03	M(broad)		h
^{19}F			
74.3	M	3	i
117.5, 120.2, 123.8, 125.0.	Overlapping AB's	2	g
211.7	M	1	h

M.Wt. 252 No.4



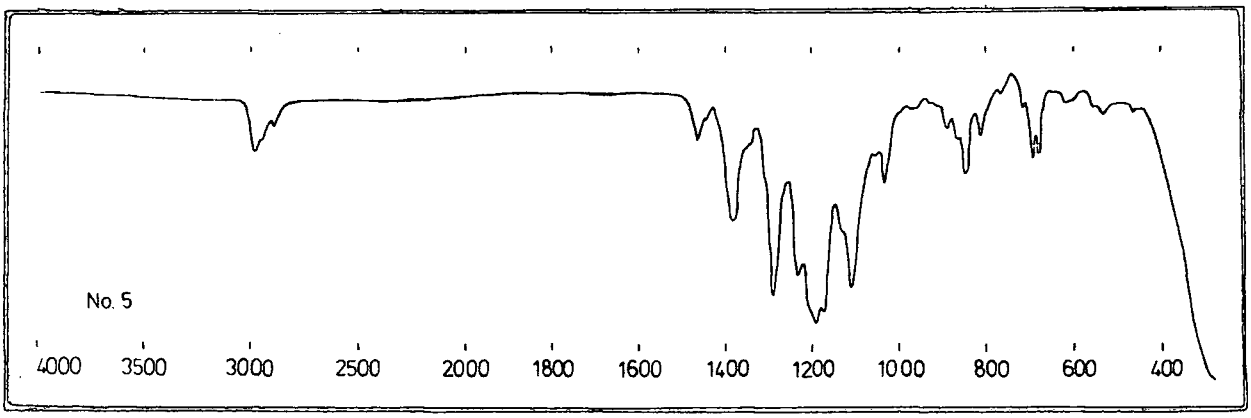
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.25	5.10	36	87.03	1.10
2	28.13	2.14	37	88.94	0.44
3	29.02	4.44	38	90.90	2.99
4	29.86	0.27	39	95.00	0.66
5	30.92	9.63	40	99.97	0.33
6	32.02	0.41	41	101.00	34.18
7	38.99	1.29	42	102.01	2.99
8	39.89	0.44	43	103.00	0.77
9	40.97	14.71	44	108.90	1.18
10	42.07	3.76	45	112.96	0.60
11	43.13	62.88	46	120.97	0.44
12	44.17	2.41	47	123.03	0.52
13	45.16	4.36	48	126.99	3.16
14	47.11	11.77	49	132.96	1.23
15	48.05	0.38	50	140.87	0.55
16	50.93	0.63	51	144.97	0.63
17	55.16	1.56	52	150.94	0.80
18	56.14	0.58	53	152.96	1.59
19	57.11	5.35	54	155.01	0.30
20	58.08	1.29	55	158.94	0.33
21	59.02	100.00	56	170.97	0.44
22	59.95	3.57	57	171.94	0.27
23	61.02	0.80	58	172.96	13.55
24	65.12	2.88	59	174.02	1.07
25	67.09	0.47	60	190.94	0.36
26	68.96	1.12	61	192.93	1.12
27	69.96	0.27	62	202.92	0.41
28	70.98	1.18	63	204.91	0.47
29	72.03	0.36	64	210.88	0.36
30	73.06	4.88	65	222.97	0.80
31	74.09	0.41	66	236.90	0.41
32	75.07	0.55	67	248.89	0.33
33	77.01	1.78	68	250.90	0.85
34	83.01	0.52			
35	85.06	0.38			



$CH_3CH_2CH(CF_2CFHCF_3)\text{-}O\text{-}CH(CF_2CFHCF_3)CH_2CH_3$

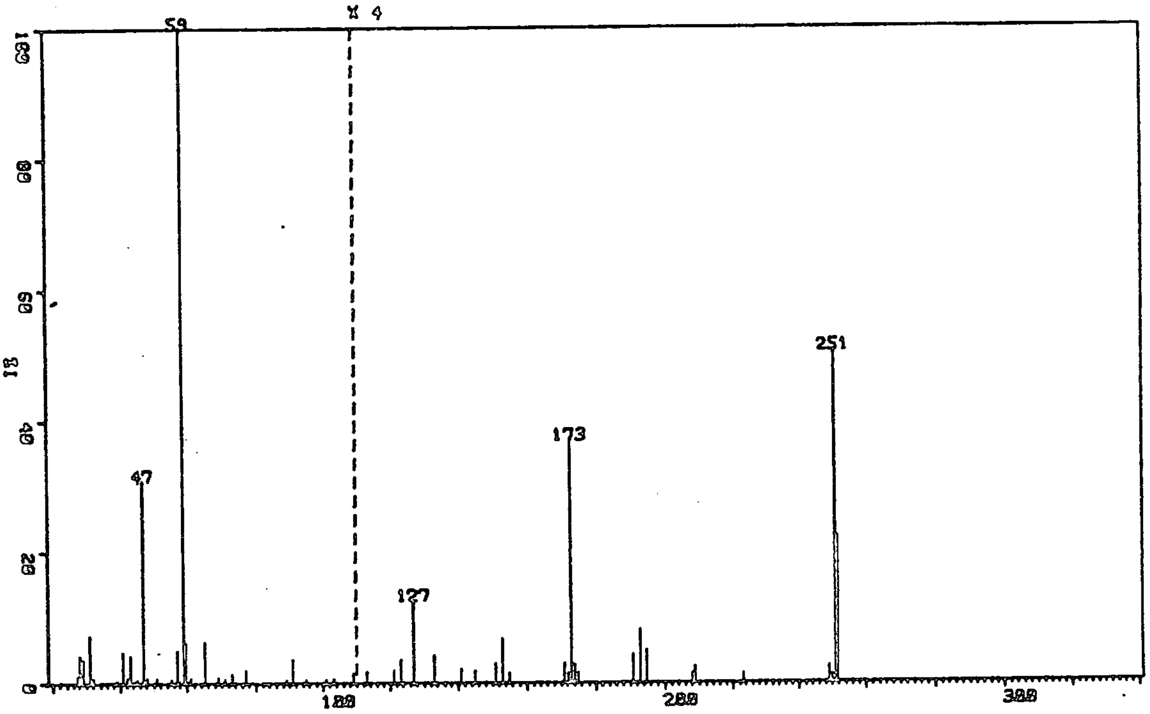
No.5

Di(1-ethyl-2,2,3,4,4,4-hexafluorobutyl) ether (13).

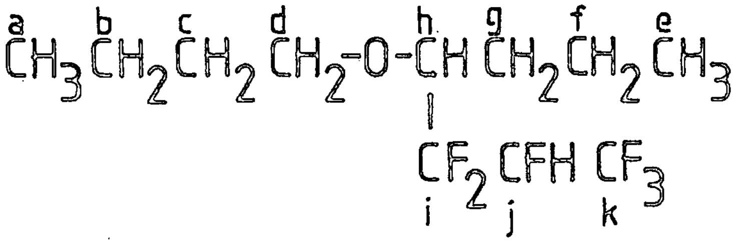


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
1.06	M	3	a , g
1.79	M	2	b , h
3.90	M	1	c , i
5.01	D of M, J_{HF}=46	1	e , k
^{19}F			
74.4	M	3	f , l
116.9, 117.9, 118.8, 119.7, 122.2, 122.7, 124.4, 125.3, 127.9.	Overlapping AB's	2	d , j
212.1	M	1	e , k

M.Wt. 402 No.5



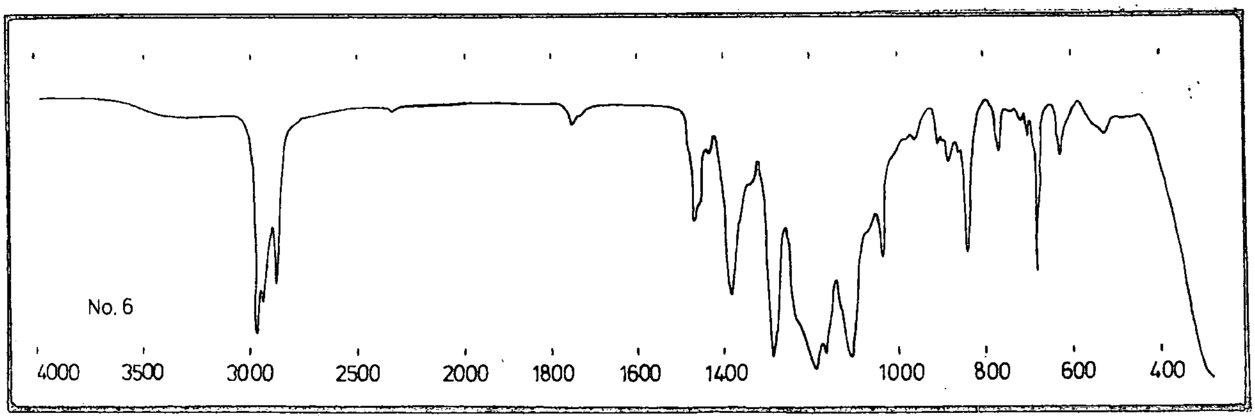
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.26	1.05	36	95.01	0.53
2	28.13	4.10	37	101.01	0.61
3	29.03	3.58	38	103.02	0.69
4	30.94	7.18	39	108.94	1.44
5	32.02	0.72	40	113.00	0.44
6	39.01	0.42	41	121.01	0.50
7	40.99	4.77	42	123.05	0.86
8	42.08	0.83	43	127.01	3.16
9	43.14	4.21	44	133.02	1.05
10	44.17	0.28	45	140.94	0.53
11	45.17	0.64	46	145.00	0.47
12	46.81	0.30	47	150.95	0.72
13	47.12	30.99	48	153.00	1.66
14	47.35	0.28	49	155.00	0.36
15	47.44	0.30	50	170.99	0.75
16	48.07	0.80	51	172.02	0.39
17	50.95	0.72	52	173.02	9.28
18	55.16	0.58	53	174.01	0.69
19	56.92	0.28	54	175.01	0.39
20	57.12	4.96	55	190.91	1.08
21	57.59	0.30	56	192.96	2.05
22	57.76	0.30	57	194.95	1.25
23	59.00	100.00	58	207.90	0.36
24	59.52	6.15	59	208.87	0.61
25	60.12	0.28	60	223.08	0.36
26	60.37	0.30	61	248.97	0.61
27	61.03	0.80	62	250.00	0.30
28	65.13	6.29	63	250.94	12.67
29	68.96	0.91	64	251.58	5.57
30	70.99	0.61			
31	73.07	1.39			
32	77.03	1.94			
33	83.04	0.28			
34	88.95	0.53			
35	90.95	3.43			



$$\overset{a}{C}H_3\overset{b}{C}H_2\overset{c}{C}H_2\overset{d}{C}H_2{-}O{-}\overset{h}{C}H(\underset{i}{C}F_2\underset{j}{C}FH\underset{k}{C}F_3)\overset{g}{C}H_2\overset{f}{C}H_2\overset{e}{C}H_3$$

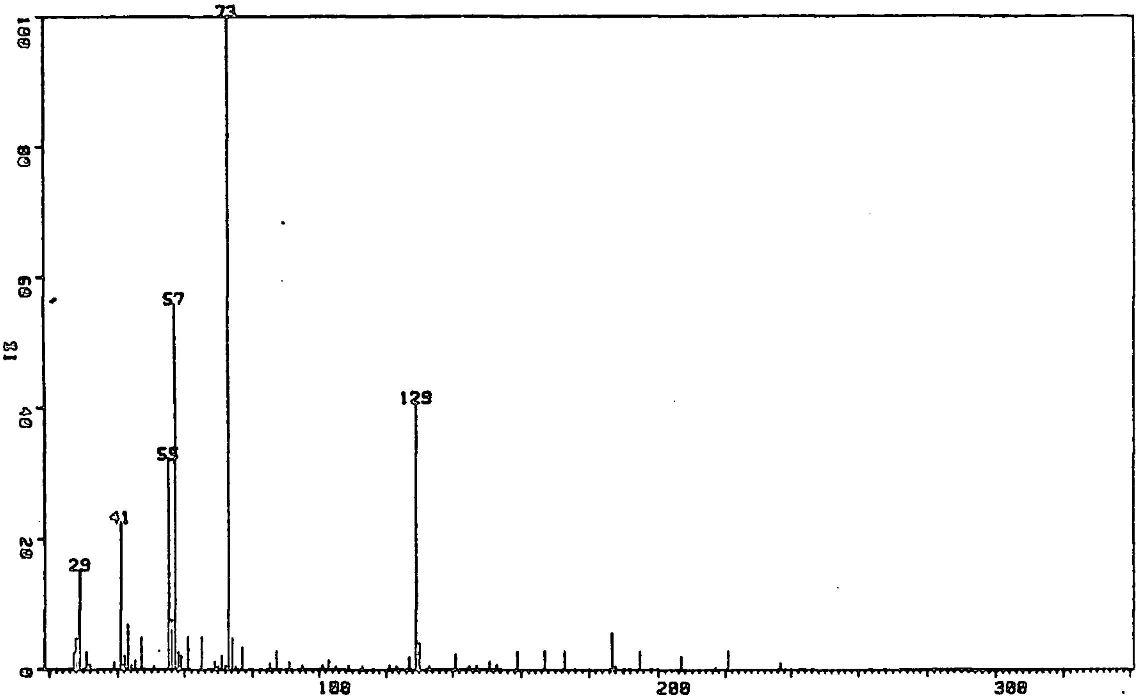
No. 6

1-Propyl-2,2,3,4,4,4-hexafluorobutyl butyl ether (14).

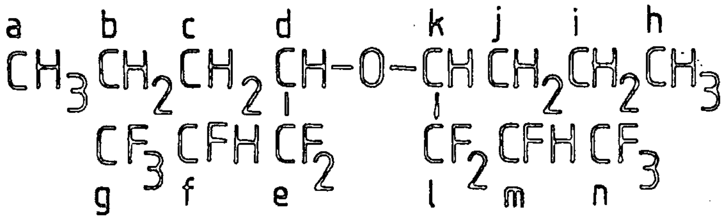


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
0.67	M	14	a , e
1.27	M		b , c ,f ,g
3.32	M	3	d , h
4.77	D of M, J_{HF}=43	1	j
^{19}F			
76.2	M	3	k
117.2, 123.0	AB, J_{FF}=273	2	i
120.3, 128.2	AB, J_{FF}=273		
213.5	M	1	j

M.Wt. 280 No.6



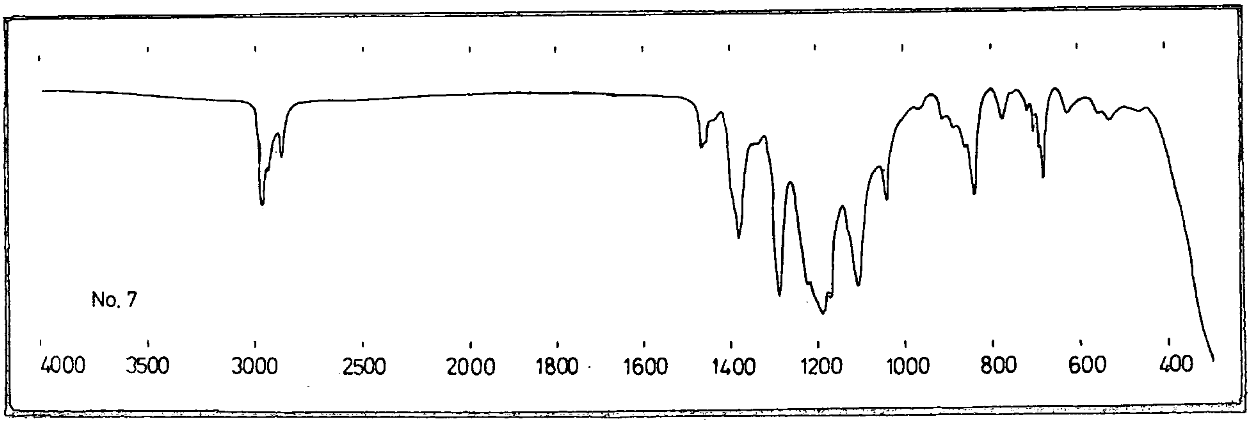
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.25	2.56	36	102.99	1.37
2	28.13	4.74	37	105.03	0.60
3	29.02	15.17	38	108.92	0.81
4	30.92	2.63	39	112.98	0.63
5	32.01	0.77	40	120.97	0.77
6	39.00	1.09	41	123.03	0.60
7	40.98	22.51	42	127.01	1.93
8	41.36	0.39	43	129.03	40.81
9	41.53	0.56	44	130.01	4.11
10	42.07	2.14	45	132.96	0.53
11	43.15	6.81	46	140.87	2.42
12	44.17	0.74	47	144.97	0.60
13	45.17	1.44	48	146.98	0.67
14	47.12	4.88	49	150.91	1.23
15	50.95	0.53	50	152.99	0.84
16	55.17	32.21	51	158.91	2.77
17	56.16	7.69	52	166.98	2.92
18	57.15	55.88	53	172.96	2.85
19	58.12	2.77	54	186.97	5.58
20	59.02	2.07	55	187.96	0.46
21	61.02	4.99	56	194.89	2.85
22	65.12	5.02	57	206.90	2.00
23	68.96	1.23	58	216.96	0.42
24	69.96	0.49	59	220.93	2.92
25	70.99	2.07	60	236.89	1.02
26	72.04	0.67			
27	73.07	100.00			
28	74.10	4.88			
29	75.10	0.49			
30	77.01	3.37			
31	85.05	1.02			
32	87.05	2.81			
33	90.92	1.19			
34	95.00	0.74			
35	100.98	0.67			



$CH_3CH_2CH_2CH(CF_2CFHCF_3)-O-CH(CF_2CFHCF_3)CH_2CH_2CH_3$

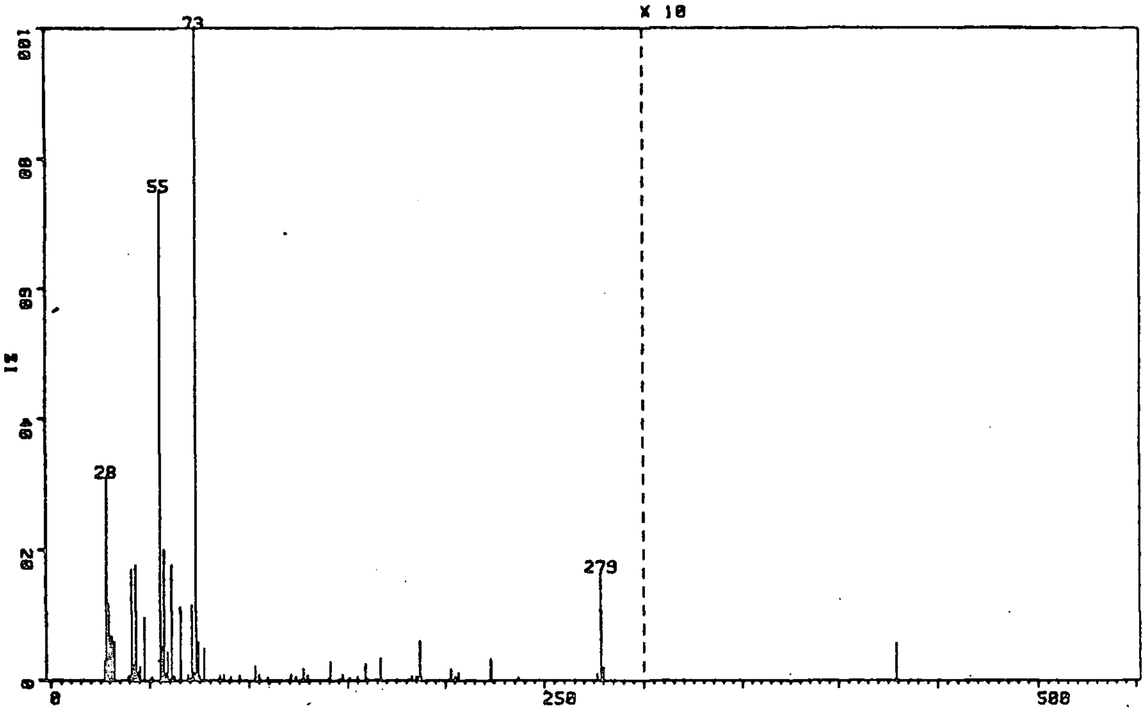
No.7

Di(1-propyl-2,2,3,4,4,4-hexafluorobutyl) ether (15).

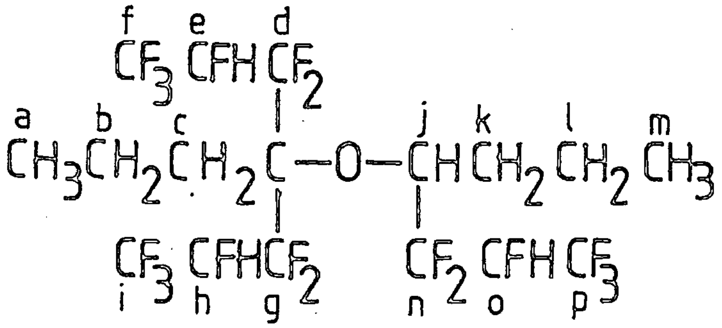


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
0.87	M	7	a, h
1.52	M		b, c, i, j
3.83	M	1	d, k
4.87	D of M, J_{HF}=44	1	f, m
^{19}F			
75.7	M	3	g, n
112.8, 114.2, 117.5, 119.0, 119.7, 120.8, 123.7, 125.3, 126.3, 130.3.	Overlapping AB's	2	e, l
212.7	M	1	f, m

MWt. 430 No.7



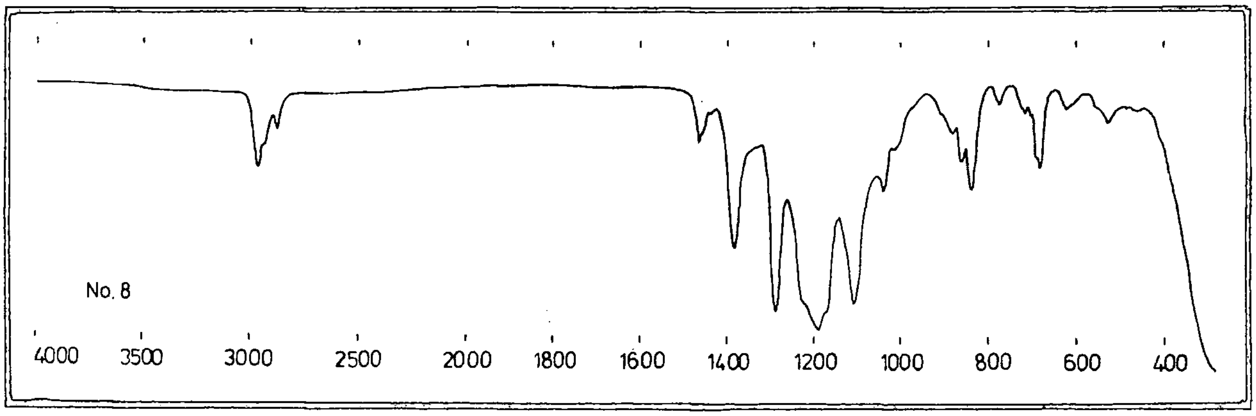
PEAK NO.	MASS	%HT. BASE
1	27.25	3.14
2	28.13	31.02
3	29.02	11.68
4	30.93	6.78
5	32.02	5.97
8	40.99	16.97
9	42.08	2.34
10	43.15	17.69
12	45.17	2.18
13	47.12	9.61
15	55.17	75.03
16	56.17	5.13
17	57.15	20.03
19	59.02	4.44
20	61.03	17.73
22	65.13	11.22
24	70.99	11.53
26	73.07	100.00
27	74.10	5.94
29	77.02	4.98
34	103.00	2.34
39	127.01	1.80
41	140.89	2.91
45	158.95	2.57
46	167.00	3.29
50	186.96	6.01
52	202.88	1.76
55	222.99	3.26
58	278.87	16.62
59	279.92	1.99
60	428.93	0.57



$$CH_3CH_2CH_2C(CF_2CFHCF_3)_2-O-CH(CF_2CFHCF_3)CH_2CH_2CH_3$$

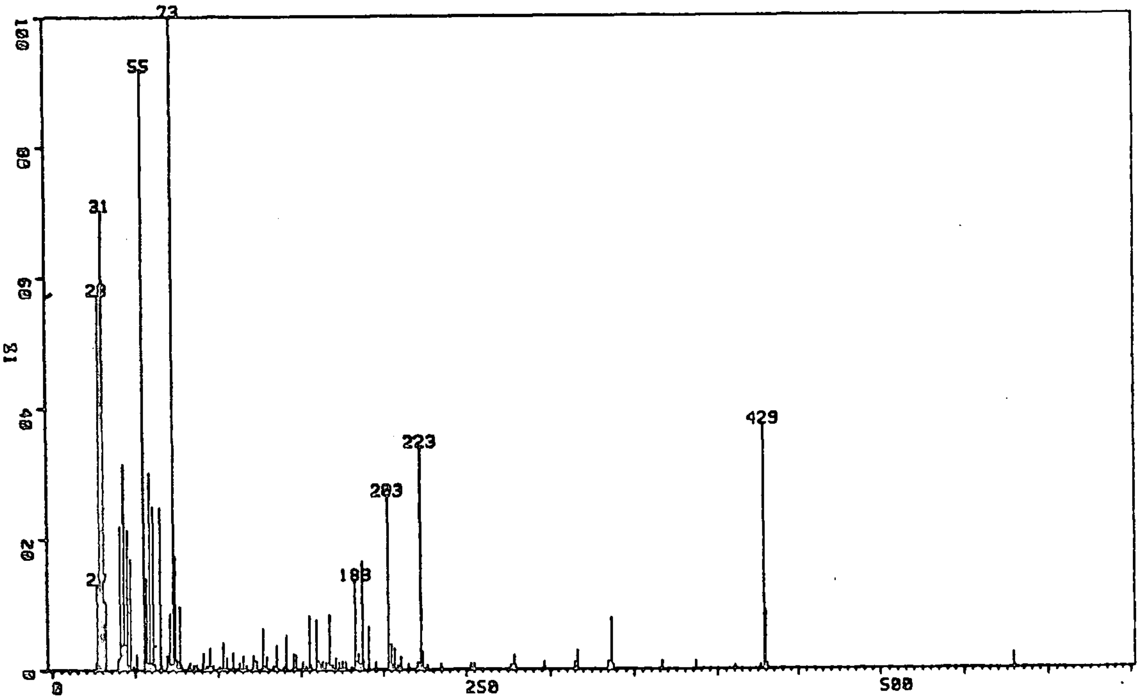
No.8

1-Propyl-2,2,3,4,4,4-hexafluorobutyl 1-propyl-1-(1,1,2,3,3,3-hexafluoropropyl)-2,2,3,4,4,4-hexafluorobutyl ether (16).

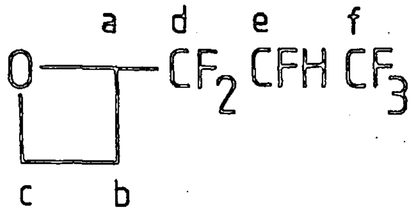


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
1.03	M	6	a, m
1.57	M	8	b, c, k, l
2.10	M		
3.97	M	1	j
4.87	D of M, J_{HF}=42	3	e, h, o
^{19}F			
74.7	M	3	f, i, p
116.7, 119.0, 122.3, 124.0	Overlapping AB's	2	d, g, n
211.2	M(broad)	1	e, h, o

M.Wt. 580 No.8

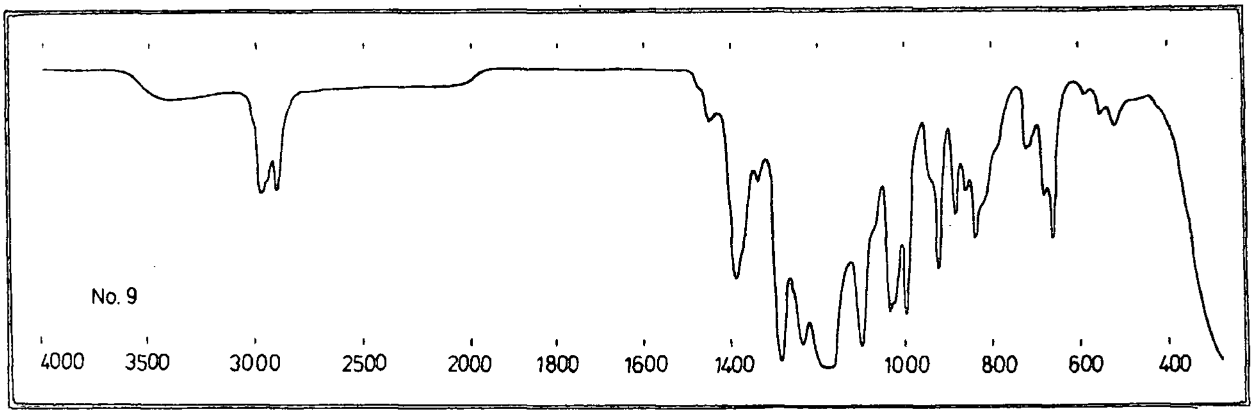


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
2	27.25	13.09	60	140.89	5.29
3	28.13	57.30	61	144.98	2.50
4	29.02	40.72	62	147.00	2.20
6	30.92	70.25	65	155.01	8.22
7	32.02	10.37	67	158.93	7.58
9	39.83	1.76	73	167.00	8.39
10	40.99	22.00	76	170.93	1.85
11	42.08	3.66	81	182.97	13.69
12	43.15	31.42	83	184.95	2.54
13	44.16	3.75	85	186.96	16.57
14	45.17	21.48	87	190.91	6.59
16	47.12	16.87	89	202.92	26.56
18	50.95	2.37	90	203.91	2.02
19	55.17	91.65	91	204.91	3.92
20	56.17	5.29	93	206.90	3.23
21	57.15	13.86	95	210.91	1.94
23	59.03	30.00	98	223.00	33.96
25	61.03	24.92	99	224.02	2.63
27	65.12	24.75	105	279.00	2.20
29	68.97	2.28	108	314.94	1.08
30	70.99	8.52	109	316.88	2.97
32	73.07	100.00	110	334.95	1.29
33	74.10	17.26	111	336.92	7.92
34	75.10	1.55	112	337.93	0.77
35	77.01	9.64	113	366.85	1.25
41	90.93	2.63	114	386.89	1.33
43	95.02	3.31	115	410.94	0.69
46	103.00	4.09	116	427.09	0.82
47	105.03	1.89	117	429.06	37.37
48	108.92	2.58	118	429.91	8.82
50	115.03	2.11	119	431.11	0.73
52	120.97	2.15	120	579.21	2.41
54	127.01	6.33			
56	129.05	2.07			
58	135.00	3.83			



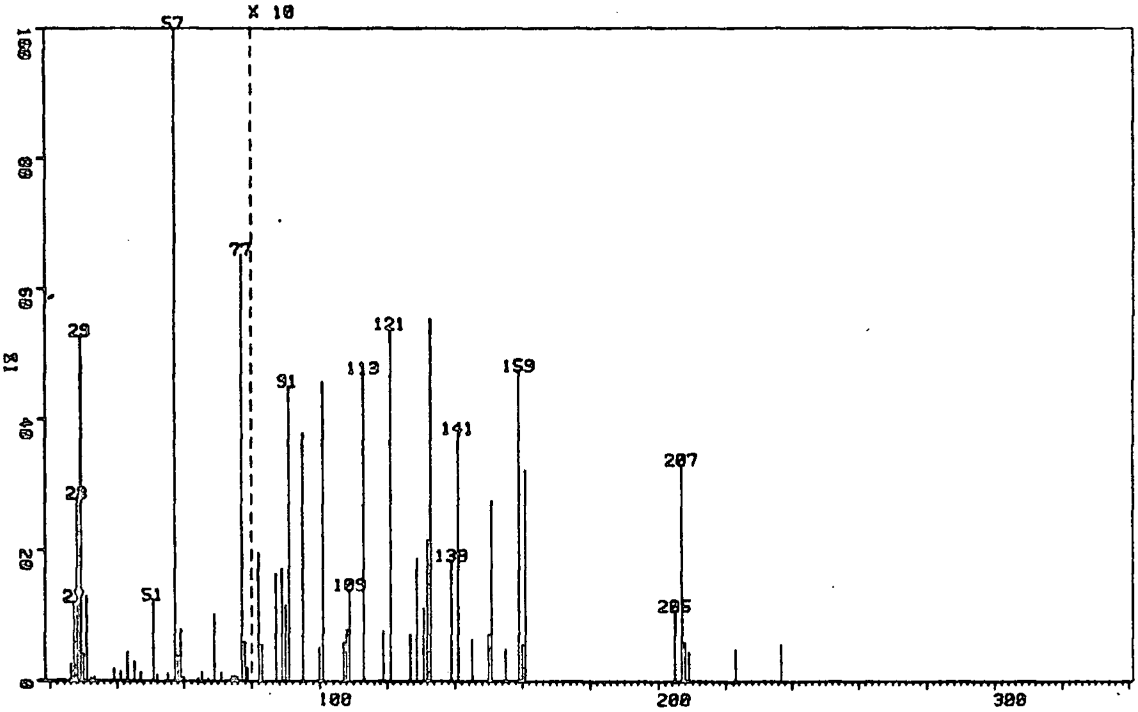
No.9

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

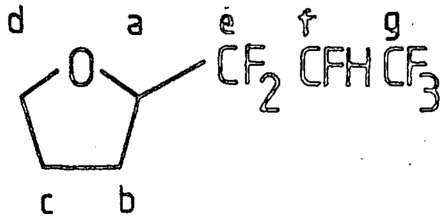


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
2.60	Q, J =7.5	2	b
4.40	T, J =7.5	4	c
5.0	M(broad)		a , e
^{19}F			
75.9	M(D of Q, J=6 and 11)	3	f (RR+SS)
76.8	M(P, J=8)		f (RS+SR)
127.9	M(Sx, J=10)	2	d (RS+SR)
132.8	M(11 peaks, J=10)		d (RR+SS)
215.8	D of Q of M, J=42 and 10	1	e (RR+SS)
219.9	D of Sx, J=44 and 10		e (RS+SR)

MWt. 208 No.9

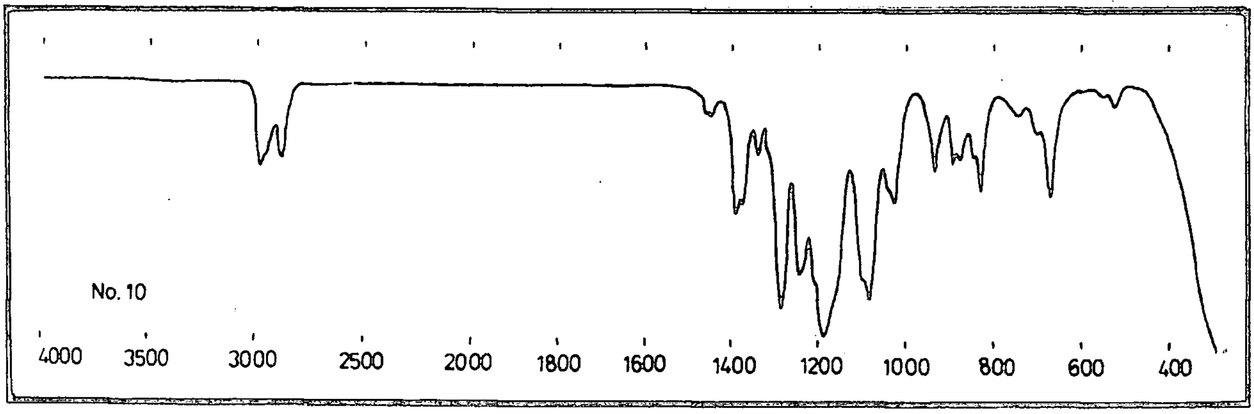


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	26.30	2.63	36	88.91	1.72
2	27.24	12.10	37	89.87	1.16
3	28.14	27.86	38	90.96	4.51
4	28.98	52.85	39	95.04	3.79
5	29.01	49.62	40	99.93	0.52
6	29.82	4.07	41	100.95	4.59
7	30.91	12.93	42	107.03	0.60
8	32.01	0.48	43	108.01	0.80
9	33.11	0.56	44	108.97	1.40
10	38.99	1.88	45	112.99	4.71
11	40.97	1.44	46	118.98	0.76
12	43.09	4.39	47	120.99	5.39
13	45.15	2.95	48	127.02	0.72
14	47.10	1.36	49	128.94	1.88
15	50.92	12.42	50	130.93	1.12
16	52.02	0.96	51	131.97	2.16
17	55.11	1.16	52	132.99	5.55
18	57.09	100.00	53	138.96	1.84
19	58.06	3.79	54	140.93	3.79
20	58.99	7.94	55	145.02	0.64
21	59.93	0.48	56	149.91	0.72
22	64.09	0.48	57	150.94	2.75
23	65.10	1.40	58	155.03	0.48
24	67.04	0.40	59	158.99	4.75
25	68.92	10.18	60	159.95	0.56
26	70.94	1.32	61	160.95	3.23
27	74.07	0.84	62	204.94	1.08
28	75.01	0.80	63	206.97	3.31
29	76.00	0.64	64	207.97	0.60
30	76.99	65.23	65	208.97	0.44
31	77.96	6.07	66	222.99	0.48
32	78.91	2.04	67	236.96	0.56
33	81.90	1.96			
34	82.95	0.56			
35	86.99	1.64			



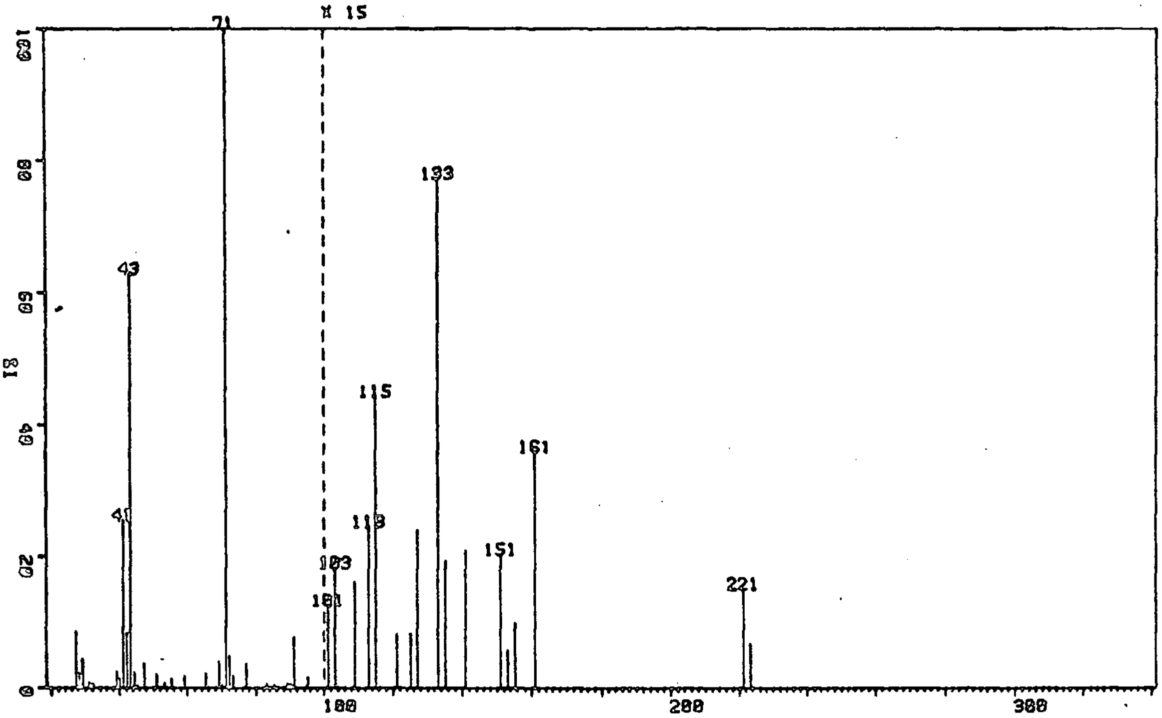
No.10

2-(1,1,2,3,3,3-Hexafluoropropyl)oxolane (21).

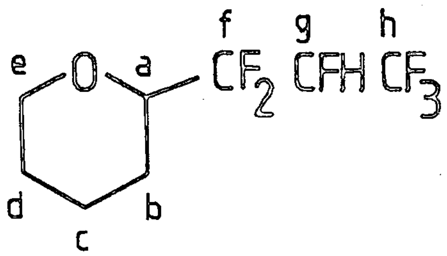


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
1.98	M	4	b , c
3.66	M	2	d
4.16	M	1	a
5.26	D of M, J_{HF}=44	1	f
^{19}F			
74.39	M	3	g (RR+SS)
74.96	M		g (RS+SR)
120.2, 124.7	AB, J_{FF}=306	2	e (RS+SR)
124.8, 131.3	AB, J_{FF}=316		e (RR+SS)
213.8	D of M, J_{FH}=42	1	f (RR+SS)
218.4	D of M, J_{FH}=44		f (RS+SR)

M.Wt. 222 No.10

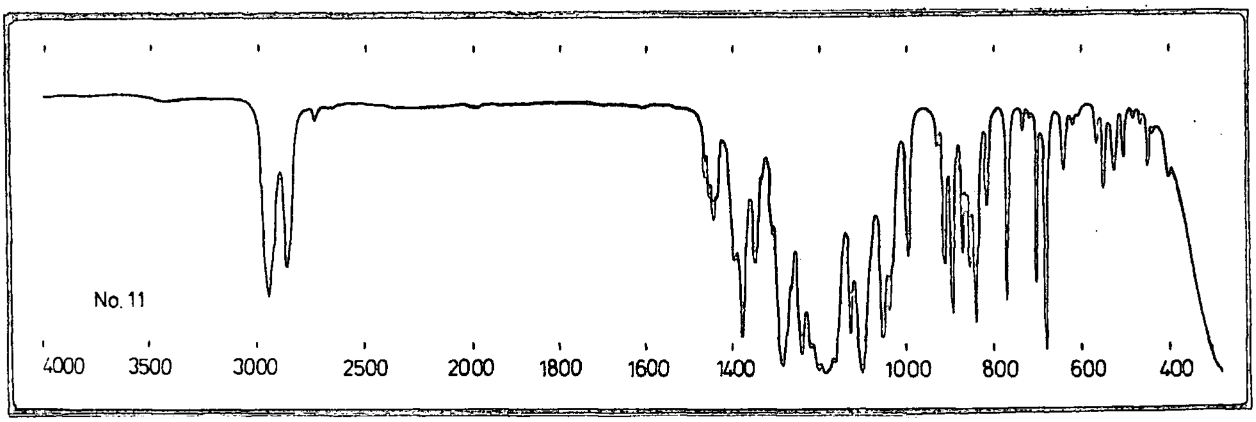


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.25	8.52	36	120.99	0.56
2	28.14	2.16	37	125.05	0.56
3	29.00	4.31	38	127.01	1.60
4	30.93	0.80	39	133.01	5.15
5	32.02	0.49	40	135.05	1.29
6	39.00	2.43	41	140.96	1.39
7	39.90	1.39	42	150.95	1.36
8	40.98	25.53	43	153.07	0.38
9	42.08	8.38	44	155.03	0.66
10	43.14	62.89	45	160.96	2.40
11	44.18	2.37	46	221.02	1.01
12	45.16	0.35	47	223.09	0.45
13	47.12	3.69			
14	50.94	2.05			
15	53.11	0.73			
16	55.16	1.50			
17	59.02	1.84			
18	65.13	2.23			
19	68.96	4.00			
20	69.93	0.38			
21	71.00	100.00			
22	72.05	4.87			
23	73.07	1.84			
24	77.03	3.69			
25	83.02	0.59			
26	85.08	0.42			
27	88.97	0.56			
28	89.92	0.45			
29	90.96	7.72			
30	95.04	1.60			
31	100.96	0.83			
32	103.04	1.22			
33	108.97	1.08			
34	112.99	1.63			
35	115.04	2.96			



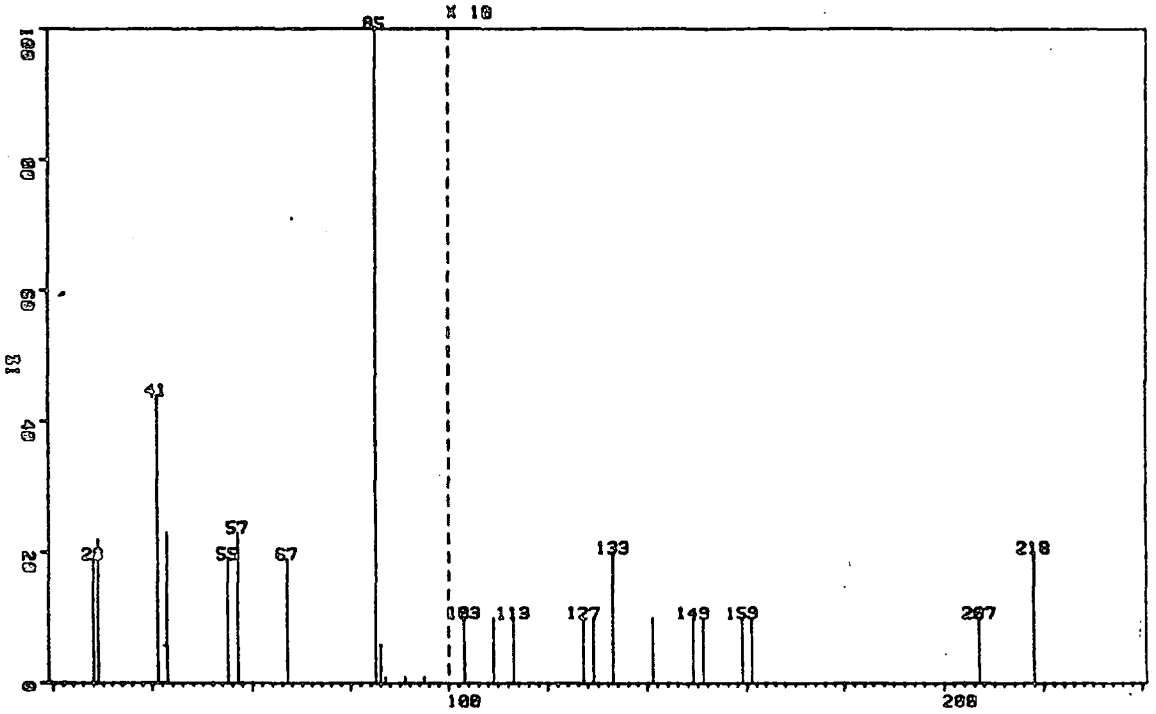
No.11

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

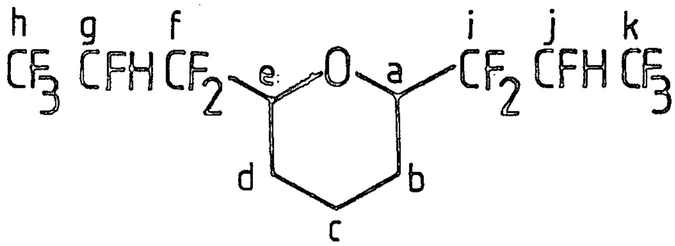


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
1.48	M	6	b, c, d
3.18, 3.83	M	3	a , e
4.85	D of M, J_{HF}=44, J=5	1	g
^{19}F			
74.9	D of Q, J=6 and 11	3	h (RR+SS)
75.8	P of M, J=8		h (RS+SR)
123.3	Oc of M, J=11	2	f (RS+SR)
128.4	Sp of M, J=11		f (RR+SS)
214.8	D of Sx of M, J=43 and 10	1	g (RR+SS)
219.7	D of Sx, J=44 and 10		g (RS+SR)

M.Wt. 236 No.11

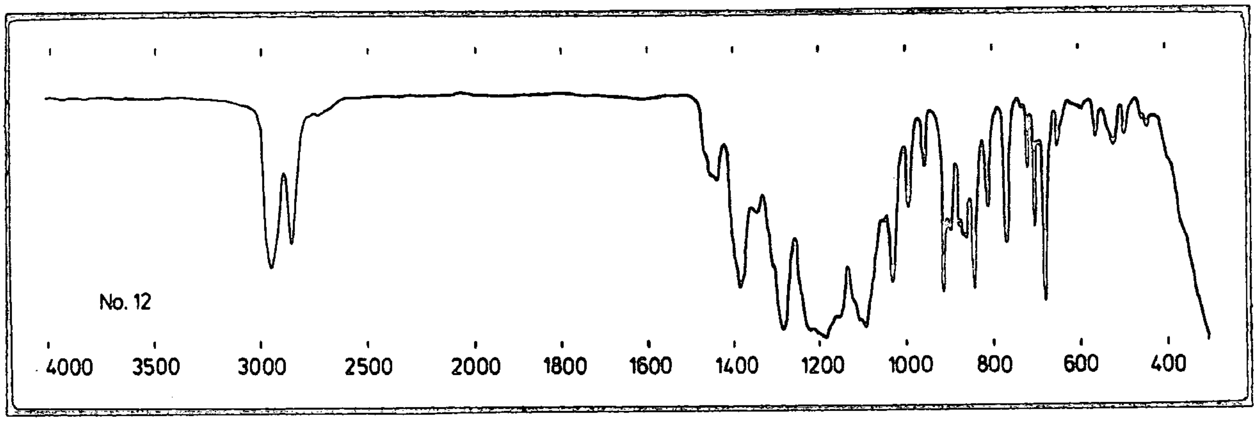


PEAK NO.	MASS	%HT. BASE
1	28.00	19.00*
2	29.00	22.00*
3	41.00	44.00*
4	43.00	23.00*
5	55.00	19.00*
6	57.00	23.00*
7	67.00	19.00*
8	85.00	100.00*
9	86.00	6.00*
10	87.00	1.00*
11	91.00	1.00*
12	95.00	1.00*
13	103.00	1.00*
14	109.00	1.00*
15	113.00	1.00*
16	127.00	1.00*
17	129.00	1.00*
18	133.00	2.00*
19	141.00	1.00*
20	149.00	1.00*
21	151.00	1.00*
22	159.00	1.00*
23	161.00	1.00*
24	207.00	1.00*
25	218.00	2.00*



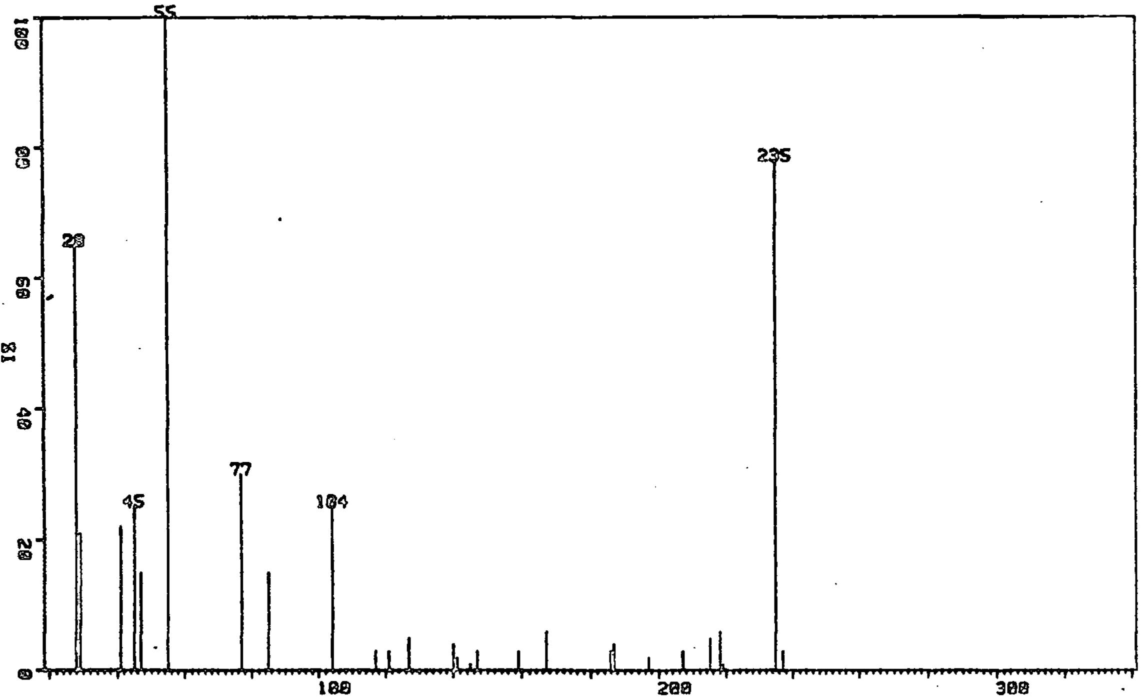
No.12

2,5-Di(1,1,2,3,3,3-hexafluoropropyl)oxane (<u>23</u>).



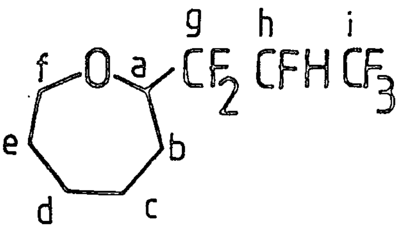
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
<u>^1H</u>			
1.57	M	6	b, c, d
3.17	M	2	a, e
3.80	M		
4.75	D of M, J_{HF}=44	2	g, j
<u>^{19}F</u>			
76.0	M	3	h , k
117.0	M	2	f , i
118.3	M		
211.7	M	1	g , j

MWt. 384 No.12

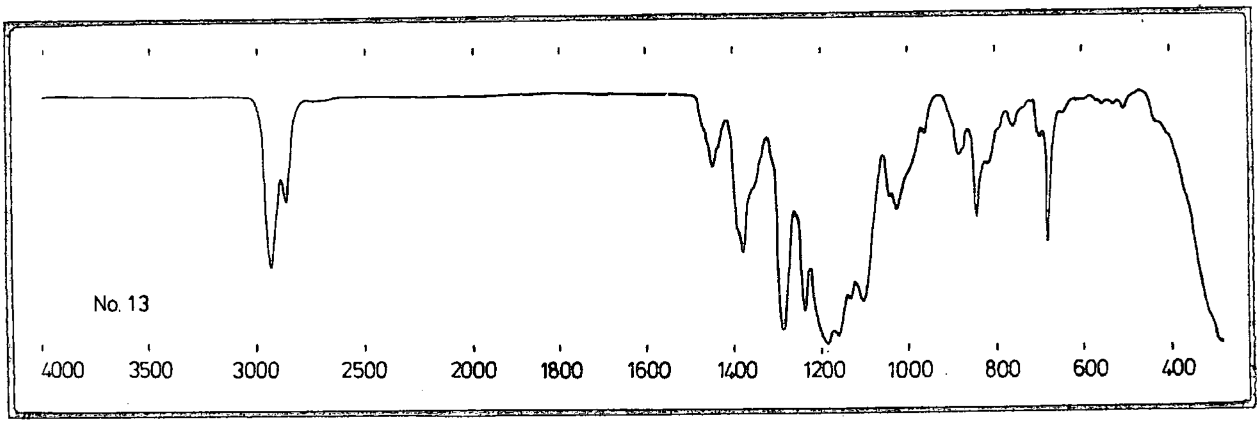


PEAK NO.	MASS	%HT. BASE
1	28.00	65.00*
2	29.00	21.00*
3	41.00	22.00*
4	45.00	25.00*
5	47.00	15.00*
6	55.00	100.00*
7	77.00	30.00*
8	85.00	15.00*
9	104.00	25.00*
10	117.00	3.00*
11	121.00	3.00*
12	127.00	5.00*
13	140.00	4.00*
14	141.00	2.00*
15	145.00	1.00*
16	147.00	3.00*
17	159.00	3.00*
18	167.00	6.00*
19	186.00	3.00*
20	187.00	4.00*
21	197.00	2.00*
22	207.00	3.00*
23	215.00	5.00*
24	218.00	6.00*
25	219.00	1.00*
26	235.00	78.00*
27	237.00	3.00*

No.13

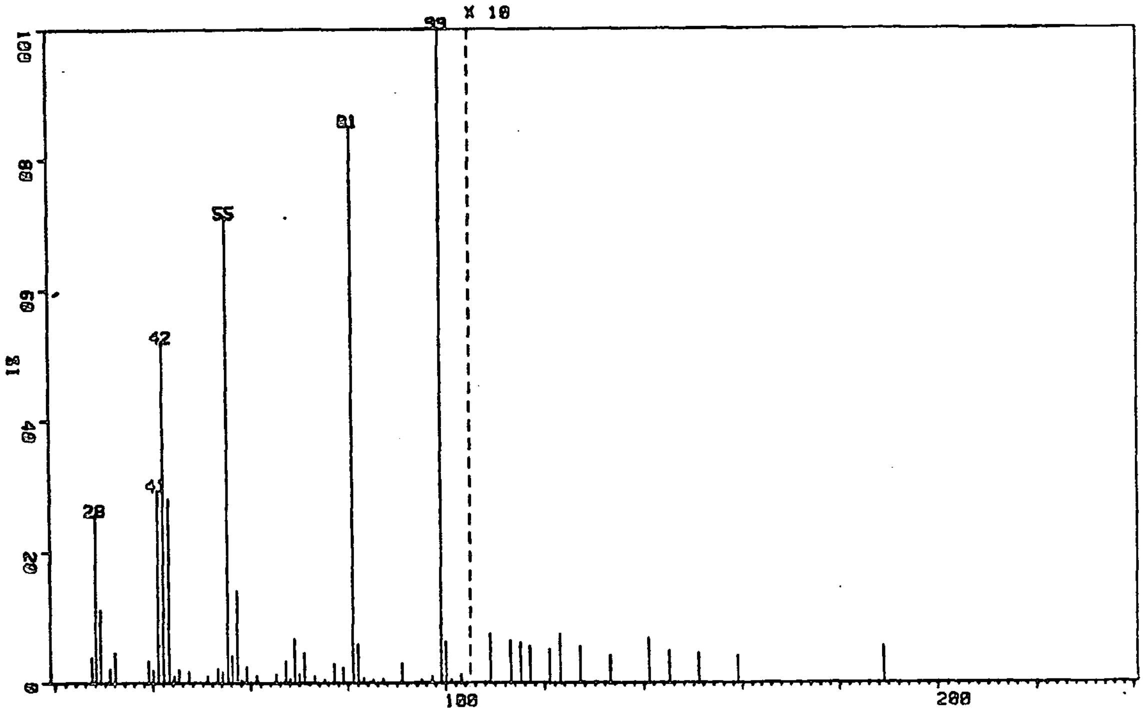


2-(1,1,2,3,3,3-hexafluoropropyl)oxepane (24).



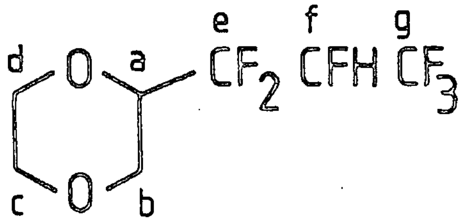
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
1.47	M	8	b, c, d, e
3.47	M	3	a , f
4.87	D of M, J_{HF}=44	1	h
^{19}F			
76.5	M	3	i
76.8	M		
117.3, 122.0, 124.2, 127.0, 129.0, 134.0.	Overlapping AB's	2	g
214.8	D of M, J_{FH}=44	1	h
219.5	D of M, J_{HF}=44		

MWt. 250 No.13

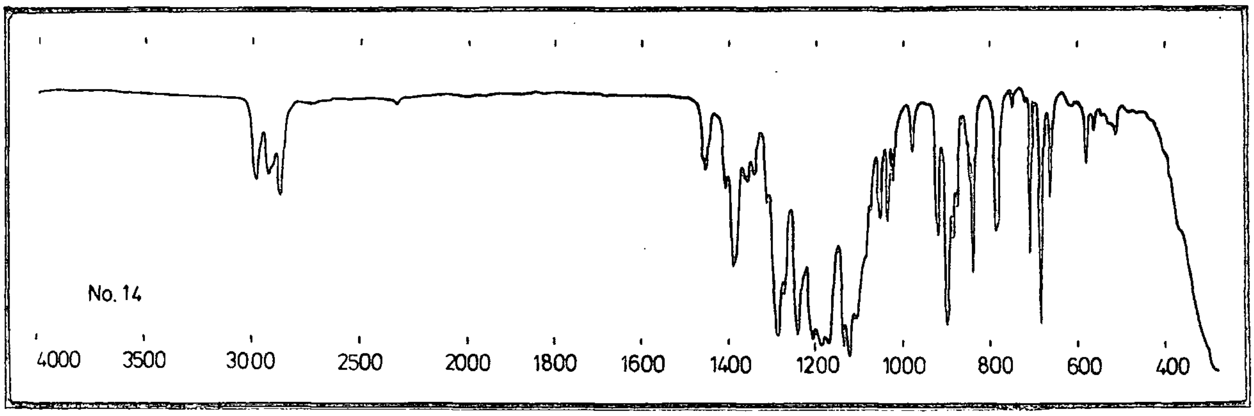


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.25	3.98	36	85.06	0.52
2	28.13	25.55	37	87.05	0.68
3	29.02	11.17	38	90.96	3.04
4	30.93	2.17	39	95.03	0.62
5	32.02	4.60	40	97.05	1.04
6	39.00	3.34	41	99.02	100.00
7	39.89	1.98	42	99.98	6.25
8	40.99	29.37	43	101.00	0.55
9	42.08	52.01	44	103.05	1.23
10	43.14	28.08	45	109.00	0.74
11	44.17	1.04	46	113.02	0.65
12	45.18	2.01	47	115.05	0.62
13	47.12	1.72	48	117.03	0.55
14	50.95	1.13	49	120.96	0.52
15	53.12	2.27	50	123.05	0.74
16	54.15	1.65	51	127.02	0.55
17	55.17	71.05	52	133.02	0.42
18	56.17	4.21	53	140.95	0.68
19	57.12	14.12	54	145.03	0.49
20	58.08	0.49	55	150.97	0.45
21	59.01	2.43	56	159.02	0.42
22	61.03	1.13	57	189.03	0.55
23	65.14	1.39			
24	67.10	3.27			
25	68.07	0.62			
26	69.00	6.74			
27	69.95	1.39			
28	71.01	4.63			
29	73.07	1.13			
30	75.12	0.62			
31	77.01	2.95			
32	78.97	2.40			
33	80.97	85.01			
34	82.03	5.86			
35	83.04	0.74			

No. 14

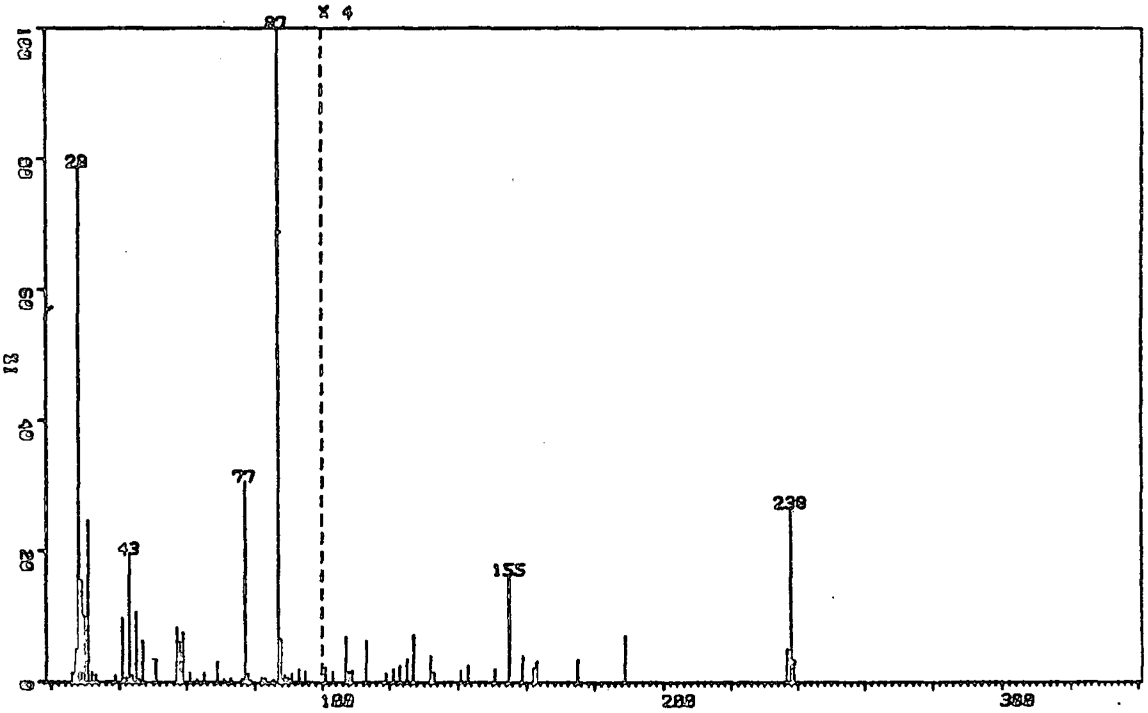


2-(1,1,2,3,3,3-Hexafluoropropyl)-1,4-dioxan (25).



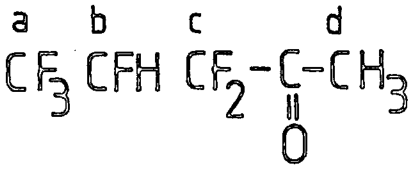
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
3.61	M	7	a, b, c, d
4.99	D of M, J_{HF}=46	1	f
^{19}F			
75.2	M, J=6 and 4	3	g (RR+SS)
76.0	M, J=8		g (RS+SR)
122.5	D of M, J=50 and 10	2	e (RS+SR)
127.7	M, J=10		e (RR+SS)
214.3	D of M, J=43 and 10	1	f (RR+SS)
218.9	D Of Q, J=43 and 10		f (RS+SR)

M.Wt. 238 No.14



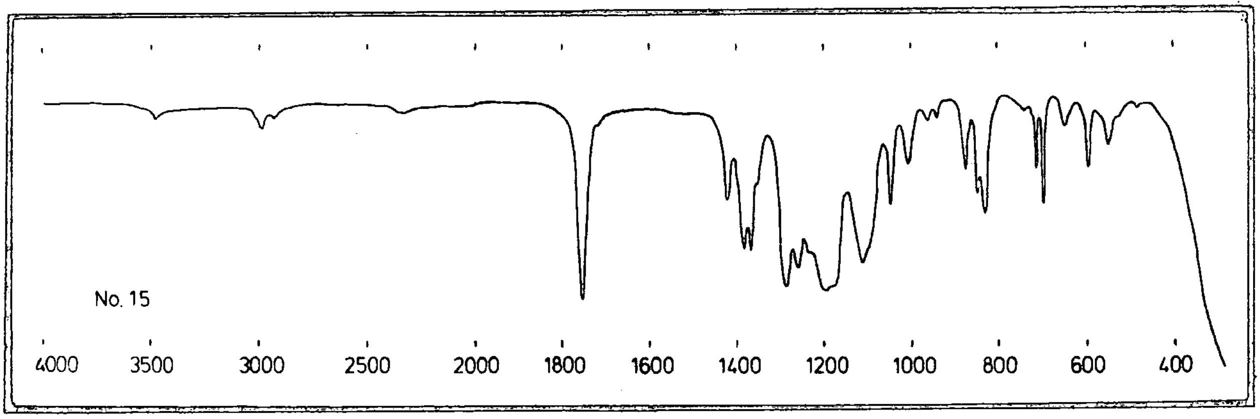
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	26.30	1.39	36	86.95	100.00
2	27.23	4.93	37	87.64	6.55
3	28.13	78.82	38	88.52	0.46
4	28.99	15.56	39	88.90	1.08
5	29.84	10.13	40	89.87	0.65
6	30.90	24.68	41	90.94	1.42
7	32.00	1.50	42	93.00	1.96
8	33.10	1.19	43	95.03	1.77
9	38.97	1.00	44	100.95	0.58
10	40.95	9.74	45	103.02	0.42
11	42.02	0.73	46	107.00	1.73
12	43.07	19.64	47	107.98	0.42
13	44.11	1.00	48	108.94	0.46
14	45.14	10.67	49	112.97	1.58
15	46.12	0.39	50	118.98	0.35
16	47.08	6.39	51	120.97	0.50
17	50.89	3.47	52	123.00	0.62
18	57.08	8.32	53	125.04	0.89
19	58.03	6.08	54	126.99	1.81
20	58.98	7.55	55	131.92	1.00
21	60.94	1.39	56	132.98	0.39
22	63.04	0.42	57	140.86	0.46
23	65.08	1.46	58	142.93	0.65
24	68.95	3.12	59	150.89	0.50
25	70.96	0.42	60	154.94	4.12
26	73.02	0.69	61	158.92	1.00
27	76.02	0.54	62	161.91	0.54
28	76.99	30.69	63	162.94	0.81
29	77.96	1.23	64	174.95	0.89
30	78.90	0.35	65	188.88	1.77
31	81.90	0.69	66	236.82	1.27
32	82.96	0.65	67	237.85	6.66
33	85.29	0.35	68	238.90	0.85
34	85.42	0.39			
35	85.74	0.35			

No. 15



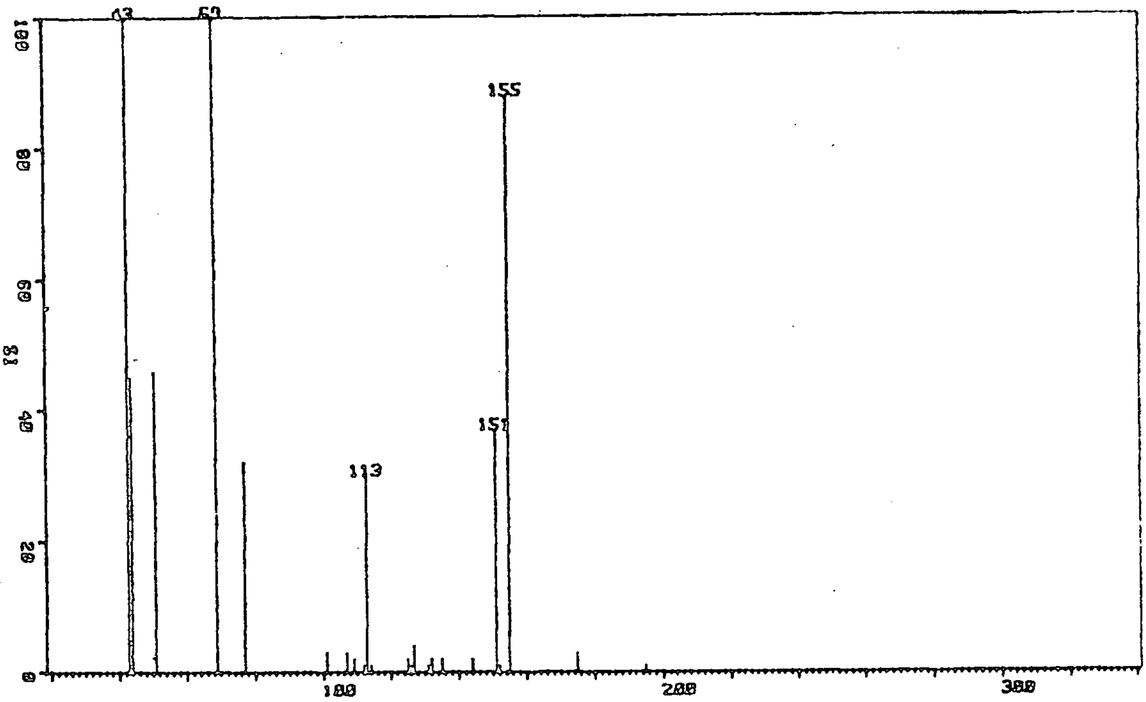
$$\overset{a}{CF_3}\,\overset{b}{CFH}\,\overset{c}{CF_2}-\underset{\underset{O}{\|}}{C}-\overset{d}{CH_3}$$

3,3,4,5,5,5-Hexafluoropentan-2-one (19).

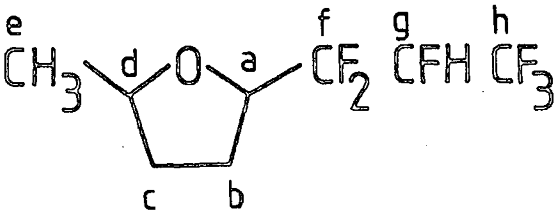


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
2.32	S	3	d
5.32	D of M, $J_{HF}=43$, $J=6$	1	b
^{19}F			
76.5	M	3	a
117.5, 125.5	AB, $J_{FF}=298$	2	c
218.1	D of M, $J_{FH}=43$, $J=6$	1	b

M.Wt. 194 No.15

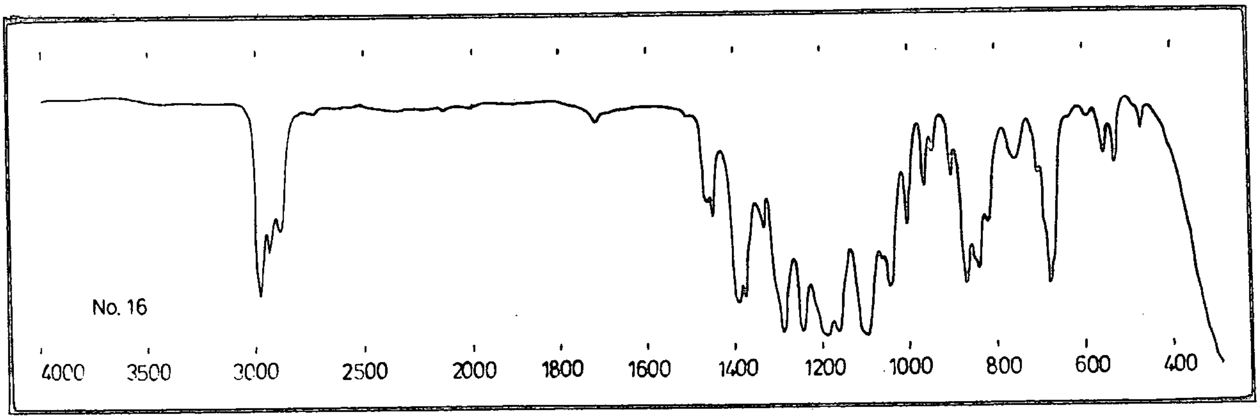


PEAK NO.	MASS	%HT. BASE
1	43.00	100.00*
2	44.00	45.00*
3	51.00	46.00*
4	69.00	100.00*
5	77.00	32.00*
6	101.00	3.00*
7	107.00	3.00*
8	109.00	2.00*
9	112.00	1.00*
10	113.00	30.00*
11	114.00	1.00*
12	125.00	2.00*
13	126.00	1.00*
14	127.00	4.00*
15	131.00	1.00*
16	132.00	2.00*
17	135.00	2.00*
18	144.00	2.00*
19	151.00	37.00*
20	152.00	1.00*
21	155.00	88.00*
22	175.00	3.00*
23	195.00	1.00*



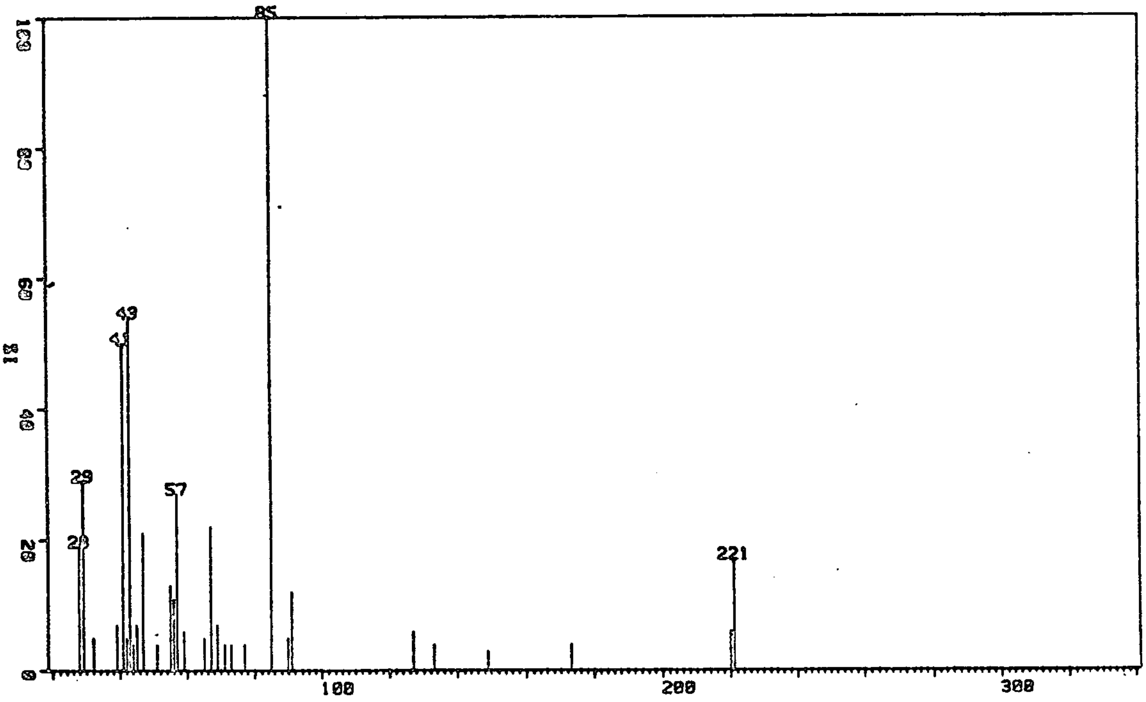
No. 16

2-Methyl-5-(1,1,2,3,3,3-hexafluoropropyl)oxolane (27).



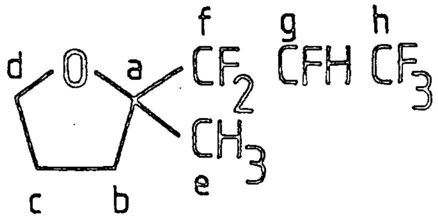
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
1.25	D	3	e
2.18	M	4	b , c
4.18	M	3	d
4.58	M		a
5.18	D of M, J_{HF}=43		g
^{19}F			
74.3	M	3	h(RR+SS)
124.0, 127.2, 128.8, 130.3, 131.6, 133.4.	Overlapping AB'S	2	f(RR+SS)
213.2	D of M, J_{FH}=43	1	g(RR+SS)

M.Wt. 236 No.16

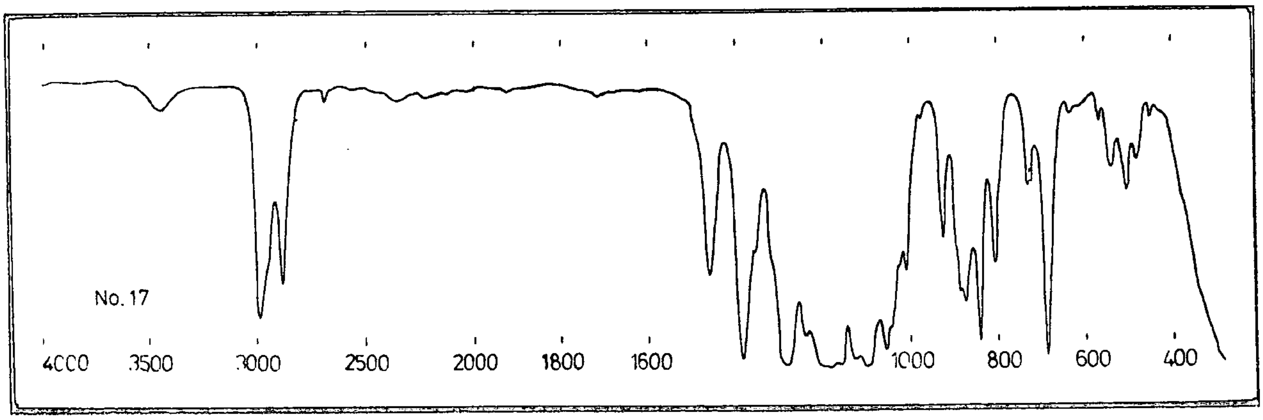


PEAK NO.	MASS	%HT. BASE
1	28.00	19.00*
2	29.00	29.00*
3	32.00	5.00*
4	39.00	7.00*
5	41.00	50.00*
6	42.00	5.00*
7	43.00	54.00*
8	44.00	4.00*
9	45.00	7.00*
10	47.00	21.00*
11	51.00	4.00*
12	55.00	5.00*
13	55.00	13.00*
14	56.00	11.00*
15	57.00	27.00*
16	59.00	6.00*
17	65.00	5.00*
18	67.00	22.00*
19	69.00	7.00*
20	71.00	4.00*
21	73.00	4.00*
22	77.00	4.00*
23	85.00	100.00*
24	90.00	5.00*
25	91.00	12.00*
26	127.00	6.00*
27	133.00	4.00*
28	149.00	3.00*
29	173.00	4.00*
30	220.00	6.00*
31	221.00	17.00*

No.17

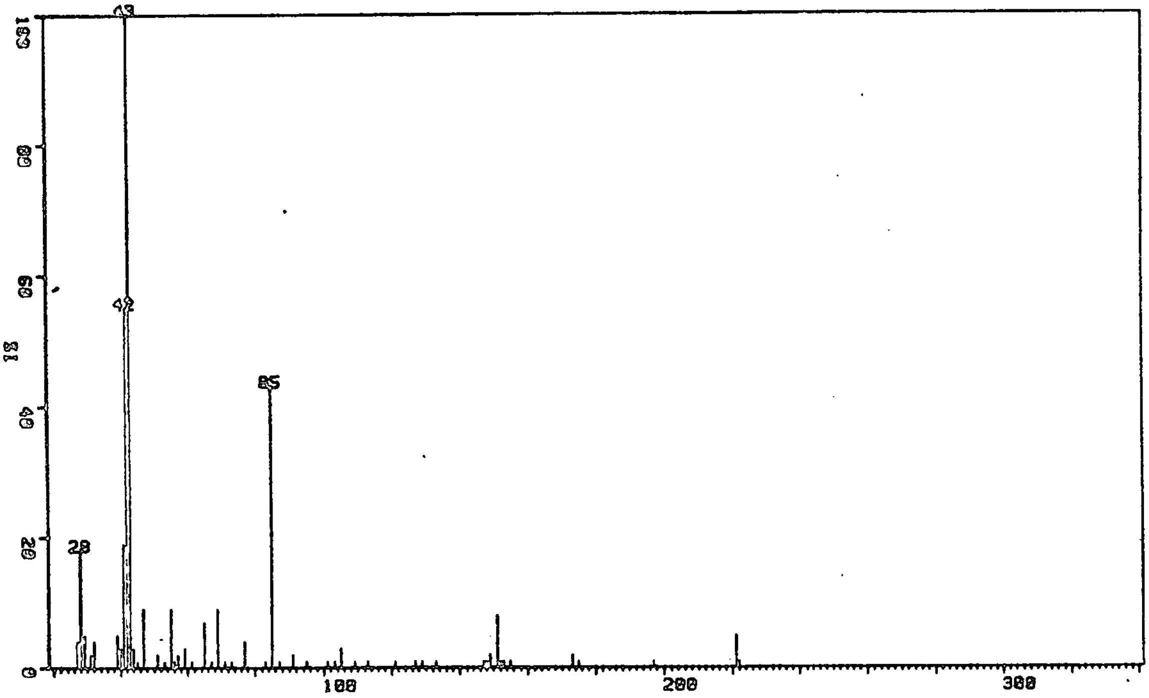


2-Methyl-2-(1,1,2,3,3,3-hexafluoropropyl)oxolane (26).



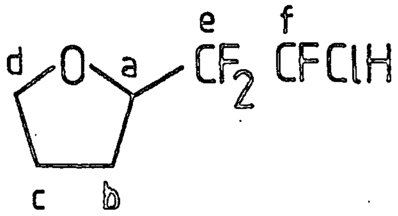
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
1.07	S	3	e
1.72	M	4	b , c
3.68	T, J=6	2	d
4.92	D of M, J_{HF}=44	1	g
^{19}F			
75.5	M	3	h
125.0, 118.1	AB, J_{FF}=282	2	f
210.5	D of Sx, J_{FH}=43, J=9	1	g

M.Wt. 236 No.17

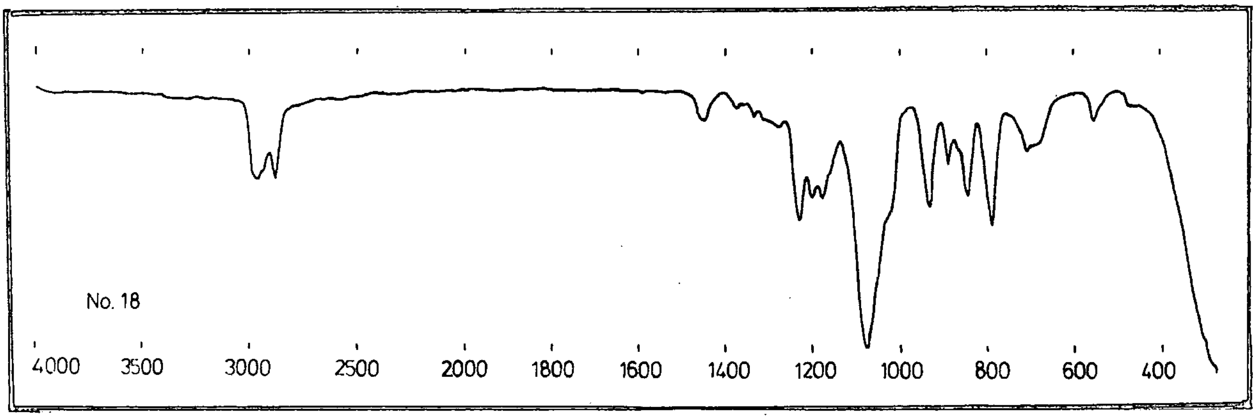


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.00	4.00*	36	105.00	3.00*
2	28.00	18.00*	37	109.00	1.00*
3	29.00	5.00*	38	113.00	1.00*
4	31.00	2.00*	39	121.00	1.00*
5	32.00	4.00*	40	127.00	1.00*
6	39.00	5.00*	41	129.00	1.00*
7	40.00	3.00*	42	133.00	1.00*
8	41.00	19.00*	43	147.00	1.00*
9	42.00	55.00*	44	148.00	1.00*
10	43.00	100.00*	45	149.00	2.00*
11	44.00	3.00*	46	151.00	8.00*
12	45.00	1.00*	47	152.00	1.00*
13	47.00	9.00*	48	153.00	1.00*
14	51.00	2.00*	49	155.00	1.00*
15	53.00	1.00*	50	173.00	2.00*
16	55.00	9.00*	51	175.00	1.00*
17	56.00	1.00*	52	197.00	1.00*
18	57.00	2.00*	53	221.00	5.00*
19	59.00	3.00*	54	222.00	1.00*
20	61.00	1.00*			
21	65.00	7.00*			
22	67.00	1.00*			
23	69.00	9.00*			
24	71.00	1.00*			
25	73.00	1.00*			
26	77.00	4.00*			
27	77.00	4.00*			
28	83.00	1.00*			
29	85.00	43.00*			
30	87.00	1.00*			
31	91.00	2.00*			
32	95.00	1.00*			
33	101.00	1.00*			
34	101.00	1.00*			
35	**103.00**	**1.00***			

No. 18

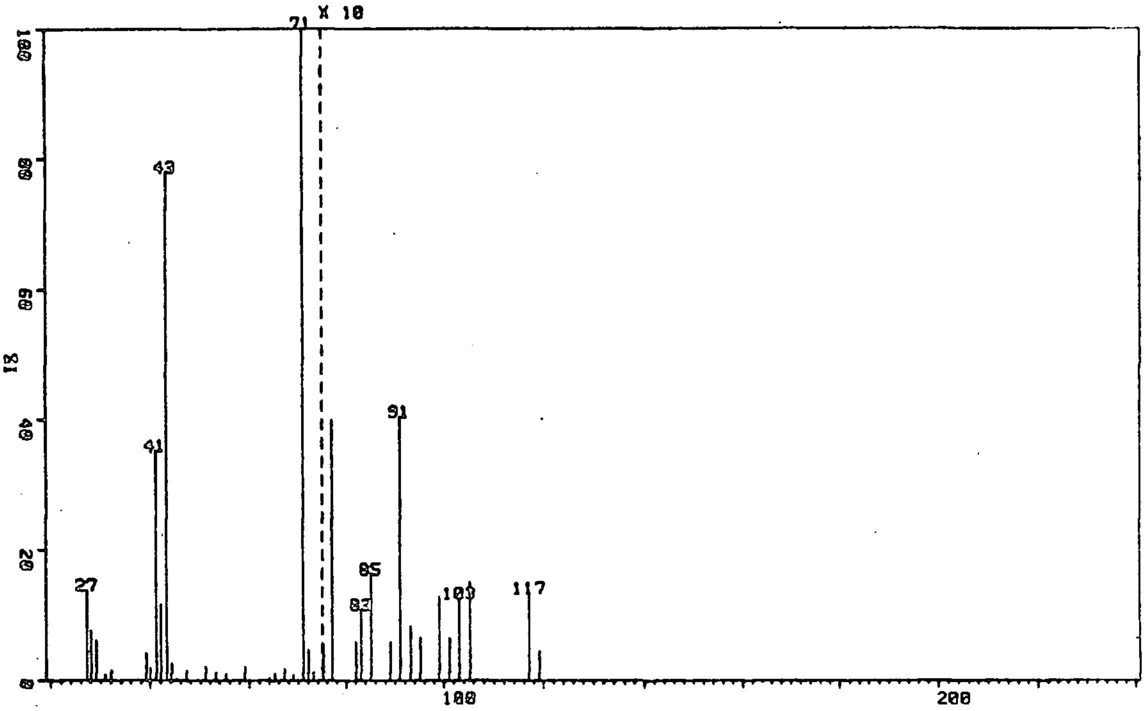


2-(2-Chloro-1,1,2-trifluoroethyl)oxolane (35).



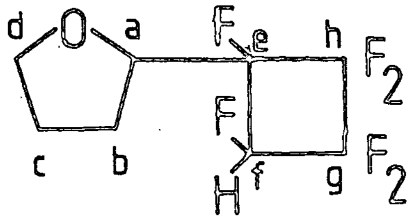
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
2.07	M	4	b, c
3.90	M	3	a, d
6.57	D of M, J_{HF}=49	1	f
^{19}F			
125.7, 129.5	AB, J_{FF}=210	2	e
127.7	M		
153.2	D of T, J_{FH}=49, J=13	1	f
161.0	D of T, J_{FH}=49, J=13		

M.Wt. 188·5 No. 18

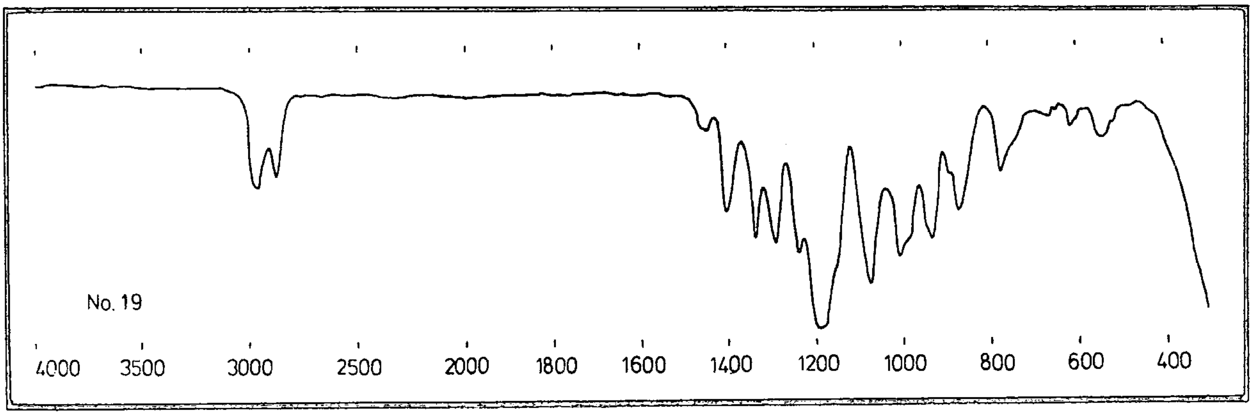


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.25	13.81	36	103.07	1.25
2	28.13	7.60	37	105.12	1.51
3	29.00	6.18	38	117.00	1.34
4	30.93	0.88	39	118.97	0.46
5	32.02	1.54			
6	39.01	4.21			
7	39.90	1.91			
8	41.00	35.17			
9	42.09	11.59			
10	43.16	77.88			
11	44.19	2.68			
12	45.18	0.26			
13	47.14	1.51			
14	50.97	2.08			
15	53.12	1.17			
16	55.18	1.00			
17	59.04	2.02			
18	64.14	0.40			
19	65.15	1.11			
20	67.04	1.65			
21	68.98	0.88			
22	71.00	100.00			
23	72.05	4.73			
24	73.07	1.31			
25	75.06	0.57			
26	77.02	3.99			
27	81.96	0.60			
28	83.02	1.08			
29	85.07	1.62			
30	88.98	0.60			
31	90.99	4.04			
32	93.04	0.83			
33	95.06	0.65			
34	98.98	1.28			
35	101.01	0.65			

No.19

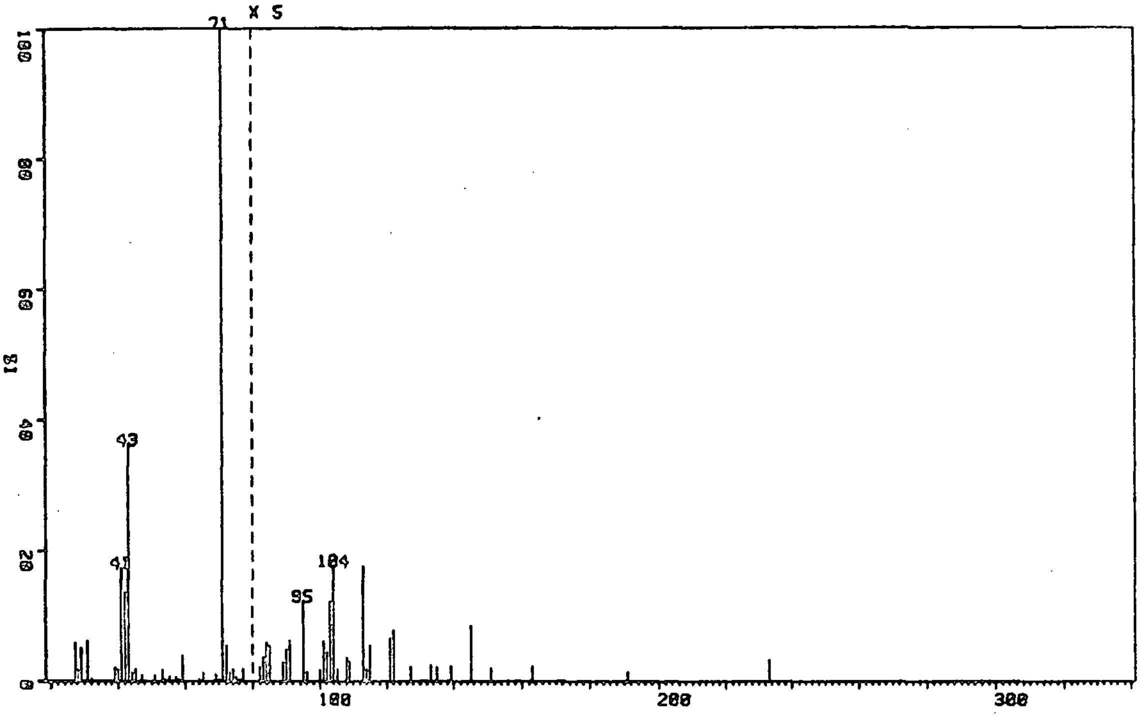


2-(1,2,3,3,4,4-Hexafluorocyclobutyl)oxolane (40).



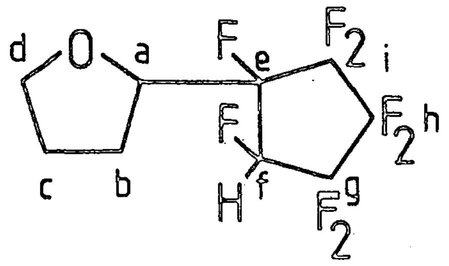
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
1.83	M	4	b, c
3.65	M	4	d
4.42	M		a
5.13	D of M, J_{HF}=44, J=5		f
^{19}F			
123.6, 136.5	AB, J_{FF}=226	2	g or h
130.0	M	2	h or g
130.7	M		
190.0	M	1	e
214.7	D of M, J_{FH}=47	1	f
217.3	D of M, J_{FH}=47		

M.Wt. 234 No.19

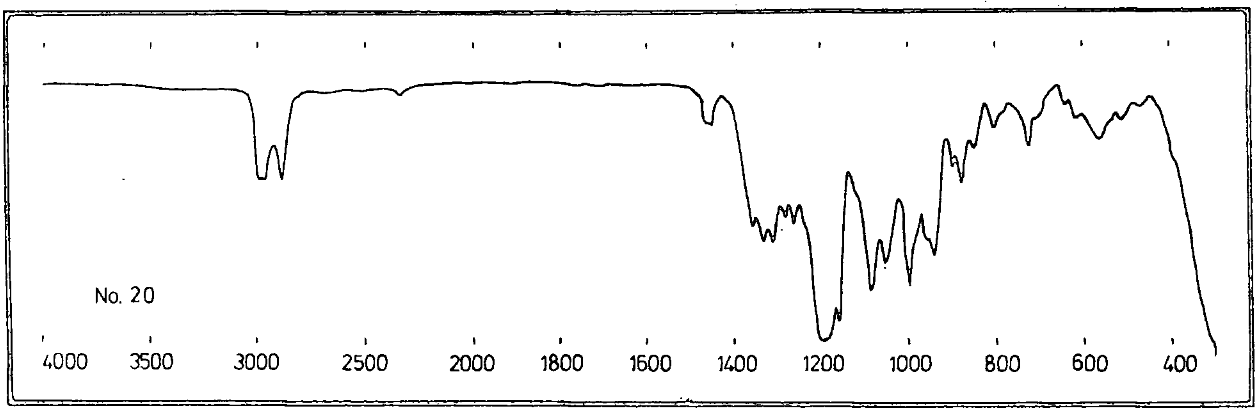


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.24	5.97	36	88.94	0.62
2	28.13	1.70	37	89.88	1.00
3	29.01	5.16	38	90.95	1.27
4	30.92	6.18	39	95.04	2.46
5	32.02	0.40	40	96.07	0.30
6	39.00	2.11	41	99.92	0.38
7	39.90	1.86	42	100.98	1.24
8	40.99	17.36	43	102.05	0.89
9	42.08	13.69	44	103.05	2.46
10	43.15	36.26	45	104.08	3.54
11	44.18	1.40	46	105.09	0.38
12	45.17	1.97	47	108.01	0.73
13	47.12	0.97	48	108.97	0.62
14	50.95	0.86	49	113.01	3.54
15	53.12	1.84	50	114.07	0.38
16	54.16	0.35	51	115.08	1.11
17	55.17	0.78	52	121.02	1.32
18	57.11	0.70	53	122.06	1.57
19	58.08	0.32	54	127.08	0.43
20	59.04	3.91	55	133.08	0.49
21	64.13	0.40	56	135.12	0.43
22	65.13	1.21	57	139.04	0.46
23	68.97	1.08	58	145.07	1.70
24	69.92	0.35	59	151.04	0.40
25	70.98	100.00	60	163.04	0.46
26	72.04	5.53	61	191.02	0.30
27	73.05	1.48	62	233.09	0.65
28	74.10	2.00			
29	75.01	0.78			
30	76.00	0.40			
31	76.99	1.97			
32	81.92	0.46			
33	82.99	0.76			
34	84.01	1.21			
35	85.02	1.08			

No. 20

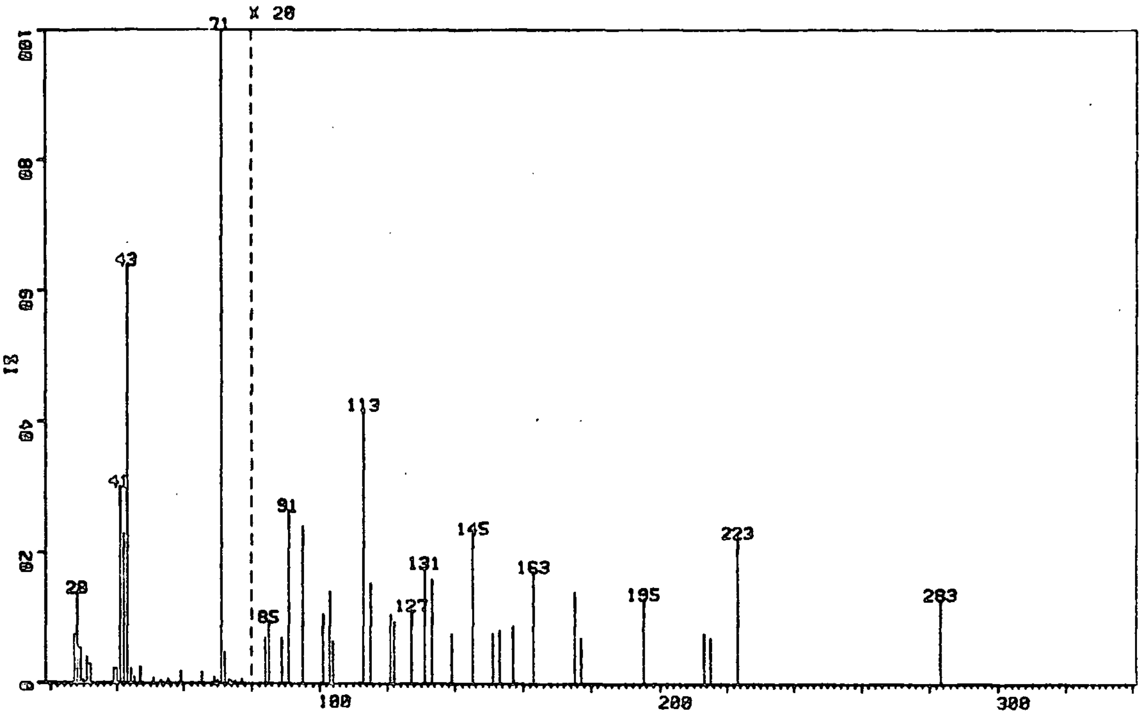


2-(1,2,3,3,4,4,5,5-Octafluorocyclopentyl)oxolane (39).

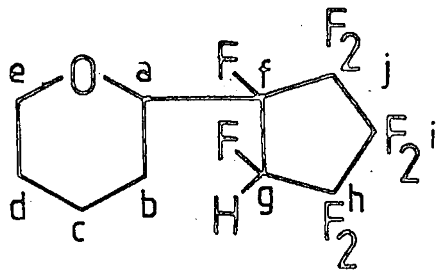


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
1.90	M	4	b, c
3.73	M	4	a, d, f
4.6	M(broad)		
^{19}F			
115.5, 117.7, 120.0, 121.3, 122.3, 124.3, 126.2, 126.7, 127.3, 127.8, 128.8, 129.7, 130.2, 131.0, 132.0, 132.7, 133.3, 134.0, 134.7, 136.0, 136.5, 137.5, 138.0, 141.0.	Overlapping AB's	6	g, h, i
187.8 and 194.8 198.7 and 200.5	M and M M and M	1	e
209.3 and 214.3 222.3 and 228.5	M and M M and M	1	f

M.Wt. 284 No.20

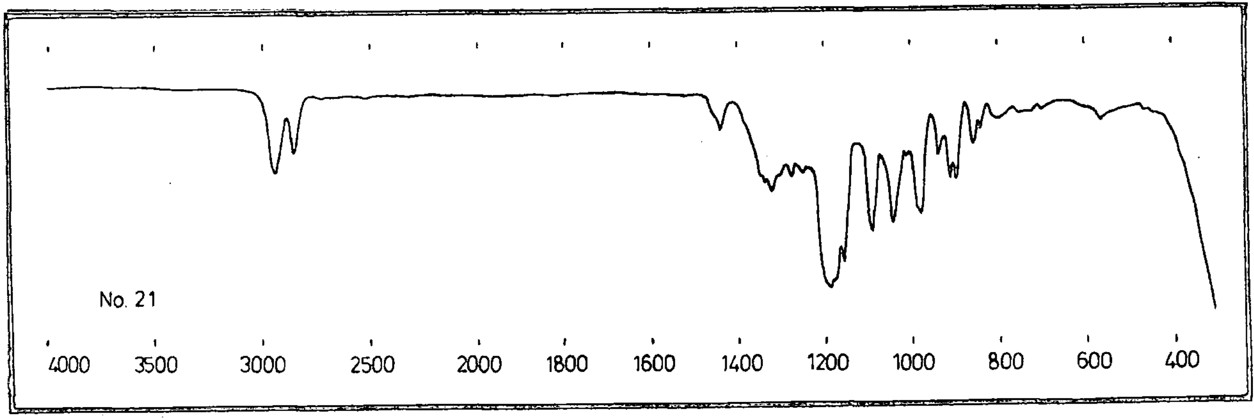


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.26	7.39	36	113.03	2.09
2	28.14	13.84	37	115.10	0.77
3	29.01	5.39	38	121.04	0.53
4	29.84	0.44	39	122.08	0.47
5	30.94	3.97	40	127.09	0.56
6	32.02	2.91	41	131.00	0.88
7	39.01	2.24	42	133.08	0.79
8	39.90	2.27	43	139.01	0.38
9	41.01	30.11	44	145.09	1.15
10	42.09	22.87	45	151.05	0.38
11	43.16	63.91	46	153.11	0.41
12	44.19	2.21	47	157.09	0.44
13	45.19	0.94	48	163.09	0.85
14	47.14	2.56	49	175.07	0.71
15	50.97	0.82	50	177.12	0.35
16	53.13	0.56	51	195.11	0.65
17	55.18	0.71	52	213.09	0.38
18	59.05	1.88	53	215.12	0.35
19	65.15	1.71	54	223.07	1.12
20	68.99	1.03	55	283.21	0.65
21	69.95	0.56			
22	71.01	100.00			
23	72.06	4.77			
24	73.08	0.68			
25	74.12	0.44			
26	75.06	0.38			
27	77.03	0.77			
28	84.06	0.35			
29	85.08	0.47			
30	88.99	0.35			
31	91.01	1.32			
32	95.07	1.21			
33	101.01	0.53			
34	103.11	0.71			
35	104.08	0.32			



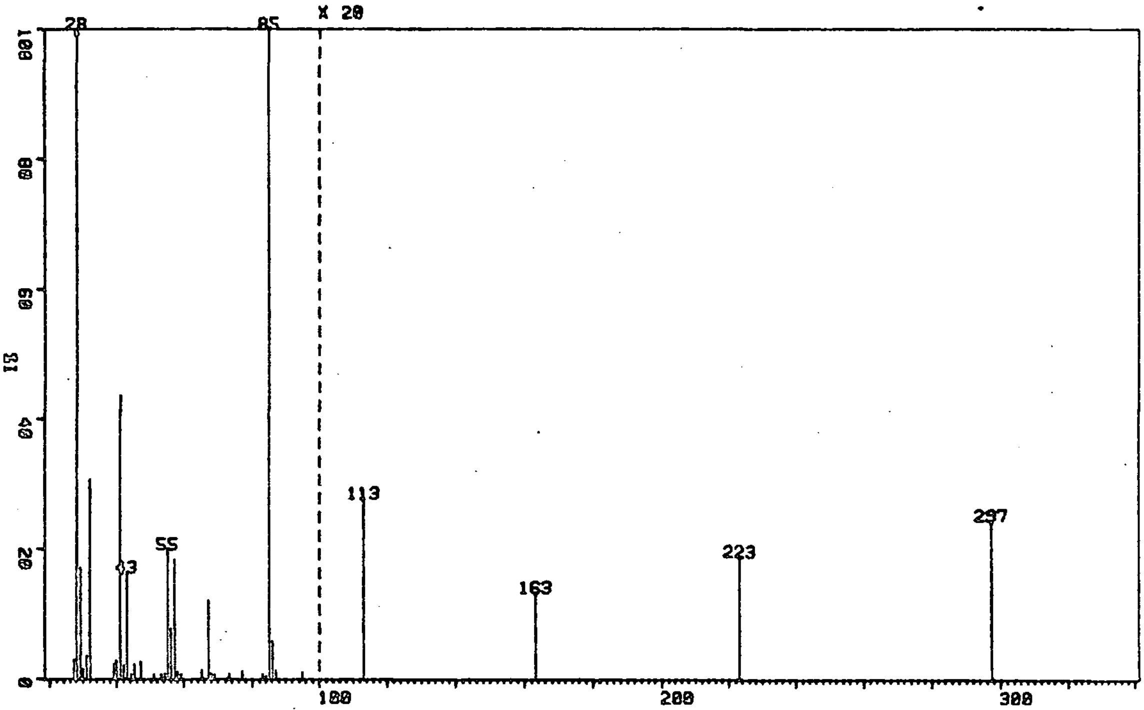
No. 21

2-(1,2,3,3,4,4,5,5-Octafluorocyclopentyl)oxane (46).



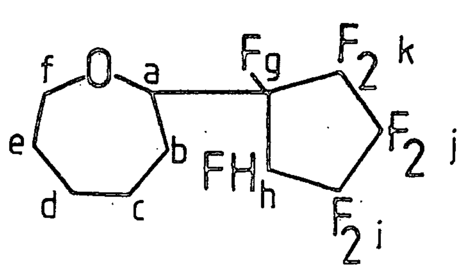
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
1.47	M	6	b, c, d
3.30	M	4	a , e
3.77	M		
4.77	D of M, J_{HF}=42		g
^{19}F			
115.2, 116.5, 118.0, 118.7, 119.8, 121.3, 122.0, 123.0, 124.3, 125.5, 126.0, 126.7, 127.5, 128.3, 129.0, 129.5, 130.7, 131.7, 132.1, 133.7, 136.5, 138.0,	Overlapping AB's	6	h, i, j
189.3 and 194.5	M and M	1	f
197.5 and 198.2	M and M		
210.7 and 211.7	D of M,J=43,andD of M,J=43	1	g
224.3 and 229.7	D of M,J=43,andD of M,J=43		

M.Wt. 298 No.21

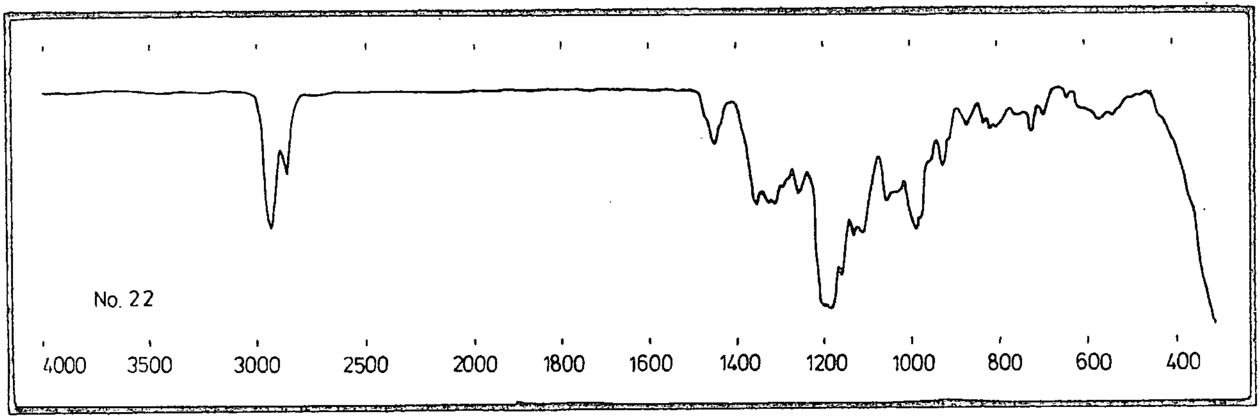


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.25	1.80	36	163.10	0.39
2	28.13	100.00	37	223.12	0.56
3	29.02	10.09	38	297.26	0.72
4	29.86	0.95			
5	30.94	2.13			
6	32.02	17.99			
7	39.01	1.41			
8	39.87	1.74			
9	41.00	25.59			
10	42.09	1.31			
11	43.13	9.67			
12	44.17	0.52			
13	45.19	1.41			
14	47.14	1.57			
15	50.96	0.49			
16	53.13	0.49			
17	54.17	0.56			
18	55.19	11.70			
19	56.20	4.55			
20	57.17	10.81			
21	58.12	0.69			
22	59.04	0.49			
23	65.16	0.82			
24	67.12	7.11			
25	68.06	0.56			
26	68.95	0.43			
27	73.09	0.52			
28	77.06	0.75			
29	83.08	0.52			
30	84.10	0.33			
31	85.12	58.68			
32	86.07	3.44			
33	87.06	0.85			
34	95.04	0.69			
35	113.04	0.82			

No.22

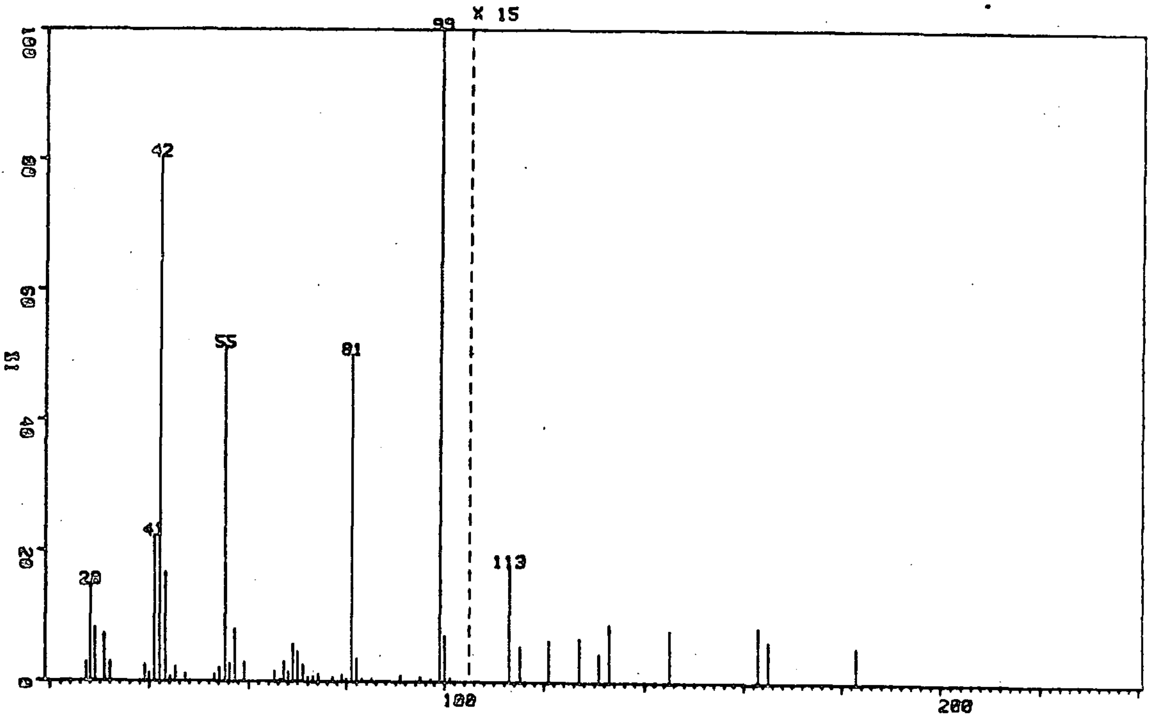


2-(1,2,3,3,4,4,5,5-Octafluorocyclopentyl)oxepane (48).



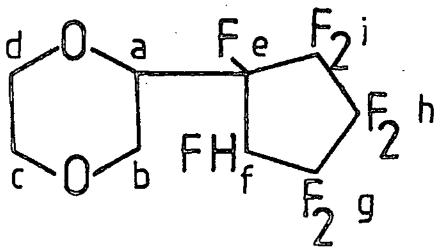
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
1.57	M	8	b, c, d, e
3.57	M	3	a , f
4.87	D of M, J=44	1	h
^{19}F			
115.7, 116.7, 118.3, 120.0, 120.7, 121.3, 123.0, 124.7, 125.0, 126.0, 126.7, 126.8, 127.7, 129.0, 130.8, 131.2, 131.7, 132.3, 133.7, 135.0, 135.7, 136.2, 138.2.	Overlapping AB's	6	i, j, k
189.8	M	1	g (trans)
191.7	M		
195.0	M		g (cis)
195.5	M		
210.3	D of M, J=44	1	h (trans)
211.7	D of M, J=44		
225.2	D of M, J=44		h (cis)
229.5	D of M, J=44		

MWt. 312 No.22

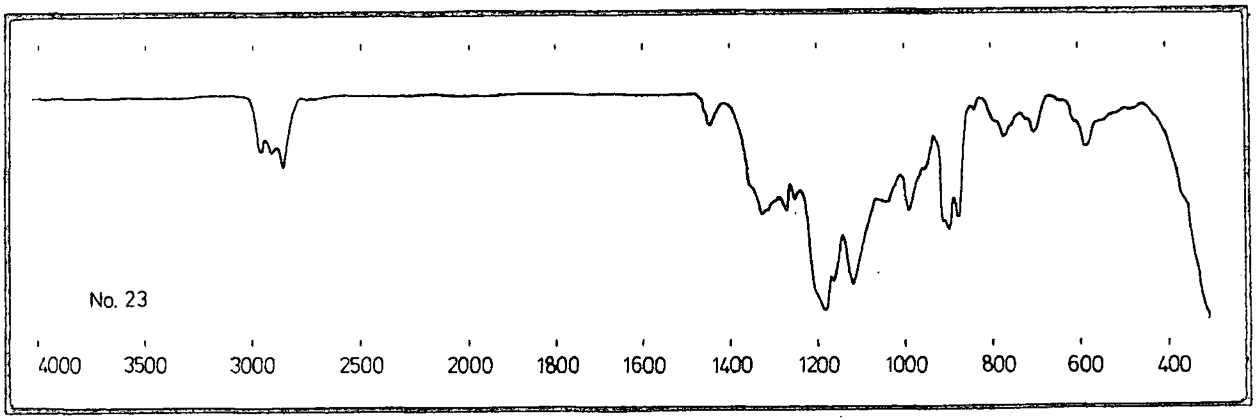


PEAK NO.	MASS	%HT. BASE
1	27.25	2.82
2	28.13	14.84
3	29.02	8.19
4	30.93	7.26
5	32.02	2.96
6	39.00	2.51
7	39.83	0.31
8	39.89	1.27
9	40.98	22.33
10	42.08	80.49
11	43.13	16.67
12	44.16	0.84
13	45.17	2.17
14	47.12	1.15
15	53.11	1.10
16	54.15	2.06
17	55.17	51.15
18	56.16	2.76
19	57.12	8.00
20	59.02	3.07
21	65.12	1.52
22	66.52	0.31
23	67.09	3.12
24	68.07	1.44
25	69.01	5.72
26	69.96	4.50
27	71.01	2.53
28	72.06	0.68
29	73.07	0.79
30	74.13	1.15
31	77.00	0.65
32	78.96	1.13
33	79.92	0.48
34	80.97	50.08
35	**82.02**	**3.52**
36	83.04	0.37
37	85.05	0.39
38	90.95	0.99
39	95.02	0.73
40	97.06	0.42
41	99.00	100.00
42	99.95	7.01
43	101.00	0.59
44	113.01	1.18
45	115.03	0.37
46	120.94	0.42
47	127.03	0.45
48	130.93	0.28
49	133.00	0.59
50	145.01	0.53
51	162.98	0.56
52	165.03	0.42
53	183.01	0.37

No. 23

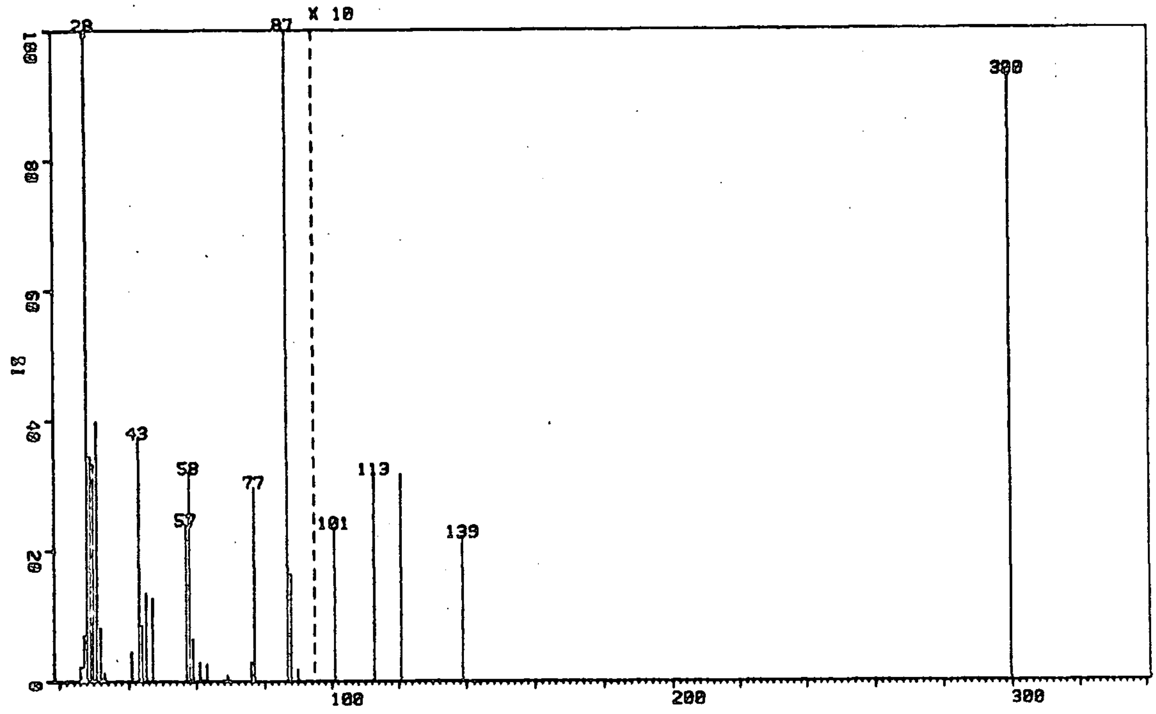


2-(1,2,3,3,4,4,5,5-Octafluorocyclopentyl)-1,4-dioxan (50).



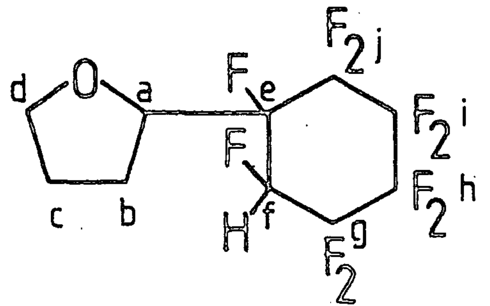
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
3.53	M(broad)	7	b, c, d
5.14	D of M, J=42	1	a
^{19}F			
115.3, 116.5, 117.3, 119.7, 121.2, 123.5, 126.0, 126.9, 128.0, 128.5, 129.3, 131.5, 132.7, 134.8, 137.0, 139.3.	Overlapping AB's	6	g, h, i
186.7	M	1	e (trans)
193.7	M		
198.3	M		e (cis)
199.5	M		
210.0	D of M, J=44	1	f (trans)
211.2	D of M, J=44		
225.0	D of M, J=44		f (cis)
229.3	D of M, J=44		

M.Wt. 300 No. 23

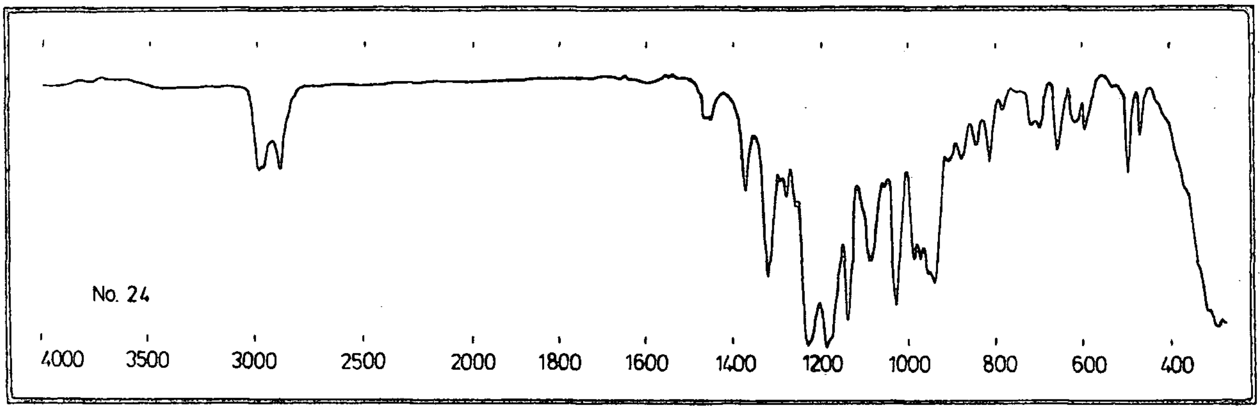


PEAK NO.	MASS	%HT. BASE
1	26.30	0.96
2	27.23	2.98
3	28.13	100.00
4	29.00	14.66
5	29.85	14.10
6	30.91	16.91
7	31.99	3.47
8	33.11	0.55
9	40.95	1.93
10	43.07	15.82
11	44.11	3.62
12	45.13	5.72
13	47.08	5.40
14	57.05	10.16
15	58.01	13.52
16	58.96	2.77
17	60.90	1.23
18	63.05	1.11
19	68.92	0.41
20	76.03	1.31
21	77.03	12.58
22	86.99	42.42
23	87.96	6.95
24	89.86	0.82
25	100.92	0.99
26	112.95	1.34
27	120.90	1.34
28	138.91	0.93
29	299.64	3.94

No. 24

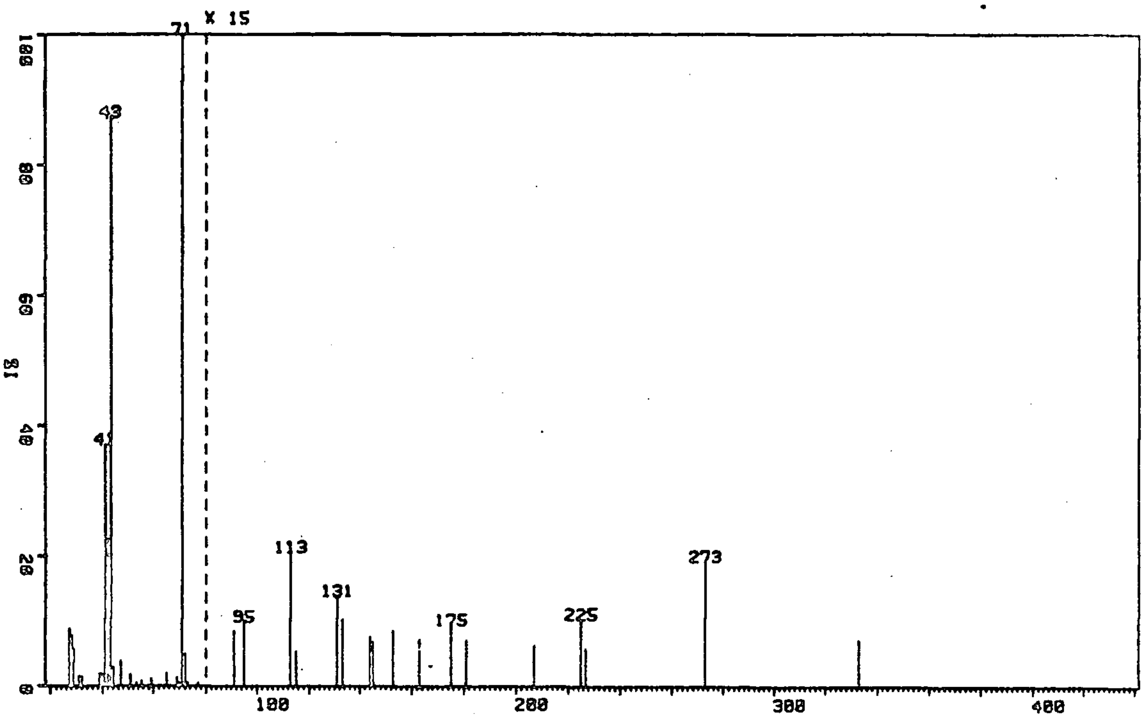


2-(1,2,3,3,4,4,5,5,6,6-Decafluorocyclohexyl)oxolane (38).

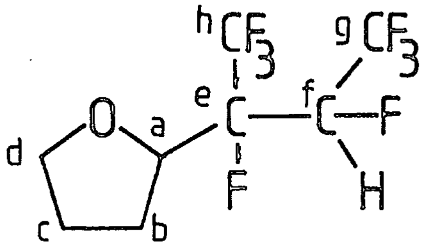


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
2.03	M(broad)	4	b , c
3.75	T, J=6	4	d
3.8 to 5.9	M(very broad)		a , f
^{19}F			
115.8, 121.0, 124.0, 127.0, 128.3, 131.0, 132.7, 134.3, 134.3, 136.2, 139.3, 144.2, 148.5.	Overlapping AB's	8	g, h, i, j
194.0	M	1	e
196.7	M		
210.3	M	1	f
229.8 and 232.5	M and M		

M.Wt. 334 No. 24

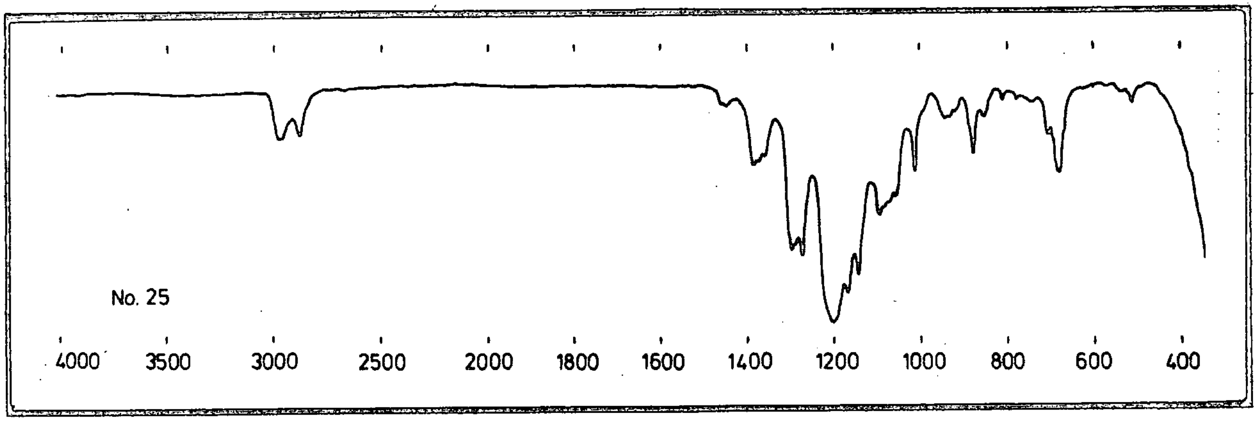


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.25	8.69	36	206.94	0.42
2	28.13	7.68	37	224.99	0.69
3	29.00	5.56	38	226.99	0.39
4	30.93	1.52	39	272.92	1.28
5	32.02	1.46	40	332.93	0.48
6	39.00	1.94			
7	39.89	1.97			
8	40.99	37.08			
9	42.08	22.53			
10	43.14	87.30			
11	44.18	3.02			
12	47.12	3.88			
13	50.94	1.76			
14	53.12	0.54			
15	55.16	0.93			
16	59.02	1.20			
17	65.12	1.94			
18	68.95	1.49			
19	69.92	0.51			
20	70.98	100.00			
21	72.02	4.99			
22	73.06	0.57			
23	77.01	0.51			
24	90.95	0.57			
25	95.02	0.66			
26	112.99	1.37			
27	115.05	0.36			
28	130.94	0.93			
29	133.04	0.69			
30	144.00	0.51			
31	145.04	0.45			
32	153.01	0.57			
33	162.99	0.48			
34	175.00	0.63			
35	180.93	0.48			



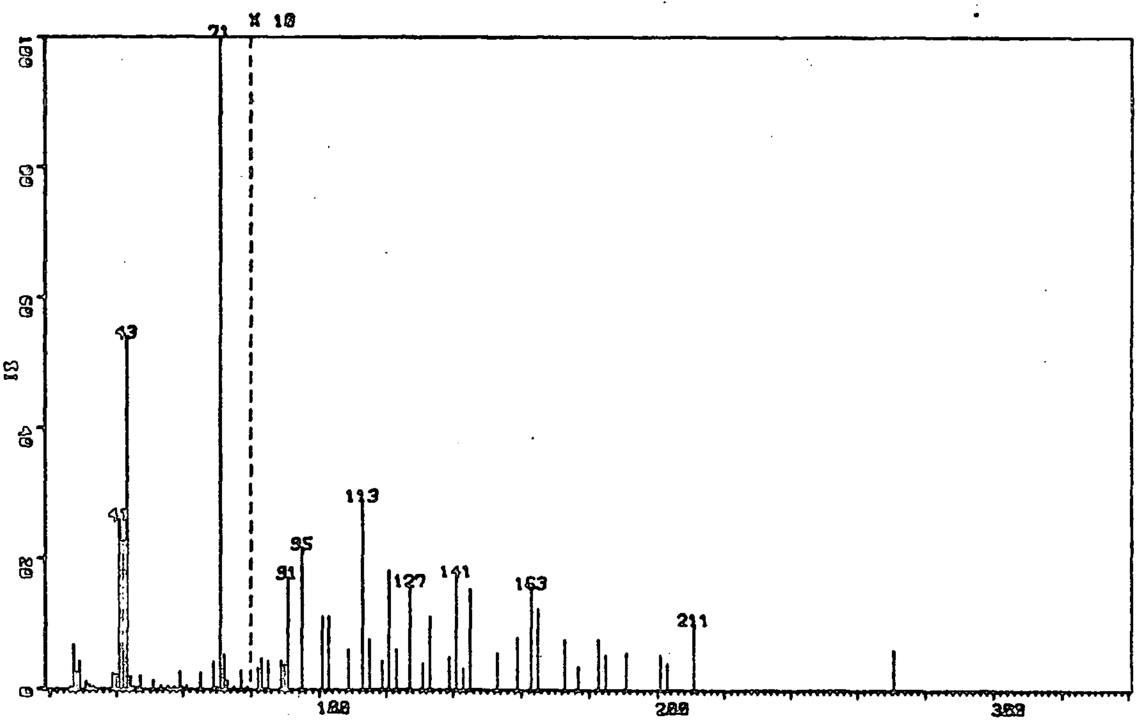
No.25

2-(1-Trifluoromethyl-1,2,3,3,3-pentafluoropropyl)oxolane (41).

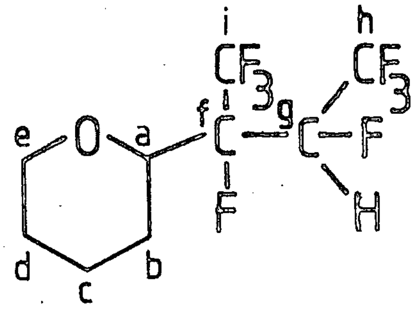


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
1,87	M	4	b, c
3.63	M	3	a, d
5.10	M(broad)	1	f
^{19}F			
75.7	M	6	g, h
180.0	M	1	e
191.8	M		
196.0	M		
212.2	M	1	f
217.3	M		

M.Wt. 272 No. 25

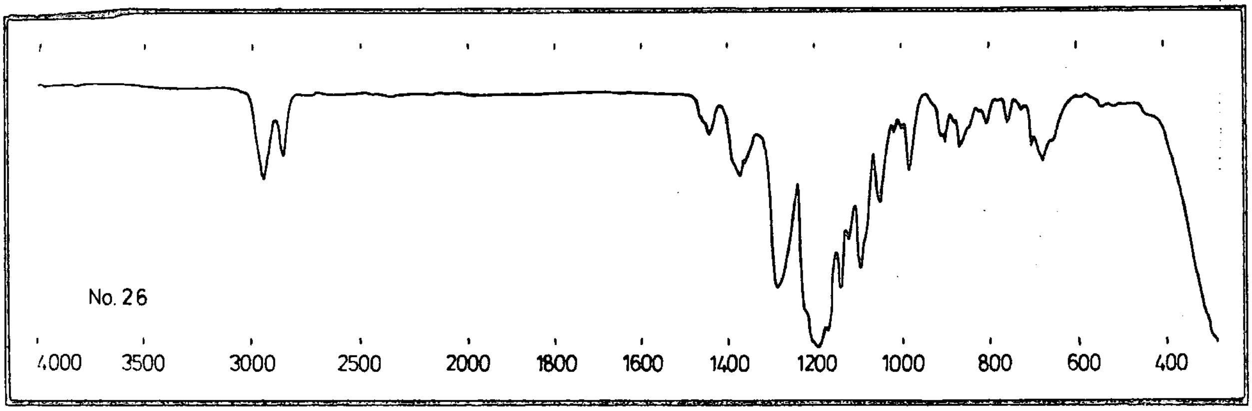


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	26.31	0.32	36	88.89	0.44
2	27.25	6.69	37	89.86	0.38
3	28.13	2.54	38	90.88	1.71
4	29.00	4.25	39	94.99	2.15
5	30.92	1.21	40	100.91	1.12
6	32.01	0.59	41	102.99	1.12
7	33.12	0.32	42	108.90	0.62
8	38.99	2.42	43	112.92	2.89
9	39.88	2.27	44	114.99	0.77
10	40.97	25.97	45	118.90	0.44
11	42.06	22.67	46	120.92	1.83
12	43.13	53.92	47	122.98	0.62
13	44.17	1.98	48	126.96	1.59
14	45.15	0.35	49	130.88	0.41
15	46.13	0.29	50	132.93	1.12
16	47.10	2.06	51	138.86	0.50
17	50.92	1.30	52	140.87	1.74
18	53.09	0.53	53	142.94	0.32
19	55.14	0.38	54	144.96	1.53
20	57.09	0.35	55	152.96	0.56
21	58.99	2.68	56	158.91	0.80
22	59.94	0.29	57	162.93	1.56
23	60.99	0.50	58	164.98	1.24
24	65.10	2.56	59	172.95	0.77
25	68.94	4.16	60	176.91	0.35
26	69.91	0.47	61	182.89	0.77
27	70.96	100.00	62	184.96	0.53
28	72.01	5.28	63	190.85	0.56
29	73.04	1.36	64	200.83	0.53
30	75.02	0.32	65	202.93	0.41
31	76.99	2.80	66	210.84	1.00
32	78.90	0.32	67	270.82	0.62
33	81.91	0.32			
34	82.96	0.47			
35	85.01	0.44			



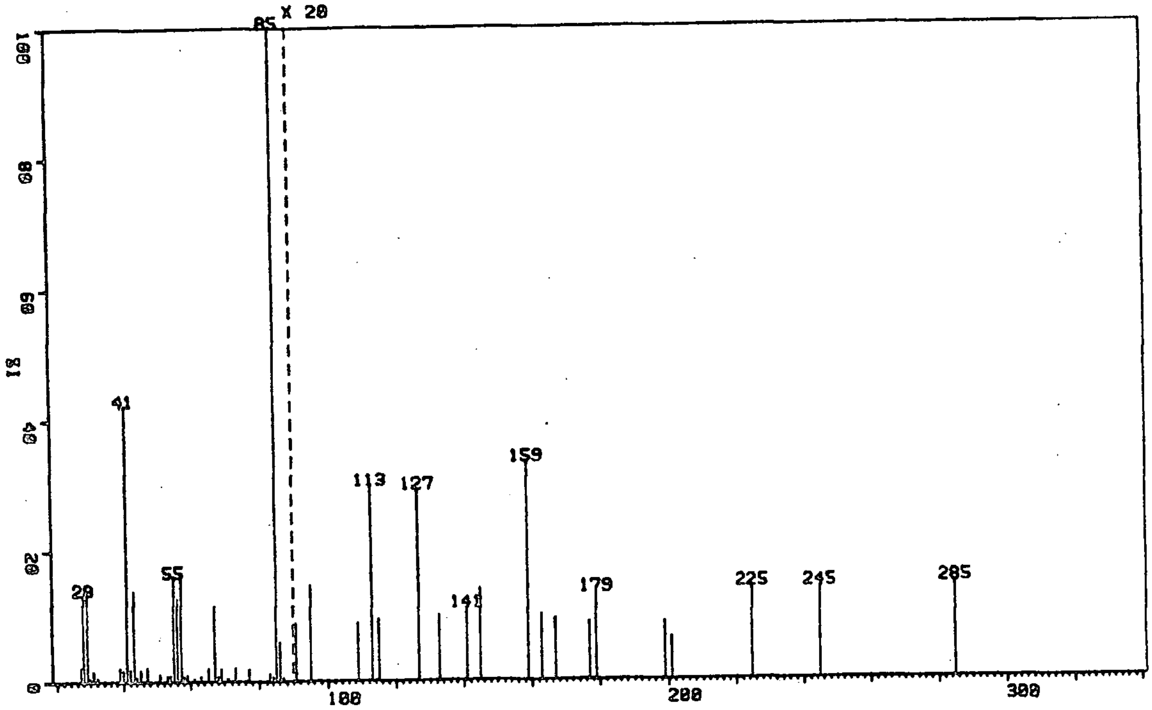
No. 26

2-(1-Trifluoromethyl-1,2,3,3,3-pentafluoropropyl)oxane (47).

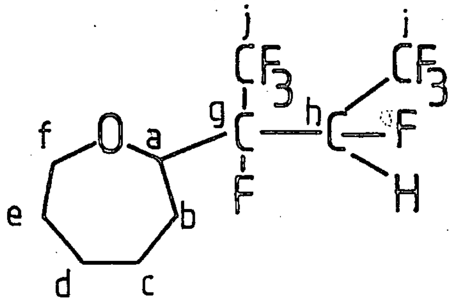


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
1.40	M	6	b, c, d
3.32	M	4	a , e
3.72	M		
5.0	M(broad)		g
^{19}F			
73.5	M	6	h , i
74.7	M		
75.5	M		
185.7	M	1	f
191.3	M		
213.3	D of M, J_{FH}=38	1	g
217.8	D of M, J_{FH}=38		

M.Wt. 286 No.26

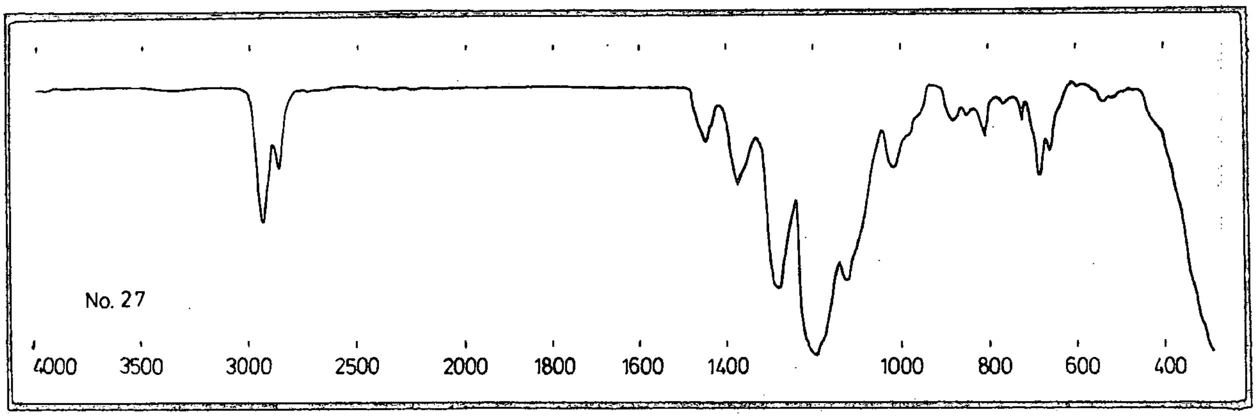


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.23	2.11	36	87.03	0.56
2	28.13	13.26	37	90.88	0.44
3	29.00	13.53	38	94.97	0.73
4	29.84	0.53	39	108.91	0.44
5	30.91	1.56	40	112.93	1.50
6	31.99	0.56	41	114.98	0.47
7	38.98	2.11	42	126.91	1.47
8	39.87	1.67	43	132.89	0.50
9	40.96	42.22	44	140.85	0.56
10	42.04	1.88	45	144.92	0.70
11	43.08	13.82	46	158.87	1.67
12	44.12	0.70	47	162.89	0.50
13	45.14	1.73	48	166.95	0.47
14	47.09	2.14	49	176.87	0.44
15	50.90	1.09	50	178.90	0.67
16	53.06	0.91	51	198.88	0.44
17	54.10	1.00	52	200.85	0.32
18	55.12	15.90	53	224.83	0.70
19	56.11	12.71	54	244.81	0.70
20	57.10	16.29	55	284.85	0.73
21	58.05	0.73			
22	58.96	0.97			
23	60.96	0.47			
24	63.04	0.85			
25	65.06	1.97			
26	67.06	11.53			
27	68.03	0.79			
28	68.92	1.91			
29	70.94	0.44			
30	73.02	2.05			
31	77.00	1.91			
32	83.01	1.17			
33	84.04	0.65			
34	85.03	100.00			
35	86.03	6.04			



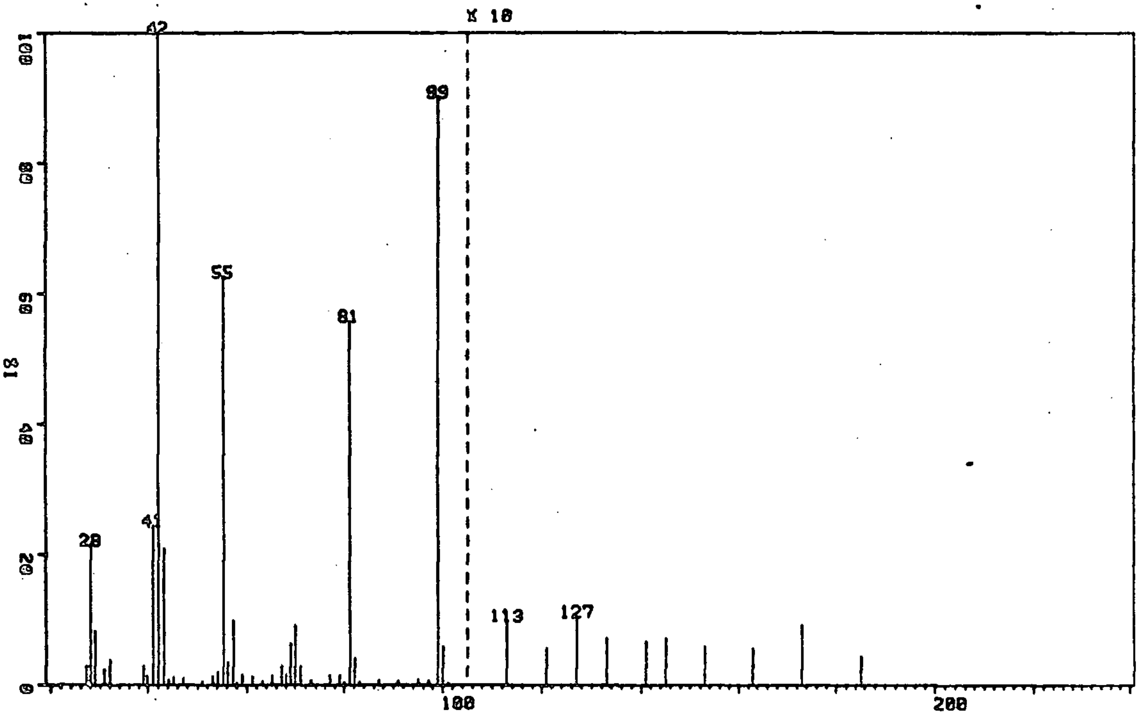
No. 27

2-(1-Trifluoromethyl-1,2,3,3,3-pentafluoropropyl)oxepane (49).

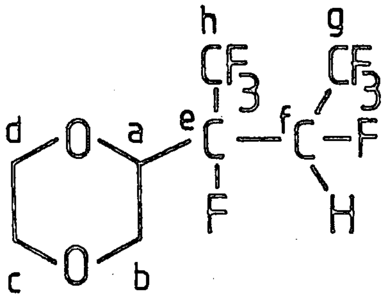


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
1.57	M	8	b, c, d, e
3.60	M	3	a , f
5.17	D of M, J_{HF}=44	1	h
^{19}F			
74.0	M	6	i , j
76.0	M		
183.0	M	1	g
188.5	M		
190.0	M		
212.3	D of M, J=44	1	h
213.0	D of M, J=44		
215.2	D of M, J=44		

M.Wt. 300 No. 27

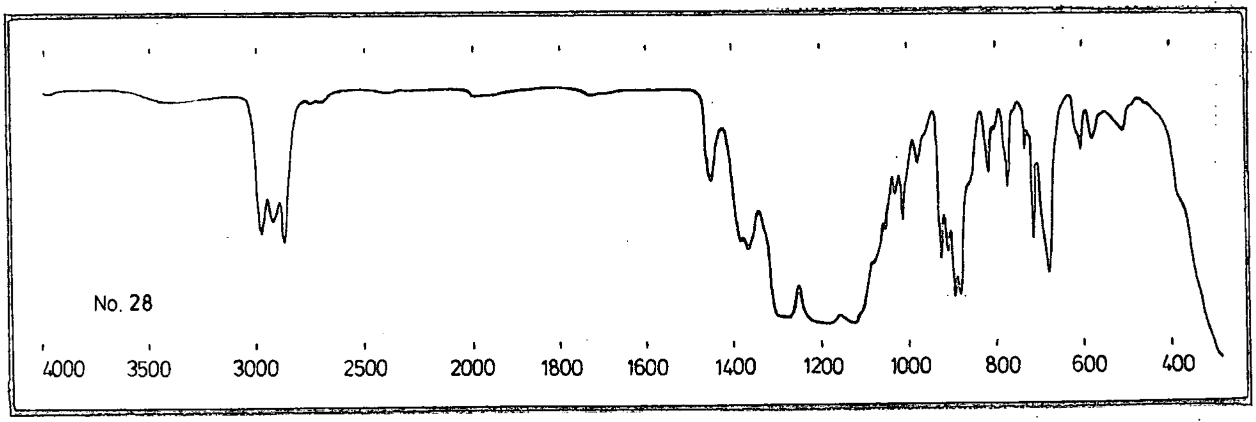


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.25	2.85	36	82.03	4.08
2	28.13	21.39	37	83.06	0.44
3	29.02	8.26	38	87.06	0.85
4	30.93	2.37	39	90.96	0.70
5	32.02	3.73	40	95.04	0.89
6	39.00	3.01	41	97.07	0.73
7	39.84	0.51	42	99.03	90.03
8	39.90	1.42	43	100.00	5.92
9	40.99	24.37	44	101.00	0.35
10	42.08	100.00	45	113.02	0.98
11	43.14	20.98	46	120.95	0.57
12	44.16	0.92	47	127.02	1.04
13	45.18	1.23	48	133.03	0.73
14	47.12	1.11	49	140.97	0.66
15	50.95	0.60	50	145.02	0.73
16	53.11	1.39	51	153.04	0.60
17	54.15	1.99	52	163.02	0.57
18	55.17	62.56	53	173.06	0.92
19	56.17	3.42	54	185.07	0.44
20	57.12	9.91			
21	58.08	0.38			
22	59.01	1.55			
23	61.03	1.33			
24	63.10	0.60			
25	65.11	1.55			
26	67.08	3.13			
27	68.04	1.61			
28	69.00	6.30			
29	69.94	9.11			
30	71.00	2.97			
31	73.05	0.85			
32	77.03	1.55			
33	78.98	1.55			
34	79.93	0.47			
35	**80.99**	**55.85**			



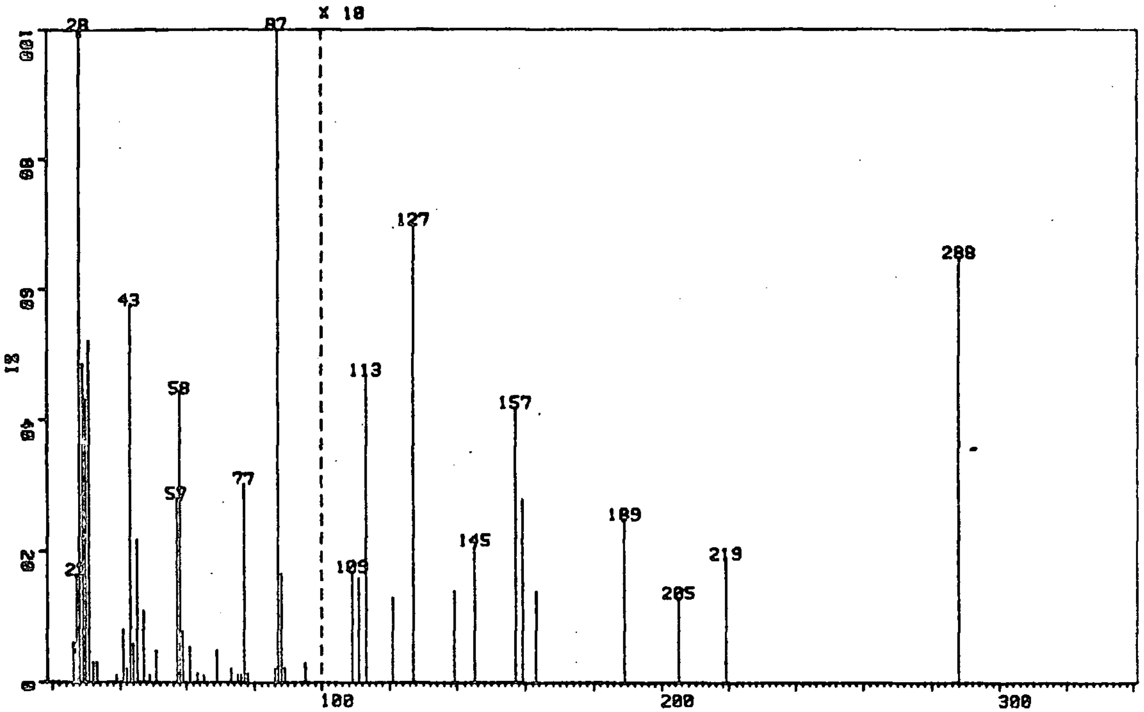
No. 28

2-(1-Trifluoromethyl-1,2,3,3,3-pentafluoropropyl)-1,4-dioxan (51).



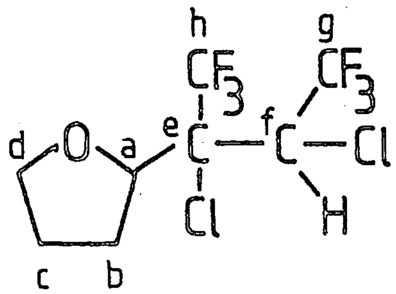
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
3.45	S	7	b, c, d
3.70	M		a
5.43	D of M, J_{HF}=44	1	f
^{19}F			
73.3	M	6	g , h
74.3	M		
187.0	M	1	e
191.3	M		
193.7	M		
212.3	M	1	f
216.7	M		

M.Wt. 288 No. 28.

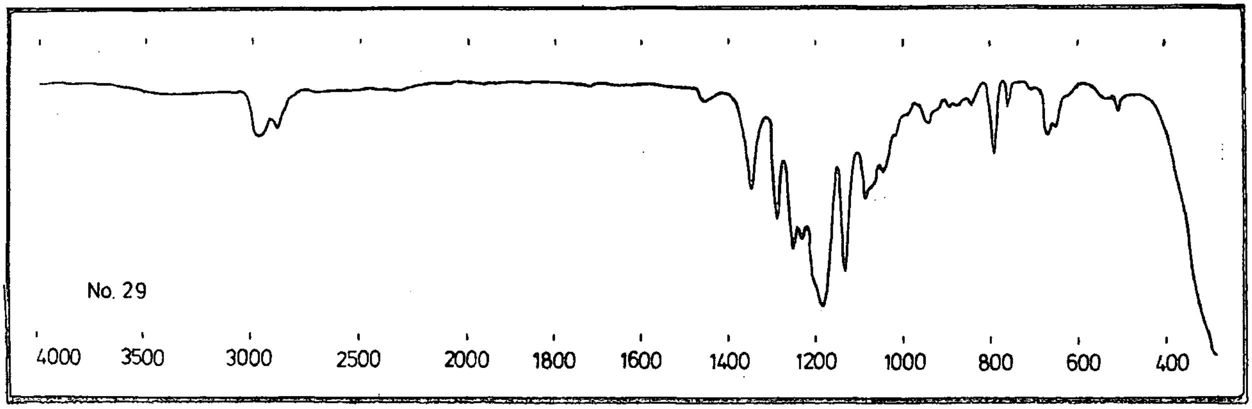


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	26.29	1.93	36	111.01	0.51
2	27.23	5.23	37	113.06	1.49
3	28.13	100.00	38	121.02	0.41
4	28.99	15.41	39	127.08	2.22
5	29.84	13.67	40	139.05	0.44
6	30.91	16.52	41	145.07	0.67
7	32.00	0.98	42	157.09	1.33
8	33.11	1.01	43	159.06	0.89
9	38.99	0.35	44	163.06	0.44
10	40.96	2.57	45	189.04	0.79
11	42.03	0.67	46	205.09	0.41
12	43.09	18.26	47	219.10	0.60
13	44.13	1.87	48	288.14	2.06
14	45.16	6.91			
15	47.10	3.46			
16	48.96	0.35			
17	50.92	1.52			
18	57.10	8.91			
19	58.07	14.01			
20	59.01	2.50			
21	60.96	1.74			
22	63.08	0.48			
23	65.12	0.35			
24	68.97	1.52			
25	73.08	0.70			
26	75.08	0.38			
27	76.11	0.38			
28	77.09	9.61			
29	78.05	0.48			
30	86.09	0.70			
31	87.07	31.71			
32	88.06	5.26			
33	89.00	0.73			
34	95.08	0.98			
35	109.04	0.54			

No. 29

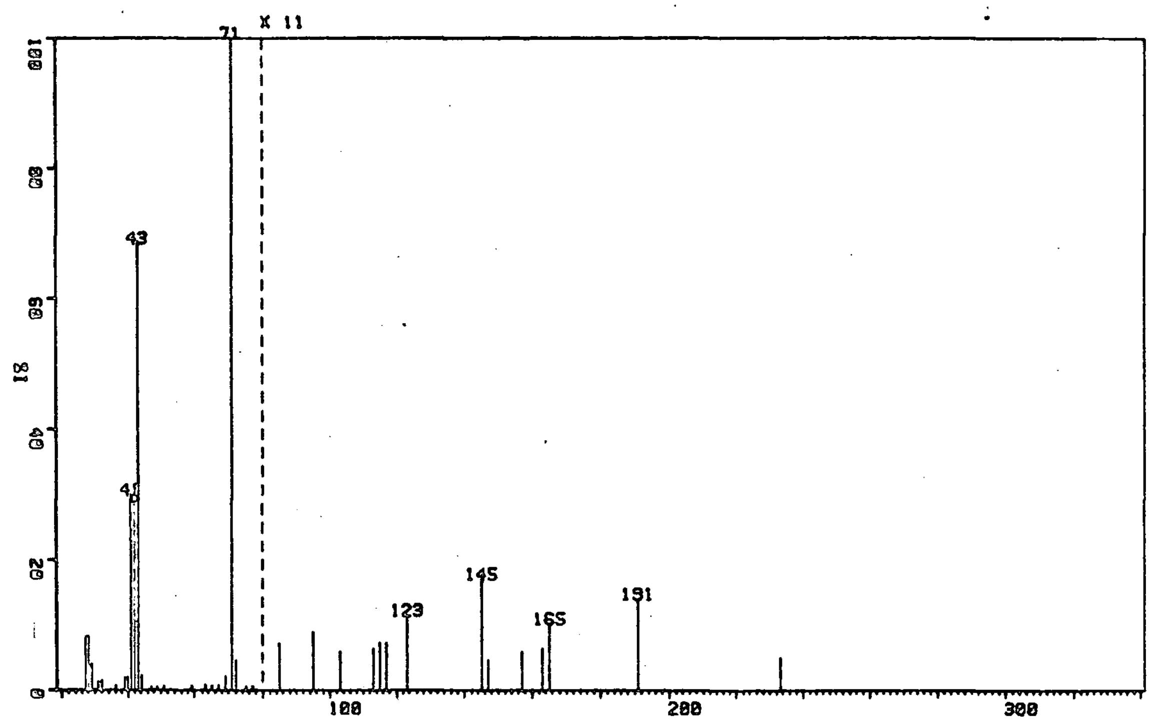


1-(1,2-Dichloro-1-trifluoromethyl-3,3-trifluoropropyl)oxolane (<u>42</u>).

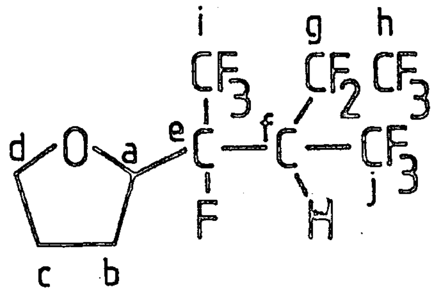


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
2.10	M	4	b , c
3.87	M	2	d
4.67	Overlapping M	2	a , f
^{19}F			
66.3	M		g , h
66.8	M		
68.2	M		
67.4	M		
69.2	M		

M.Wt. 305 No. 29

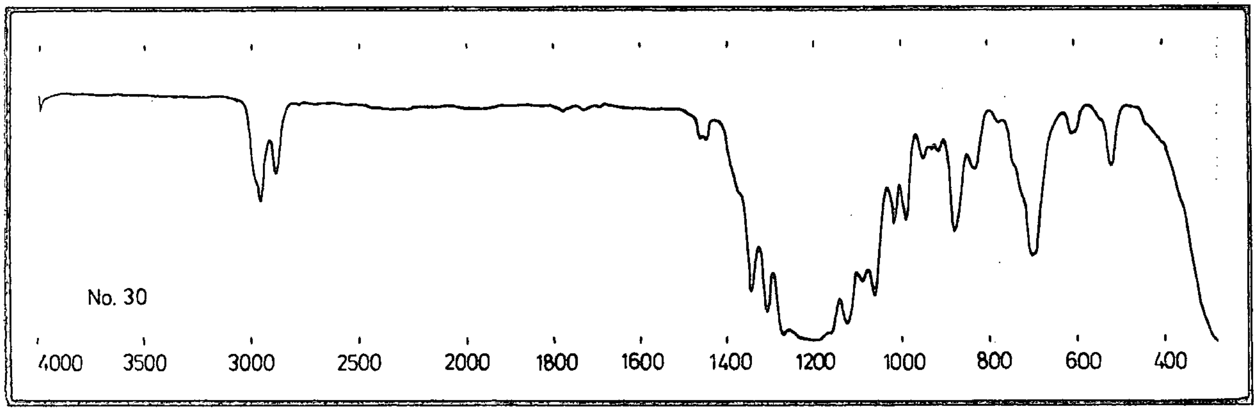


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.25	8.16	36	165.09	0.93
2	28.13	8.31	37	191.01	1.28
3	28.99	4.06	38	233.09	0.46
4	30.93	1.28			
5	32.02	1.47			
6	36.15	0.73			
7	39.01	1.93			
8	39.90	1.97			
9	41.00	29.97			
10	42.09	28.89			
11	43.16	68.48			
12	44.19	2.28			
13	47.13	0.50			
14	48.96	0.50			
15	50.95	0.58			
16	59.03	0.81			
17	63.09	0.93			
18	65.13	0.73			
19	67.03	0.81			
20	68.96	2.13			
21	70.99	100.00			
22	72.04	4.60			
23	75.04	0.62			
24	77.03	0.66			
25	84.98	0.66			
26	95.05	0.81			
27	103.08	0.54			
28	113.03	0.58			
29	115.09	0.66			
30	117.02	0.66			
31	123.06	1.04			
32	145.04	1.55			
33	147.01	0.43			
34	157.03	0.54			
35	163.07	0.58			



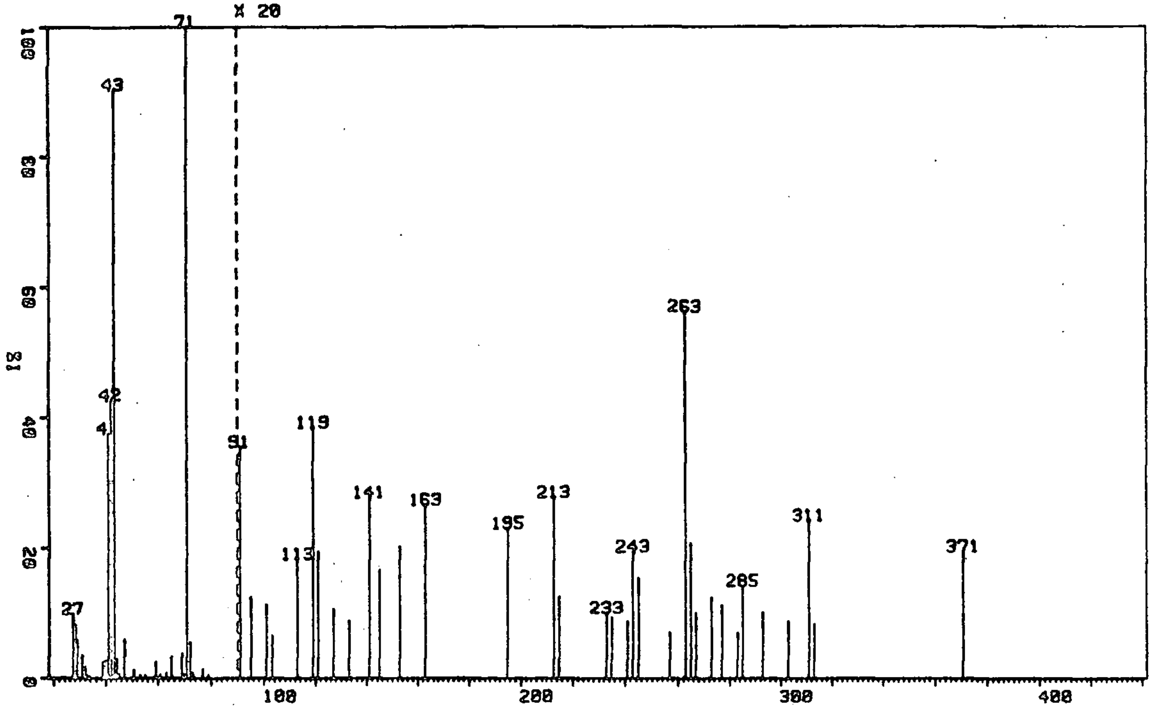
No. 30

2-(1,2-Di(trifluoromethyl)-1,3,3,4,4,4-hexafluorobutyl)oxolane (43).



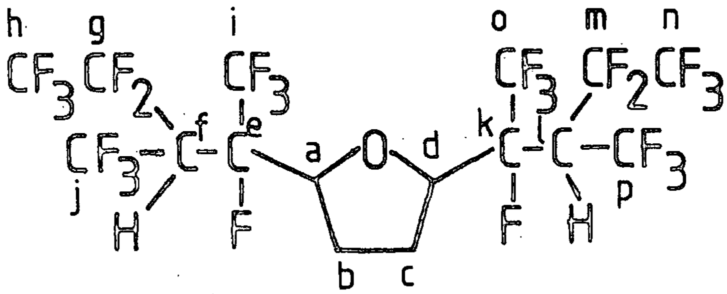
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
1.78	M	4	b , c
3.57	M	4	d
4.08	M(broad)		a , f
^{19}F			
60.0	M	3	j
60.8	M		
72.0	M	3	i
73.5	M		
86.3	M	3	h
88.0	M		
109.9, 115.9	AB, J_{FF}=282	2	g
114.0	M		
180.0	M	1	e

M.Wt. 372 No. 30

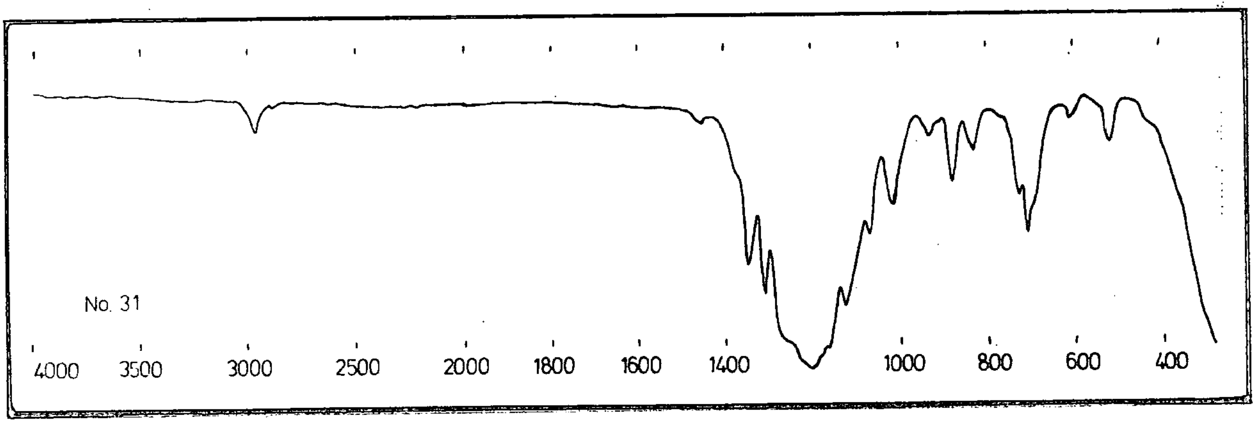


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.25	9.90	36	126.99	0.53
2	28.13	8.21	37	132.98	0.44
3	29.00	5.81	38	140.92	1.39
4	30.93	3.56	39	144.95	0.83
5	32.02	1.69	40	152.93	1.01
6	33.13	0.33	41	162.90	1.33
7	39.00	2.49	42	194.88	1.16
8	39.89	2.73	43	212.83	1.39
9	40.99	37.63	44	214.93	0.62
10	42.08	42.76	45	232.91	0.50
11	43.14	90.40	46	234.91	0.47
12	44.17	3.05	47	240.85	0.44
13	45.17	0.71	48	242.86	0.98
14	47.11	6.01	49	244.90	0.77
15	50.93	1.30	50	256.82	0.36
16	53.09	0.44	51	262.83	2.81
17	55.14	0.47	52	264.92	1.04
18	59.00	2.55	53	266.89	0.50
19	60.99	0.56	54	272.94	0.62
20	63.07	0.92	55	276.95	0.56
21	65.10	3.35	56	282.94	0.36
22	68.94	3.85	57	284.94	0.71
23	69.90	0.50	58	292.88	0.50
24	70.99	100.00	59	302.91	0.44
25	72.03	5.63	60	310.84	1.21
26	73.07	0.92	61	312.93	0.41
27	77.04	1.48	62	370.80	0.98
28	78.98	0.47			
29	90.93	1.78			
30	95.01	0.62			
31	100.95	0.56			
32	103.01	0.33			
33	112.99	0.92			
34	118.91	1.93			
35	120.92	0.98			

No. 31

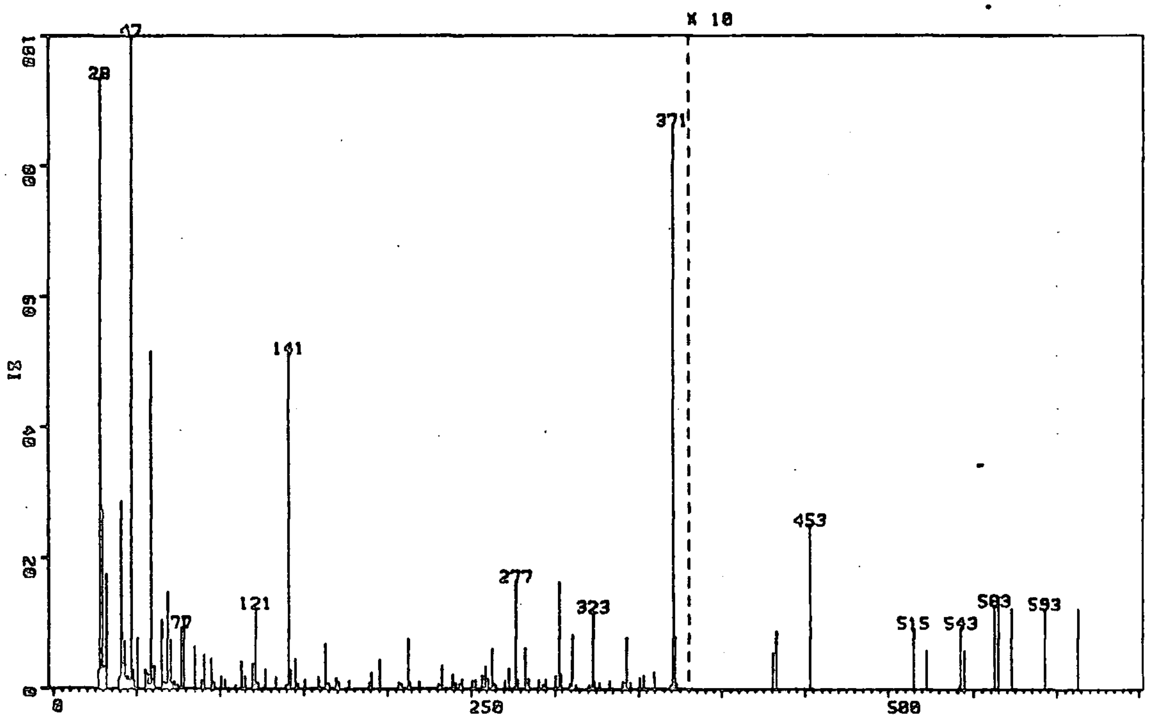


2,5-Di(1,2-di(trifluoromethyl)-1,3,3,4,4,4-hexafluorobutyl)oxolane (<u>44</u>).

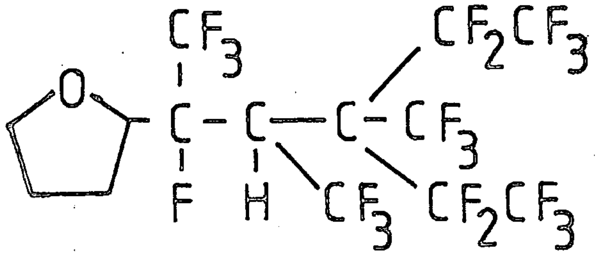


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
2.13	M	4	b , c
3.18 to 4.70	M(very broad)	4	a, d, f, l
^{19}F			
61.5	M	3	j , p
73.5	M	3	i , o
74.7	M		
87.2	M	3	h , n
89.0	M		
111.6, 115.9	AB, J_{FF}=310	2	g , m
114.8	M		
180.0	M	1	e , k

M.Wt. 672 No. 31



PEAK NO.	MASS	%HT. BASE
1	27.25	2.72
2	28.13	93.43
3	28.99	23.31
4	29.03	27.21
5	29.86	1.23
6	30.94	3.26
7	32.02	17.48
8	39.01	1.48
9	39.84	1.63
10	39.90	1.09
11	40.99	28.59
12	42.07	3.75
13	43.13	7.26
14	44.15	1.73
15	45.17	1.93
16	46.15	1.28
17	47.12	100.00
18	48.07	2.81
19	48.97	1.23
20	50.94	7.65
21	55.15	2.86
22	56.15	1.68
23	57.13	2.27
25	59.00	51.60
26	59.94	1.33
27	61.02	3.41
28	65.11	10.57
31	68.94	14.77
32	69.91	2.07
33	70.98	7.46
35	73.06	1.14
37	77.04	9.33
38	78.97	11.01
39	85.08	6.47
40	88.96	1.28
41	90.94	5.14
42	95.00	4.64
44	100.95	1.93
45	103.02	1.43
47	112.98	4.20
48	115.03	1.93
49	118.92	3.80
50	120.93	12.35
53	126.99	2.91
54	132.97	1.73
56	140.92	51.31
57	141.94	2.81
58	144.97	4.54
60	150.93	1.38
61	158.91	1.73
62	162.93	6.86
64	168.89	1.73
65	170.94	1.04
66	176.95	1.23
68	190.85	2.47
69	194.95	4.49
72	212.91	7.70
74	218.88	1.04
76	232.97	3.56
77	238.91	2.27
80	244.93	1.48
81	250.90	1.28
82	252.91	1.38
83	256.89	2.12
84	258.92	3.41
85	260.88	1.63
86	262.92	6.17
89	270.98	1.33
90	273.01	3.21
91	276.97	16.44
92	277.98	1.43
93	282.96	6.27
95	284.96	1.53
96	290.94	1.38
98	294.93	1.48
99	300.86	2.02
100	302.94	16.35
101	304.01	2.17
103	310.92	8.30
106	322.94	11.80
107	323.97	1.09
109	332.87	1.23
110	340.97	1.19
111	342.92	7.90
112	344.99	1.04
113	350.93	1.73
114	352.94	2.12
115	358.98	2.67
117	370.90	86.17
118	371.83	8.05
120	430.90	0.54
121	432.84	0.89
122	452.92	2.52
123	514.84	0.94
124	522.89	0.59
125	542.98	0.94
126	544.81	0.59
127	562.81	1.28
128	564.81	1.43
129	572.93	1.23
130	592.90	1.23
131	612.90	1.23



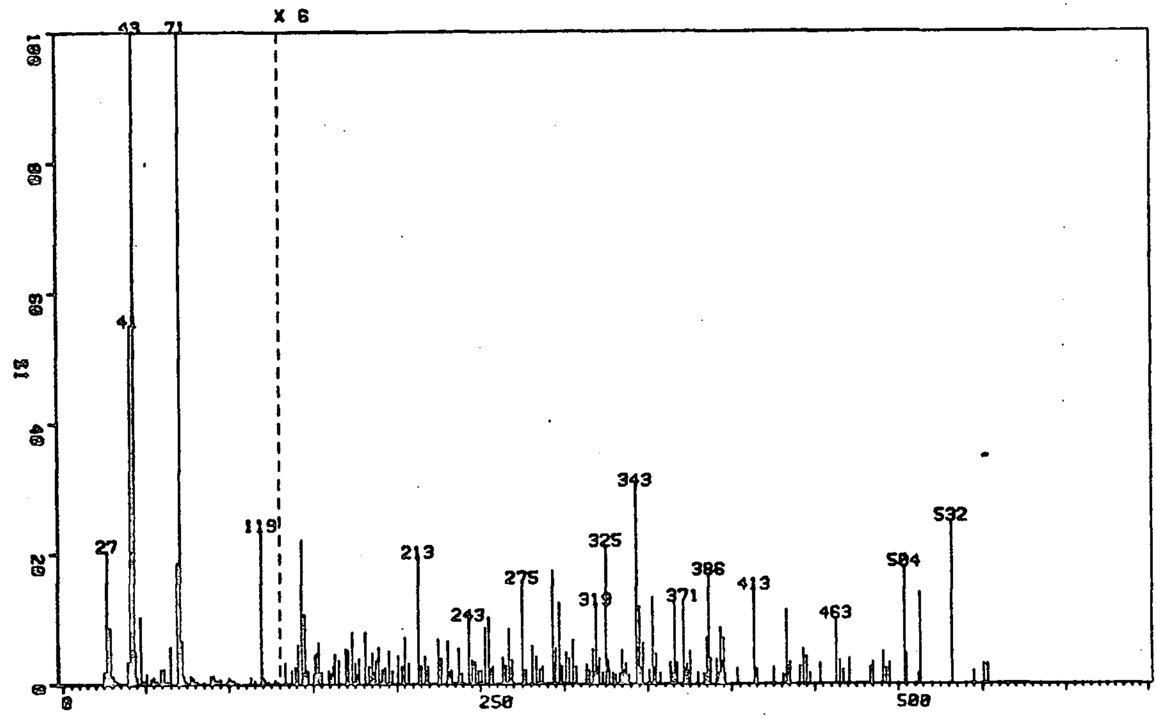
No.32

2-(1,2,3-Tri(trifluoromethyl)-3-pentafluoroethyl-1,4,4,5,5,5-hexafluoropentyl)oxolane (<u>45</u>).

No Spectrum.

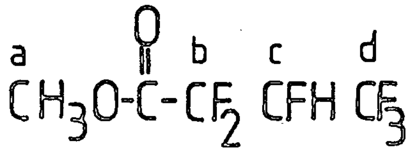
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
	No Spectrum.		

M.Wt.572 No.32



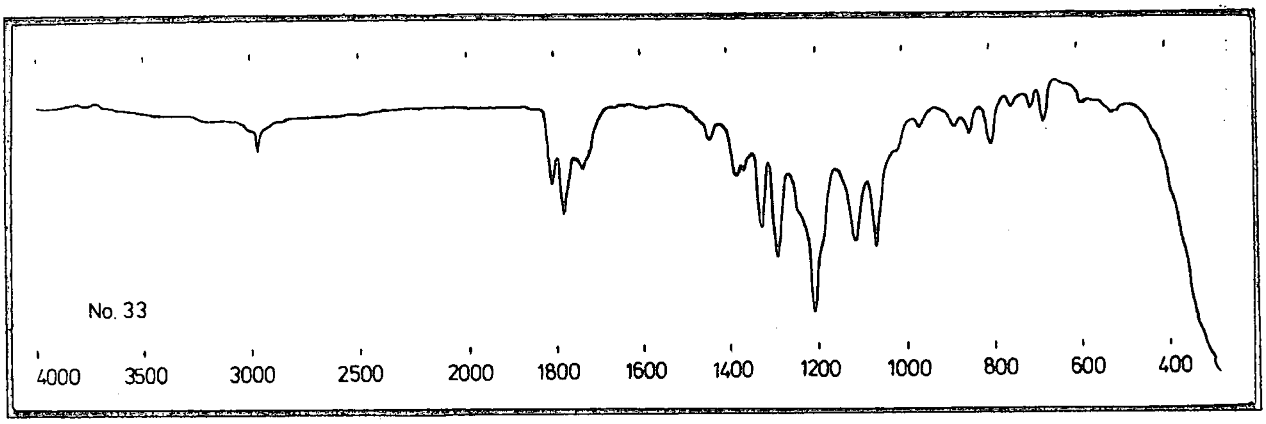
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
5	27.24	20.42	210	435.09	0.56
6	28.13	2.69	211	441.08	0.46
7	29.00	8.57	212	443.11	0.90
13	39.05	3.37	213	445.04	0.71
15	40.98	54.99	214	447.07	0.29
16	42.08	26.06	215	453.06	0.54
19	43.14	100.00	216	463.05	1.68
22	44.17	5.13	217	465.08	0.61
24	47.12	10.31	218	467.11	0.39
33	59.01	2.22	219	471.04	0.66
34	61.02	2.34	220	483.15	0.44
36	65.12	5.79	221	485.09	0.56
37	68.95	18.63	222	491.07	0.83
40	70.98	100.00	223	493.18	0.42
43	72.05	6.64	224	495.13	0.54
63	118.76	23.59	225	504.03	3.00
73	143.00	3.69	226	505.07	0.76
110	213.01	3.25	227	512.20	0.27
138	275.05	2.59	228	513.33	2.34
145	293.09	2.88	229	532.27	4.18
148	297.05	2.08	230	545.18	0.34
159	318.94	2.03	231	551.15	0.51
163	325.04	3.54	232	553.13	0.51
173	342.99	5.08			
179	352.98	2.22			
185	365.60	2.17			
187	370.96	2.12			
195	386.05	2.81			
203	403.09	0.42			
204	413.32	2.42			
205	415.08	0.39			
206	425.09	0.46			
207	431.05	0.24			
208	433.04	1.90			
209	434.10	0.44			

No. 33



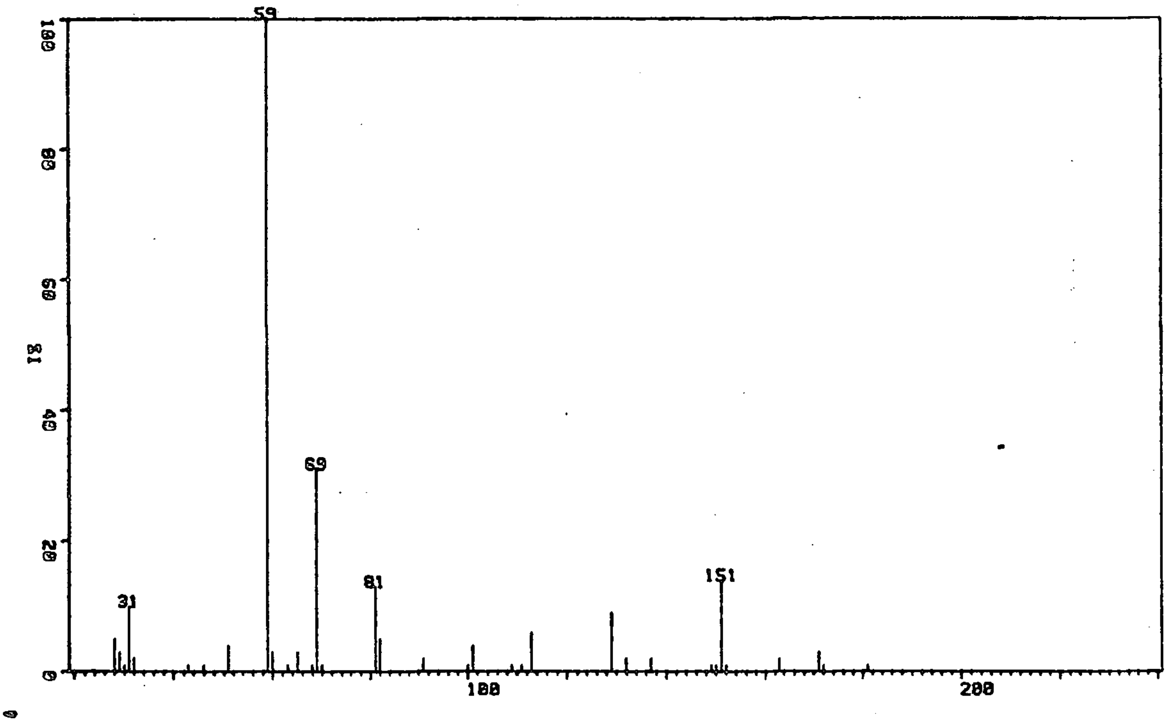
$$\overset{a}{CH_3}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{b}{CF_2}\ \overset{c}{CFH}\ \overset{d}{CF_3}$$

Methyl 2,2,3,4,4,4-hexafluorobutanoate (54).

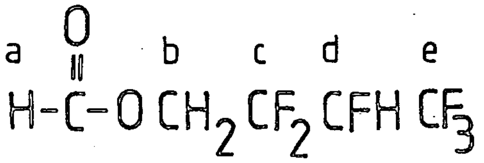


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
3.50	S	3	a
4.88	D of M, J_{HF}=44	1	c
^{19}F			
76.7	M	3	d
118.0, 122.0	AB, J_{FF}=271	2	b
216.0	D of M, J_{FH}=42	1	c

M.Wt. 210 No. 33



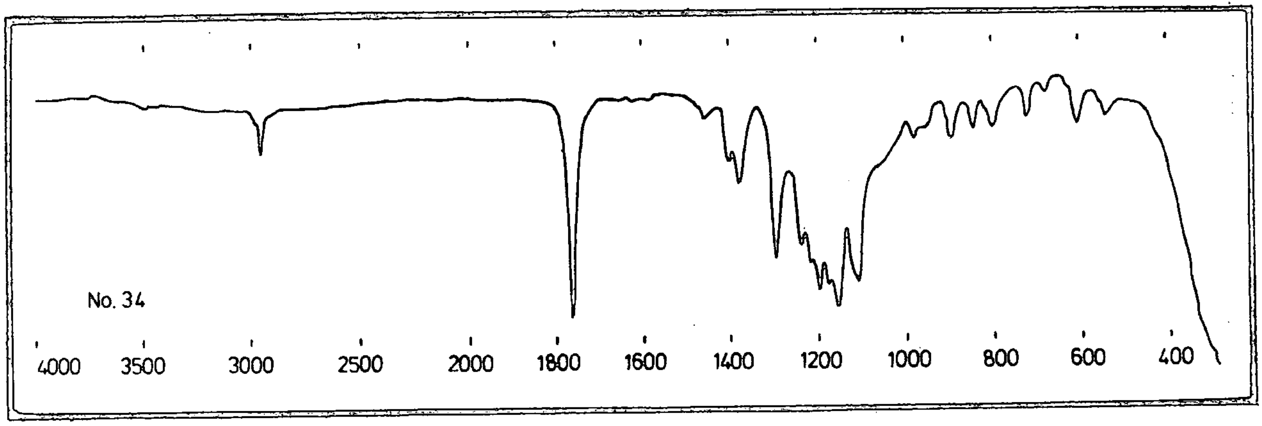
PEAK NO.	MASS	%HT. BASE
1	28.00	5.00*
2	29.00	3.00*
3	30.00	1.00*
4	31.00	10.00*
5	32.00	2.00*
6	43.00	1.00*
7	46.00	1.00*
8	51.00	4.00*
9	59.00	100.00*
10	60.00	3.00*
11	63.00	1.00*
12	65.00	3.00*
13	68.00	1.00*
14	69.00	31.00*
15	70.00	1.00*
16	81.00	13.00*
17	82.00	5.00*
18	91.00	2.00*
19	100.00	1.00*
20	101.00	4.00*
21	109.00	1.00*
22	111.00	1.00*
23	113.00	6.00*
24	129.00	9.00*
25	132.00	2.00*
26	137.00	2.00*
27	149.00	1.00*
28	150.00	1.00*
29	151.00	14.00*
30	152.00	1.00*
31	163.00	2.00*
32	171.00	3.00*
33	172.00	1.00*
34	181.00	1.00



$$\overset{a}{H}-\overset{\overset{O}{\|}}{C}-O\overset{b}{CH_2}\overset{c}{CF_2}\overset{d}{CFH}\overset{e}{CF_3}$$

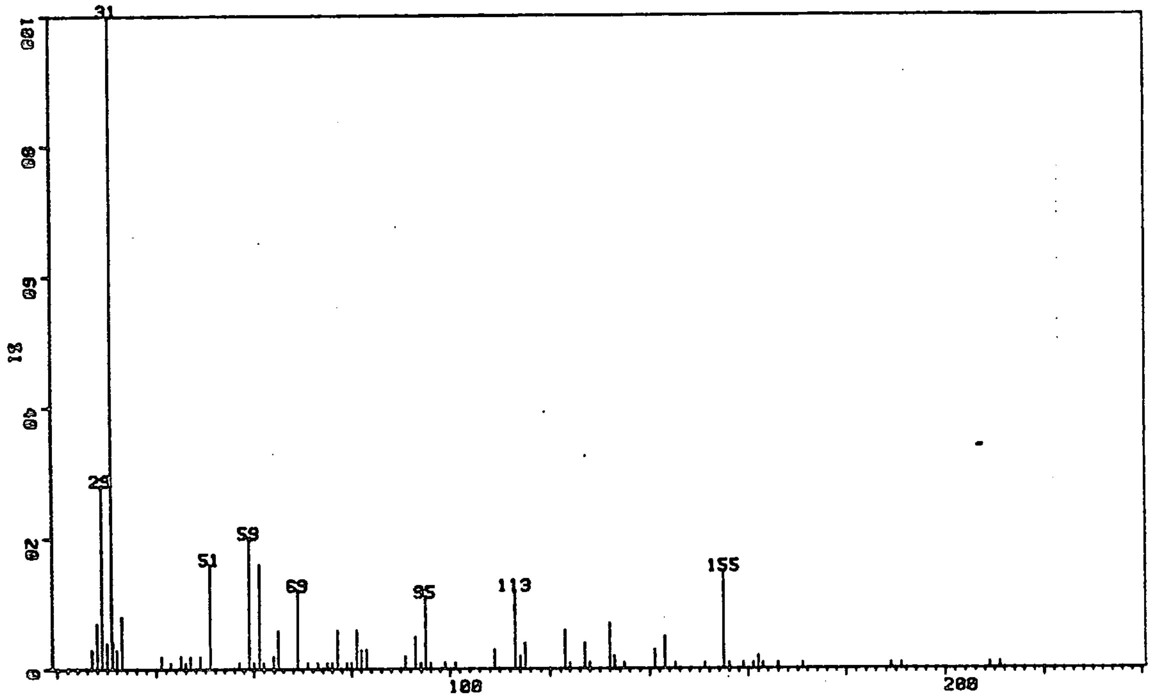
No. 34

2,2,3,4,4,4-Hexafluorobutyl formate (55).

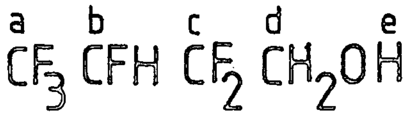


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
4.59	M	2	b
5.10	D of M, $J_{HF}=44$	1	d
8.13	S	1	a
^{19}F			
76.5	M	3	e
117.4, 122.1	AB, J=271	2	c
208.5	D of M, $J_{FH}=42$	1	d

M.Wt. 210 No. 34



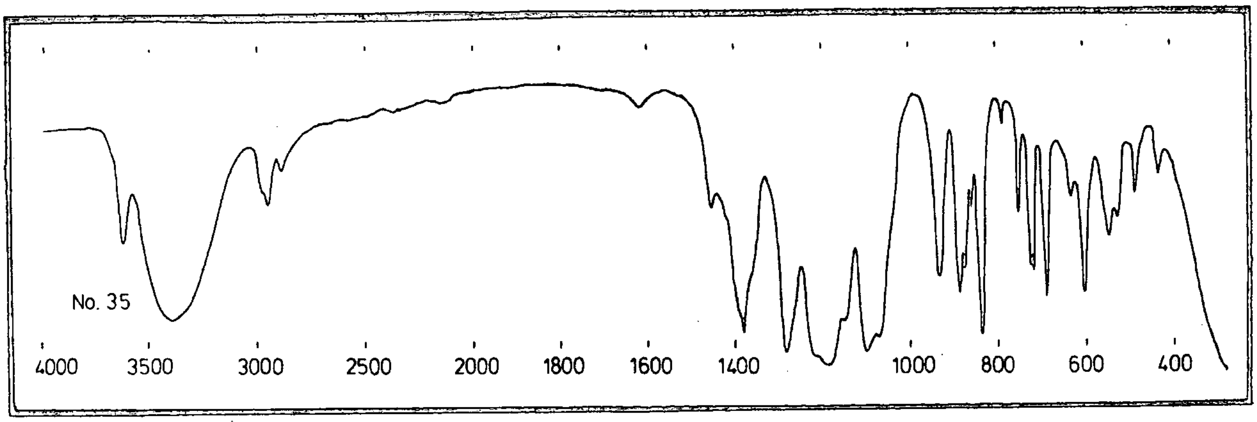
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.00	3.00*	36	94.00	1.00*
2	28.00	7.00*	37	95.00	11.00*
3	29.00	28.00*	38	96.00	1.00*
4	30.00	4.00*	39	99.00	1.00*
5	31.00	100.00*	40	101.00	1.00*
6	31.00	4.00*	41	109.00	3.00*
7	32.00	3.00*	42	113.00	12.00*
8	33.00	8.00*	43	114.00	2.00*
9	41.00	2.00*	44	115.00	4.00*
10	43.00	1.00*	45	123.00	6.00*
11	45.00	2.00*	46	124.00	1.00*
12	46.00	1.00*	47	127.00	4.00*
13	47.00	2.00*	48	128.00	1.00*
14	49.00	2.00*	49	132.00	7.00*
15	51.00	16.00*	50	133.00	2.00*
16	57.00	1.00*	51	135.00	1.00*
17	59.00	20.00*	52	141.00	3.00*
18	60.00	1.00*	53	143.00	5.00*
19	61.00	16.00*	54	145.00	1.00*
20	62.00	1.00*	55	151.00	1.00*
21	64.00	2.00*	56	155.00	15.00*
22	65.00	6.00*	57	156.00	1.00*
23	69.00	12.00*	58	159.00	1.00*
24	71.00	1.00*	59	161.00	1.00*
25	73.00	1.00*	60	162.00	2.00*
26	75.00	1.00*	61	163.00	1.00*
27	76.00	1.00*	62	166.00	1.00*
28	77.00	6.00*	63	171.00	1.00*
29	79.00	1.00*	64	189.00	1.00*
30	80.00	1.00*	65	191.00	1.00*
31	81.00	6.00*	66	209.00	1.00*
32	82.00	3.00*	67	211.00	1.00*
33	83.00	3.00*			
34	91.00	2.00*			
35	93.00	5.00			



$\overset{a}{CF_3}\,\overset{b}{CFH}\,\overset{c}{CF_2}\,\overset{d}{CH_2}O\overset{e}{H}$

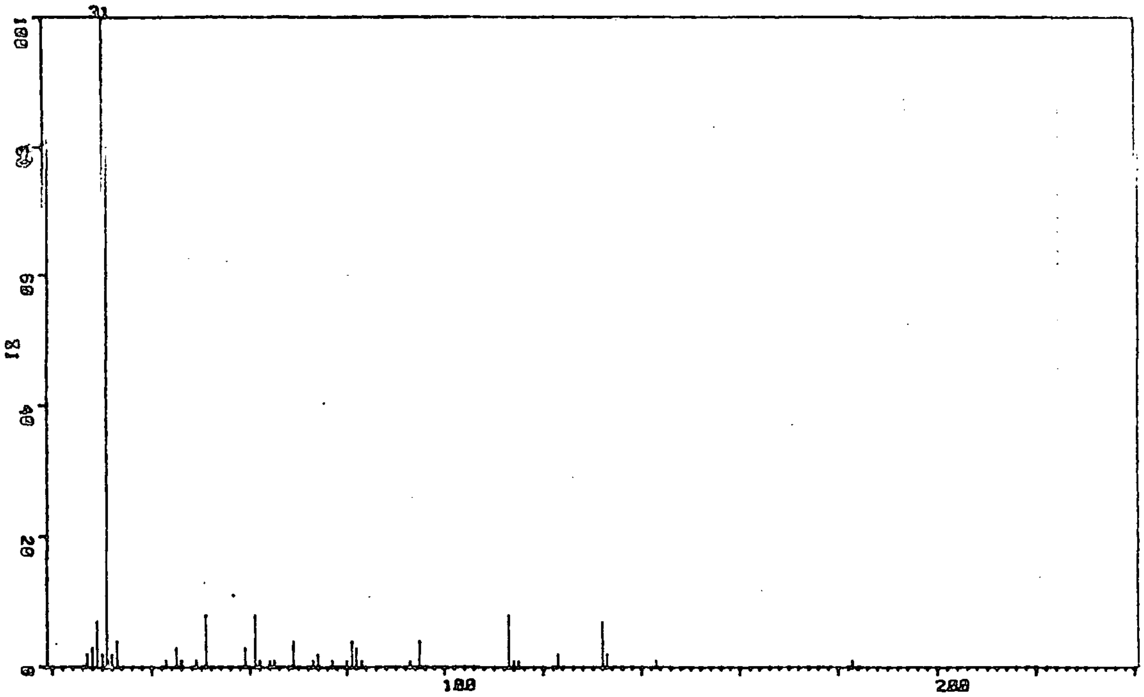
No. 35

2,2,3,4,4,4-Hexafluorobutan-1-ol (56).



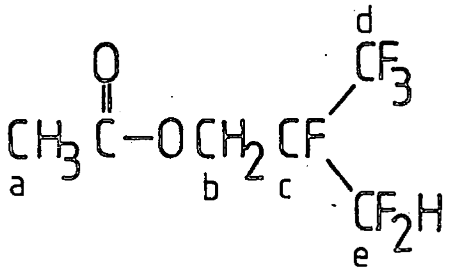
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
3.83	M	2	d
4.47	S	1	e
4.77	D of M, J_{HF}=44, J=6	1	b
^{19}F			
76.2	D of Q, J=6 and 10	3	a
118.3	(M) AB, J=271	2	c
123.2	(Sx, J=10)		
213.7	D of Sx, J=42 and 7	1	b

M. Wt. 182 No. 35

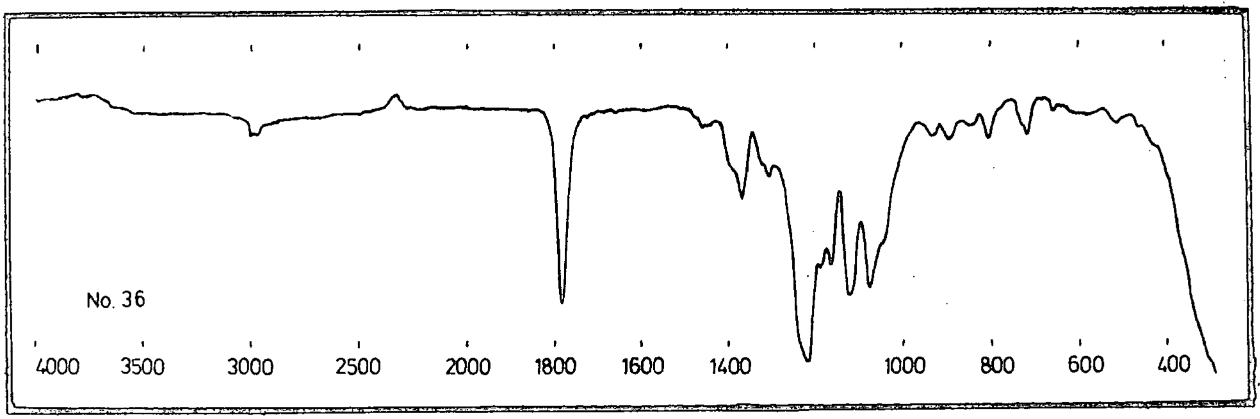


PEAK NO.	MASS	%HT. BASE
1	27.25	1.64
2	28.13	3.16
3	29.00	6.88
4	29.83	2.21
5	30.93	100.00
6	31.24	0.69
7	32.04	1.77
8	33.13	4.20
9	41.00	0.48
10	43.07	0.39
11	43.12	0.52
12	45.16	2.55
13	46.14	0.56
14	48.96	1.30
15	50.94	7.53
16	59.04	3.11
17	60.98	7.96
18	62.04	0.74
19	64.13	0.61
20	65.09	1.47
21	68.93	4.37
22	73.04	0.74
23	74.11	1.90
24	76.99	0.95
25	78.89	0.48
26	79.83	0.56
27	80.93	3.68
28	81.97	2.68
29	83.00	0.56
30	93.01	0.65
31	95.02	4.24
32	112.97	8.26
33	113.98	1.43
34	114.96	0.65
35	122.98	2.42
36	131.96	6.88
37	132.99	2.12
38	142.98	0.74
39	183.00	0.56

No. 36

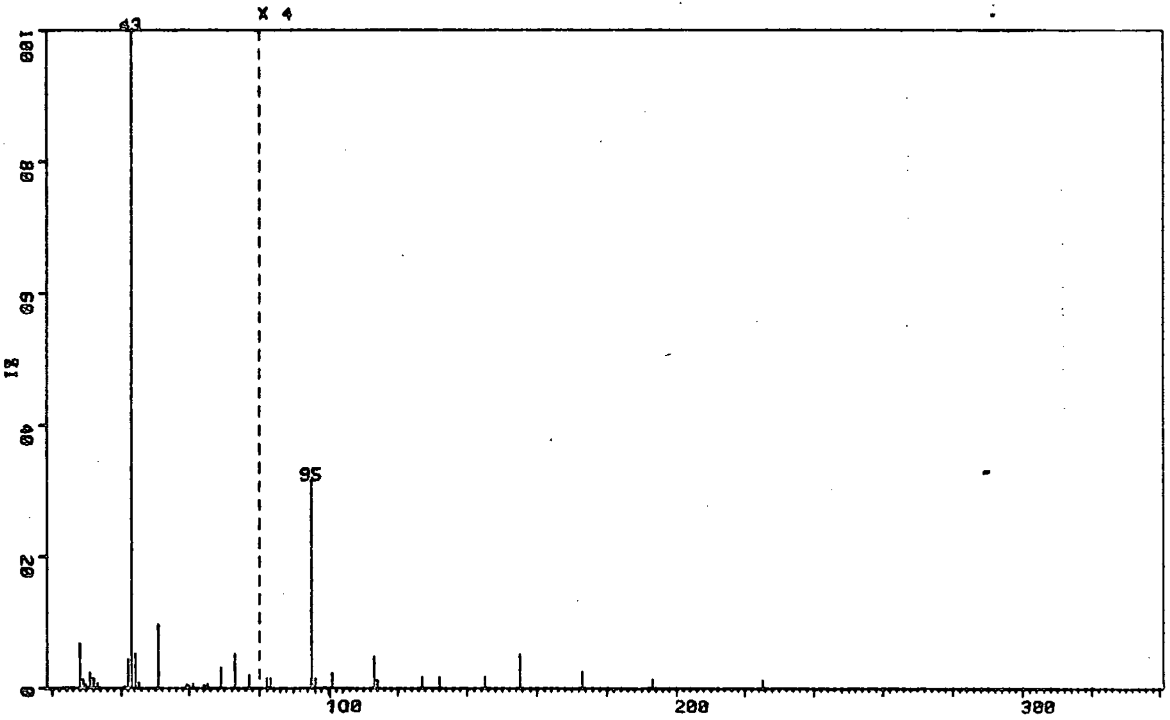


2-Trifluoromethyl-2,3,3-trifluoropropyl acetate (59).



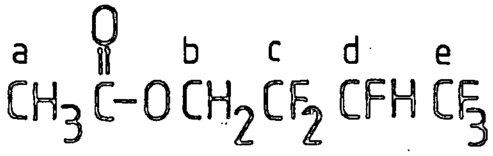
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
1.67	S	3	a
4.20	D, J=18	2	b
5.78	T of D, J=53 and 6	1	e
^{19}F			
77.2	M (Q, J=7)	3	d
135.7	D of M, J=52 and 7	2	e
191.2	M	1	c

M.Wt.224 No.36



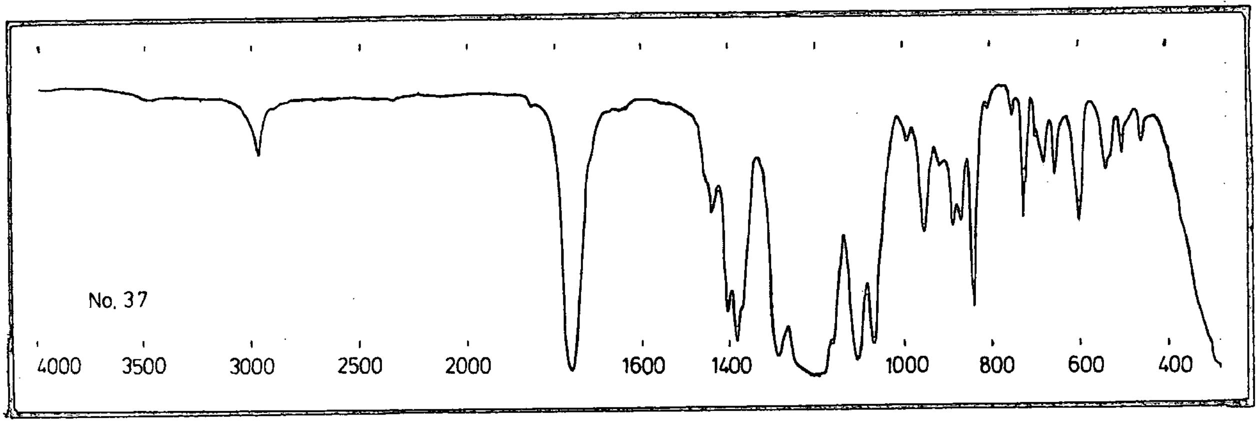
PEAK NO.	MASS	%HT. BASE
1	28.13	6.81
2	28.99	1.29
3	29.84	0.37
4	30.93	2.39
5	32.02	1.47
6	33.13	0.66
7	41.00	0.24
8	42.06	4.40
9	43.12	100.00
10	44.16	5.30
11	45.17	0.88
12	50.96	9.65
13	59.04	0.44
14	59.95	0.32
15	61.03	0.61
16	64.14	0.39
17	65.15	0.61
18	68.96	3.10
19	73.07	5.32
20	77.05	1.93
21	81.98	0.39
22	83.03	0.39
23	95.06	7.94
24	96.08	0.37
25	100.99	0.59
26	113.04	1.22
27	114.07	0.32
28	127.09	0.44
29	132.07	0.42
30	145.08	0.46
31	155.13	1.32
32	173.08	0.66
33	193.09	0.34
34	225.16	0.32

No. 37



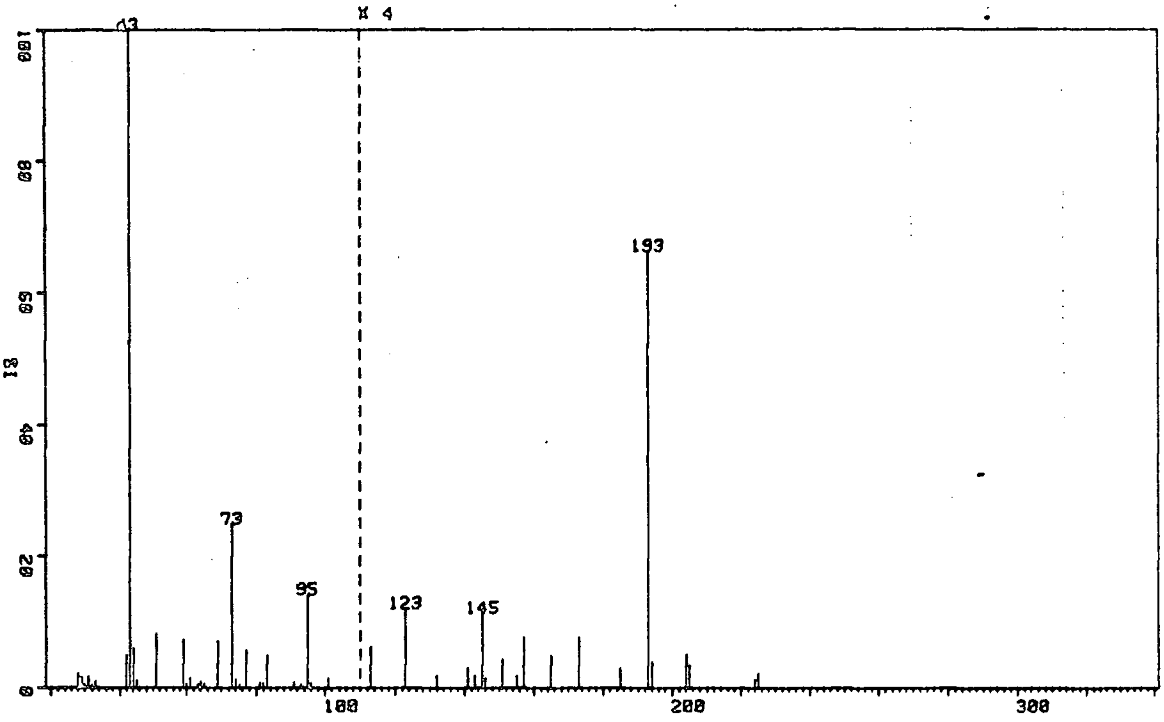
$$\overset{a}{CH_3}\overset{O}{\overset{\|}{C}}\text{-}O\overset{b}{CH_2}\overset{c}{CF_2}\overset{d}{CFH}\overset{e}{CF_3}$$

2,2,3,4,4,4-Hexafluorobutyl acetate (<u>57</u>).

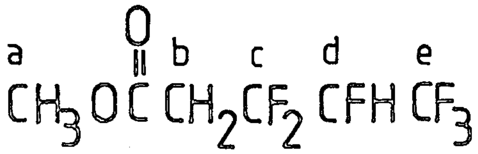


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
1.97	S	3	a
4.37	M	2	b
5.07	D of M, J_{HF}=44	1	d
^{19}F			
76.0	M	3	e
117.3, 121.7	AB, J_{FF}=270	2	c
213.8	D of M, J_{FH}=44	1	d

M.Wt. 224 No.37



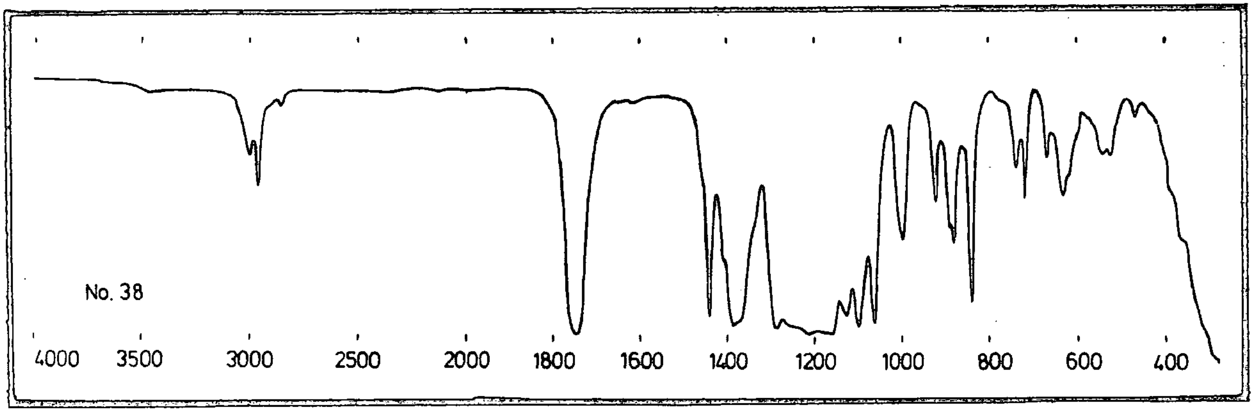
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	2.15	36	145.01	2.86
2	29.00	1.64	37	146.03	0.34
3	29.83	0.42	38	150.95	1.07
4	30.93	1.61	39	155.05	0.46
5	32.02	0.37	40	157.02	1.93
6	33.13	0.95	41	165.03	1.20
7	42.05	5.03	42	173.00	1.93
8	43.12	100.00	43	185.03	0.76
9	44.16	5.91	44	193.00	16.61
10	45.17	1.07	45	194.01	1.00
11	50.96	8.23	46	204.01	1.29
12	59.01	7.35	47	205.04	0.85
13	59.94	0.59	48	224.04	0.32
14	61.01	1.44	49	225.05	0.56
15	63.11	0.37			
16	64.13	0.98			
17	65.11	0.54			
18	68.93	7.11			
19	73.03	24.93			
20	74.05	1.27			
21	75.04	0.42			
22	77.00	5.67			
23	80.91	0.85			
24	81.94	0.71			
25	82.98	5.01			
26	90.91	0.85			
27	92.99	0.39			
28	95.02	14.19			
29	96.02	0.51			
30	100.93	1.42			
31	112.98	1.59			
32	123.02	3.03			
33	132.00	0.46			
34	140.95	0.73			
35	143.01	0.46			



$$\overset{a}{\mathrm{CH_3}}\mathrm{O}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\,\overset{b}{\mathrm{CH_2}}\overset{c}{\mathrm{CF_2}}\,\overset{d}{\mathrm{CFH}}\,\overset{e}{\mathrm{CF_3}}$$

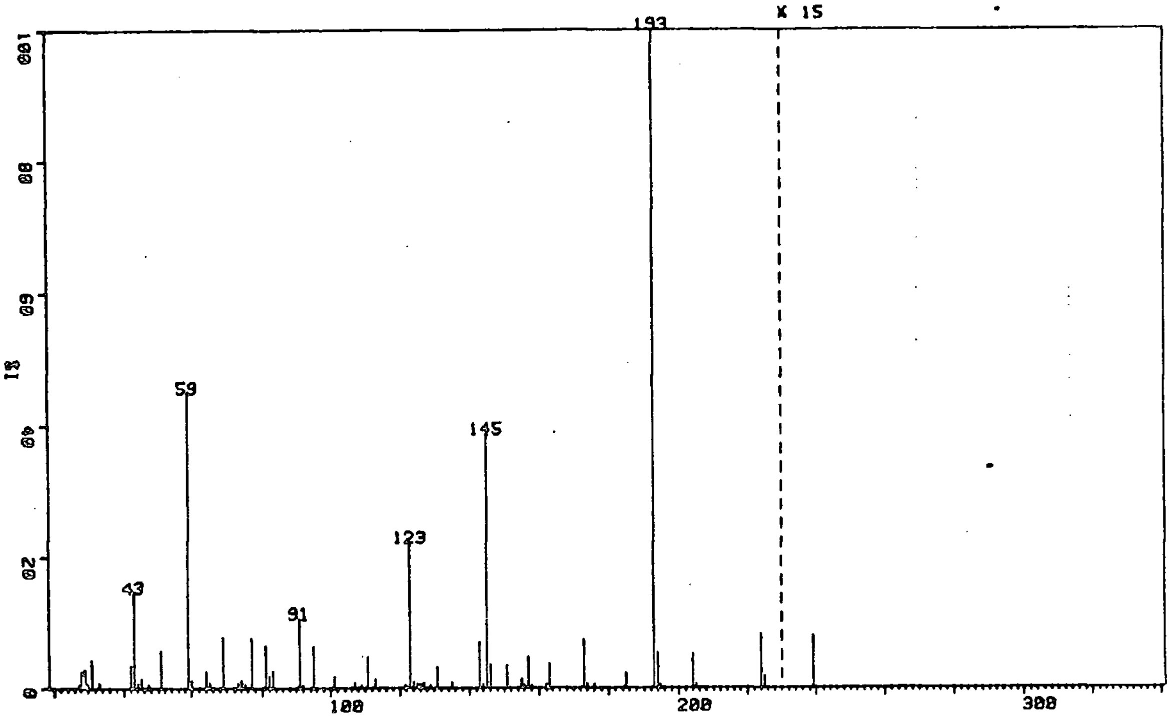
No. 38

Methyl 3,3,4,5,5,5-hexafluoropentanoate (58).

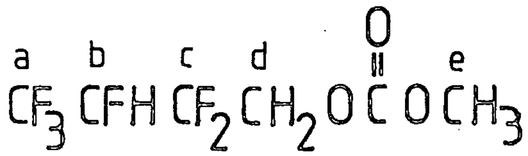


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
2.77	M	2	b
3.32	S	3	a
5.08	D of M, J_{HF}=43	1	d
^{19}F			
76.0	M	3	e
109.3	M	2	c
213.8	D of M, J_{FH}=41	1	d

M.Wt. 224 No. 38



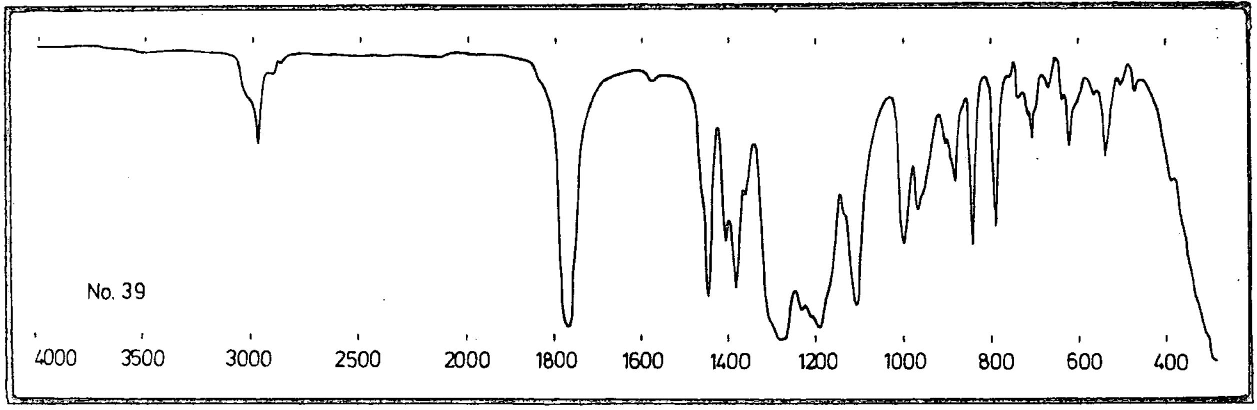
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.26	0.41	36	124.03	0.94
2	28.13	2.59	37	125.03	0.44
3	29.00	2.85	38	126.03	0.50
4	29.84	0.68	39	127.03	0.85
5	30.94	4.32	40	128.96	0.38
6	33.14	0.88	41	130.95	3.23
7	42.05	3.50	42	135.05	0.91
8	43.12	14.60	43	143.01	7.05
9	44.16	0.73	44	144.02	0.47
10	45.17	1.44	45	145.01	38.67
11	47.11	0.44	46	146.03	3.56
12	50.96	5.67	47	150.95	3.50
13	59.01	44.87	48	155.03	1.38
14	59.94	1.20	49	155.44	0.32
15	64.13	2.56	50	156.04	0.32
16	65.11	0.79	51	157.02	4.73
17	68.93	7.73	52	158.03	0.32
18	73.03	0.71	53	162.03	0.44
19	74.06	1.15	54	163.02	3.67
20	75.03	0.44	55	173.00	7.38
21	77.00	7.58	56	174.02	0.65
22	80.91	6.55	57	176.03	0.59
23	81.94	1.91	58	185.03	2.29
24	82.98	2.67	59	192.97	100.00
25	90.91	10.58	60	194.01	5.44
26	91.95	0.38	61	194.95	0.38
27	95.02	6.41	62	204.01	5.32
28	100.93	1.67	63	205.01	0.68
29	107.00	0.85	64	224.04	8.20
30	108.91	0.41	65	225.05	1.73
31	110.91	4.76	66	239.08	0.53
32	112.98	1.35			
33	121.48	0.29			
34	122.02	0.32			
35	123.02	22.19			



$\overset{a}{CF_3}\,\overset{b}{CFH}\,\overset{c}{CF_2}\,\overset{d}{CH_2}\,O\overset{O}{\overset{\|}{C}}\,O\overset{e}{CH_3}$

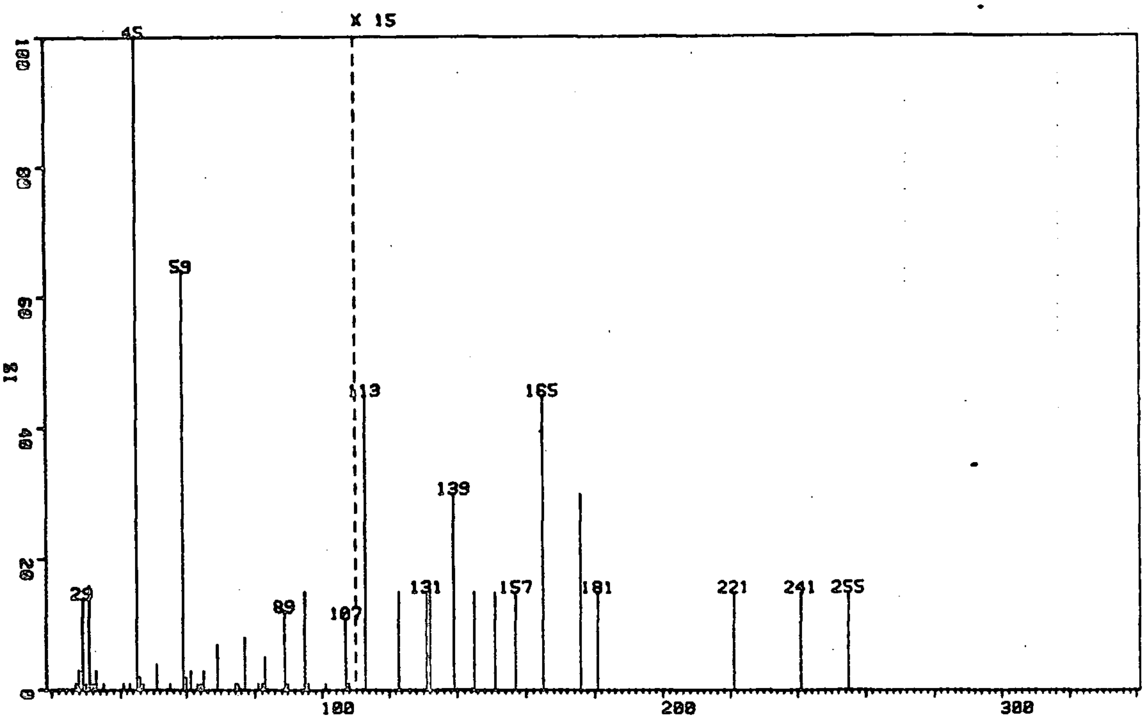
No.39

2,2,3,4,4,4-Hexafluorobutyl methyl carbonate (60).



SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
3.57	S	3	e
4.30	D of D of D, J=15, 10, 4.5	2	d
4.92	D of M, J=44	1	b
^{19}F			
76.3	M	3	a
119.3, 123.9	AB, J_{FF}=277	2	c
215.8	D of M, J_{FH}=43	1	b

M.Wt. 240 No. 39

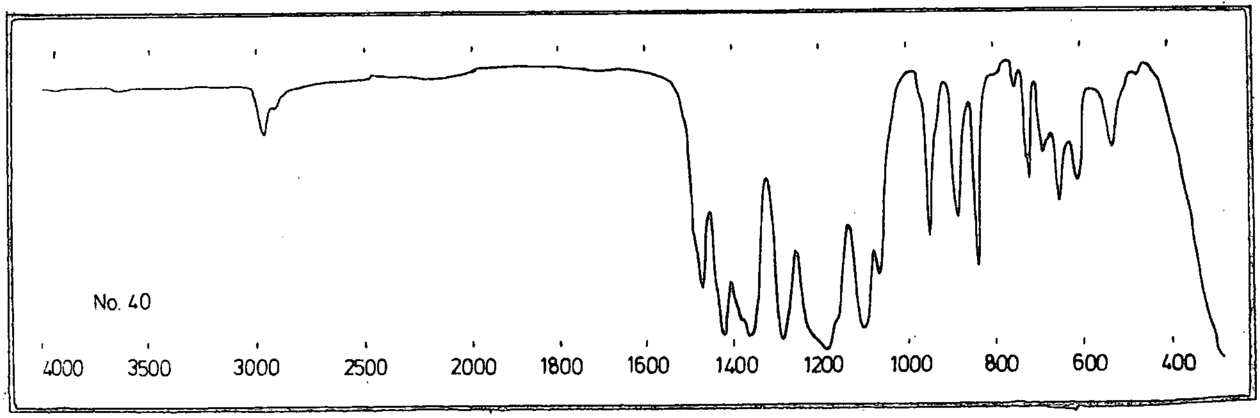


PEAK NO.	MASS	%HT. BASE
1	27.00	1.00*
2	28.00	3.00*
3	29.00	14.00*
4	30.00	1.00*
5	31.00	16.00*
6	32.00	1.00*
7	33.00	3.00*
8	35.00	1.00*
9	41.00	1.00*
10	43.00	1.00*
11	45.00	100.00*
12	46.00	2.00*
13	47.00	1.00*
14	51.00	4.00*
15	55.00	1.00*
16	59.00	64.00*
17	60.00	2.00*
18	61.00	3.00*
19	63.00	1.00*
20	64.00	1.00*
21	65.00	3.00*
22	69.00	7.00*
23	74.00	1.00*
24	75.00	1.00*
25	77.00	8.00*
26	81.00	1.00*
27	82.00	1.00*
28	83.00	5.00*
29	89.00	12.00*
30	90.00	1.00*
31	95.00	15.00*
32	96.00	1.00*
33	101.00	1.00*
34	107.00	11.00*
35	108.00	1.00
36	113.00	3.00*
37	123.00	1.00*
38	131.00	1.00*
39	132.00	1.00*
40	139.00	2.00*
41	145.00	1.00*
42	151.00	1.00*
43	157.00	1.00*
44	165.00	3.00*
45	176.00	2.00*
46	181.00	1.00*
47	221.00	1.00*
48	241.00	1.00*
49	255.00	1.00*

$\overset{e}{B}(O\overset{a}{CH_2}\overset{b}{CF_2}\overset{c}{CFH}\overset{d}{CF_3})_3$

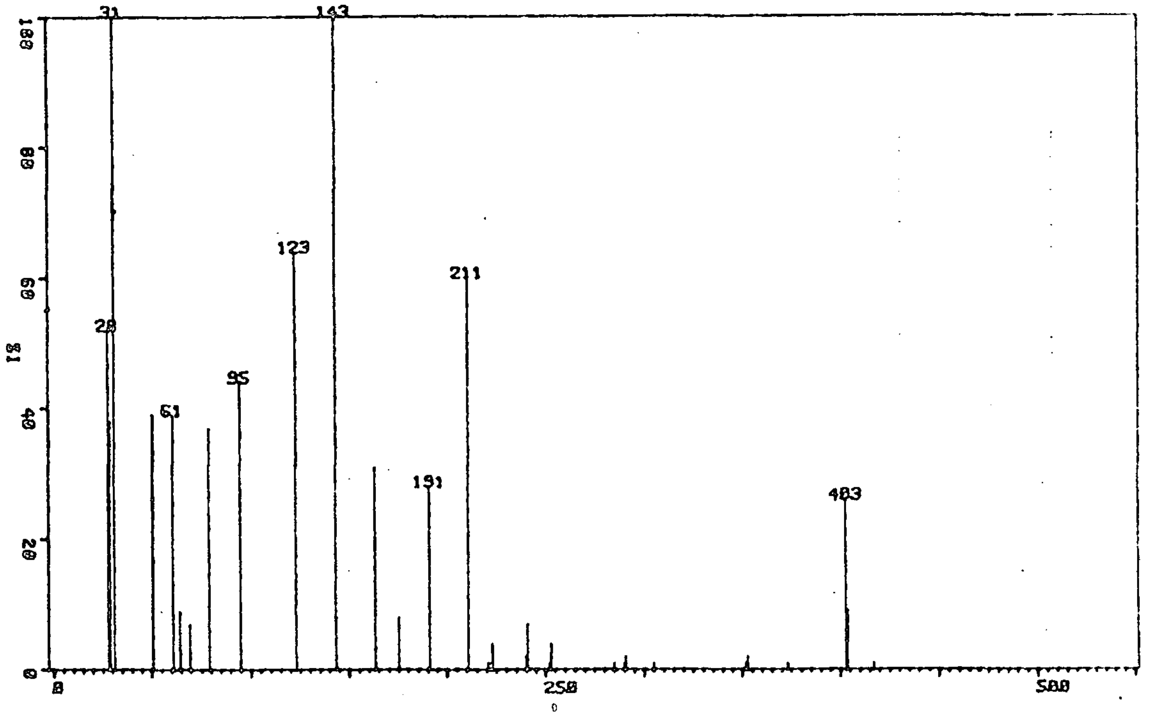
No. 40

Tri(2,2,3,4,4,4-hexafluorobutyl)borate (<u>63</u>).

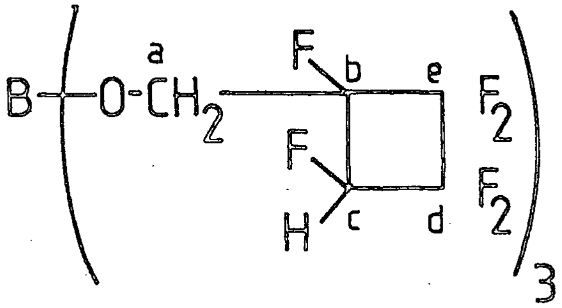


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
3.97	M, J=12	2	a
4.67	D of M, J_{HF}=42, J=6	1	c
^{19}F			
75.5	D of Q, J=7 and 11	3	d
119.0	AB, J=263 (M)	2	b
123,0	(Sx, J=10)		
214.3	D of Sx, J_{HF}=43, J=8	1	c
^{11}B			
-3.5 ($B(OMe)_3$ as reference)	S(very broad)	-	e

M.Wt. 554 No. 40

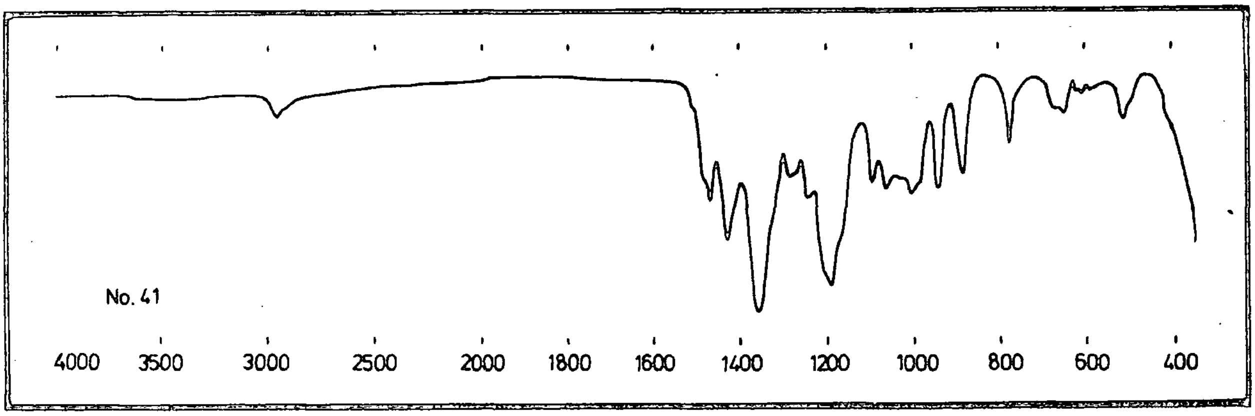


PEAK NO.	MASS	%HT. BASE
1	28.00	52.00*
2	29.00	38.00*
3	31.00	100.00*
4	51.00	39.00*
5	51.00	39.00*
6	61.00	39.00*
7	64.00	9.00*
8	69.00	7.00*
9	79.00	37.00*
10	95.00	44.00*
11	123.00	64.00*
12	143.00	100.00*
13	163.00	31.00*
14	175.00	8.00*
15	191.00	28.00*
16	211.00	60.00*
17	221.00	1.00*
18	222.00	1.00*
19	223.00	4.00*
20	240.00	2.00*
21	241.00	7.00*
22	252.00	1.00*
23	253.00	4.00*
24	285.00	1.00*
25	290.00	1.00*
26	291.00	2.00*
27	305.00	1.00*
28	352.00	1.00*
29	353.00	2.00*
30	373.00	1.00*
31	403.00	26.00*
32	404.00	9.00*
33	417.00	1.00*



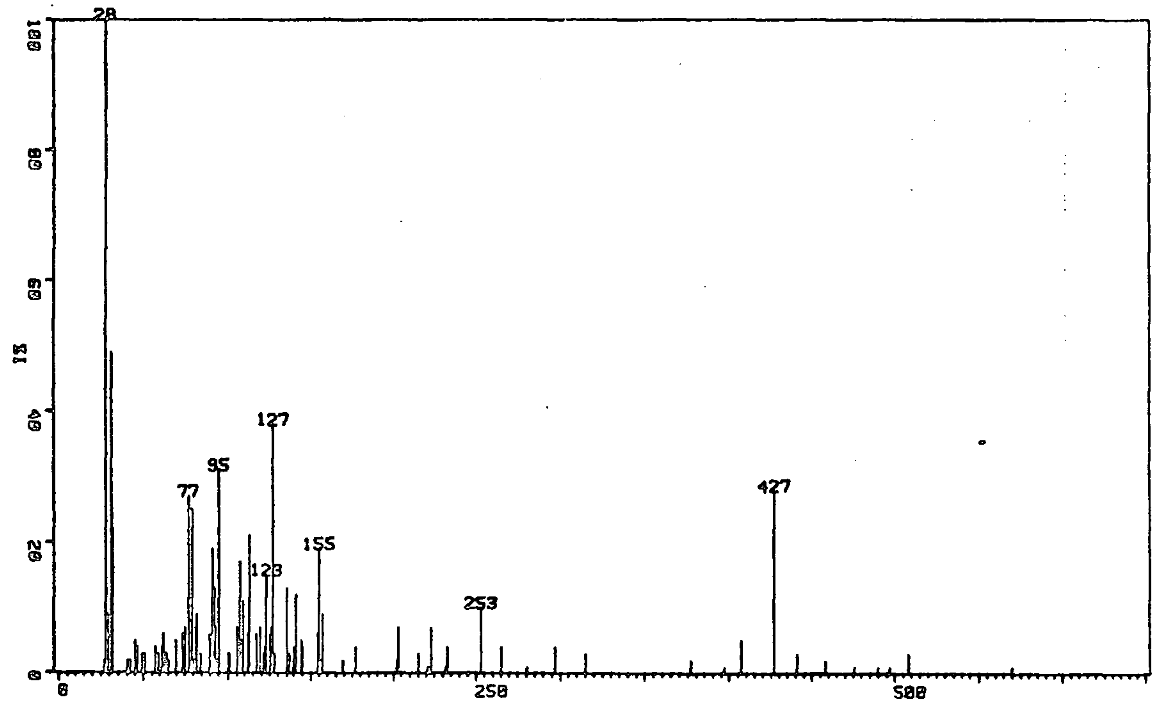
No. 41

Tri((1,2,3,3,4,4-hexafluorocyclobutyl)methyl) borate (<u>64</u>).

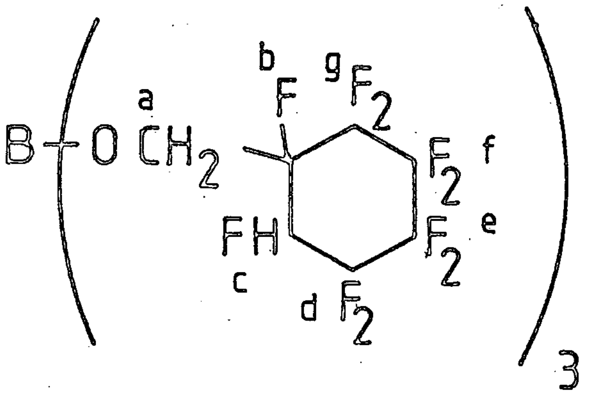


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
4.13	S	2	a
4.50	S		
5.23	D of M, $J_{HF}=45$	1	c
^{19}F			
118.8, 134.2	AB, $J_{FF}=230$	2	d or e (cis)
121.1, 135.1	AB, $J_{FF}=231$		d or e(Trans)
129.0, 131.1	AB, $J_{FF}=231$	2	e or d (cis) and(trans)
180.5	M	1	b (trans)
198.2	M		b (cis)
217.8	D of M, $J_{FF}=47$	1	c (trans)
219.7	D of M, $J_{FF}=47$		c (cis)

M.Wt. 588 No. 41

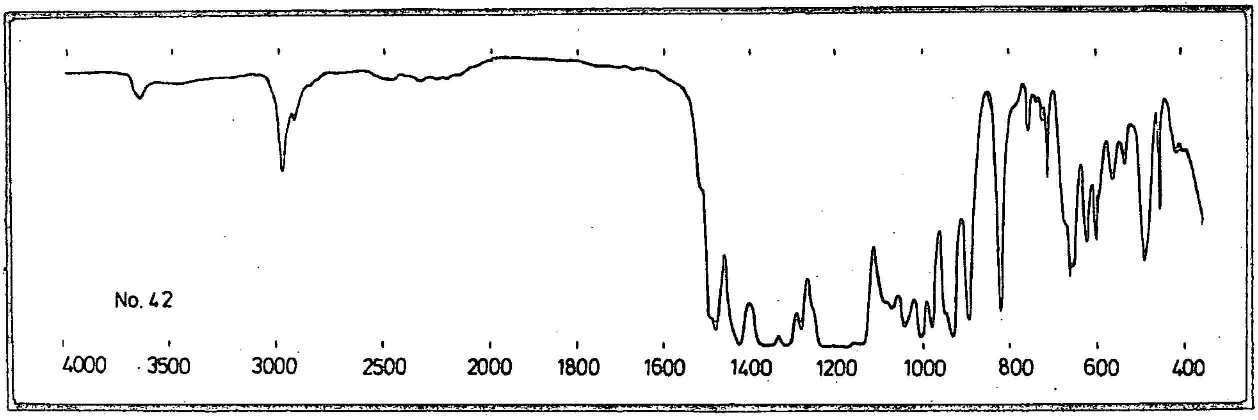


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.00	2.00*	36	94.00	2.00*	71	221.00	1.00*
2	28.00	100.00*	37	95.00	31.00*	72	223.00	7.00*
3	29.00	9.00*	38	100.00	3.00*	73	232.00	1.00*
4	29.00	6.00*	39	101.00	3.00*	74	233.00	4.00*
5	31.00	49.00*	40	105.00	7.00*	75	253.00	10.00*
6	32.00	22.00*	41	107.00	17.00*	76	265.00	4.00*
7	40.00	2.00*	42	108.00	5.00*	77	281.00	1.00*
8	42.00	2.00*	43	109.00	11.00*	78	297.00	4.00*
9	45.00	5.00*	44	112.00	6.00*	79	315.00	3.00*
10	46.00	4.00*	45	113.00	21.00*	80	377.00	2.00*
11	49.00	3.00*	46	117.00	6.00*	81	397.00	1.00*
12	51.00	3.00*	47	119.00	7.00*	82	407.00	5.00*
13	57.00	4.00*	48	121.00	3.00*	83	427.00	28.00*
14	59.00	3.00*	49	122.00	4.00*	84	441.00	3.00*
15	61.00	4.00*	50	123.00	15.00*	85	458.00	2.00*
16	62.00	6.00*	51	125.00	6.00*	86	476.00	1.00*
17	63.00	3.00*	52	126.00	7.00*	87	490.00	1.00*
18	64.00	3.00*	53	127.00	38.00*	88	497.00	1.00*
19	65.00	2.00*	54	128.00	3.00*	89	508.00	3.00*
20	69.00	5.00*	55	135.00	13.00*	90	570.00	1.00*
21	73.00	6.00*	56	137.00	3.00*			
22	74.00	6.00*	57	139.00	2.00*			
23	75.00	7.00*	58	140.00	4.00*			
24	77.00	27.00*	59	141.00	12.00*			
25	78.00	8.00*	60	144.00	5.00*			
26	79.00	25.00*	61	145.00	4.00*			
27	80.00	2.00*	62	154.00	6.00*			
28	81.00	7.00*	63	155.00	19.00*			
29	82.00	9.00*	64	156.00	2.00*			
30	84.00	3.00*	65	157.00	9.00*			
31	89.00	6.00*	66	169.00	2.00*			
32	90.00	5.00*	67	177.00	4.00*			
33	91.00	19.00*	68	202.00	2.00*			
34	92.00	13.00*	69	203.00	7.00*			
35	93.00	7.00	70	215.00	3.00			



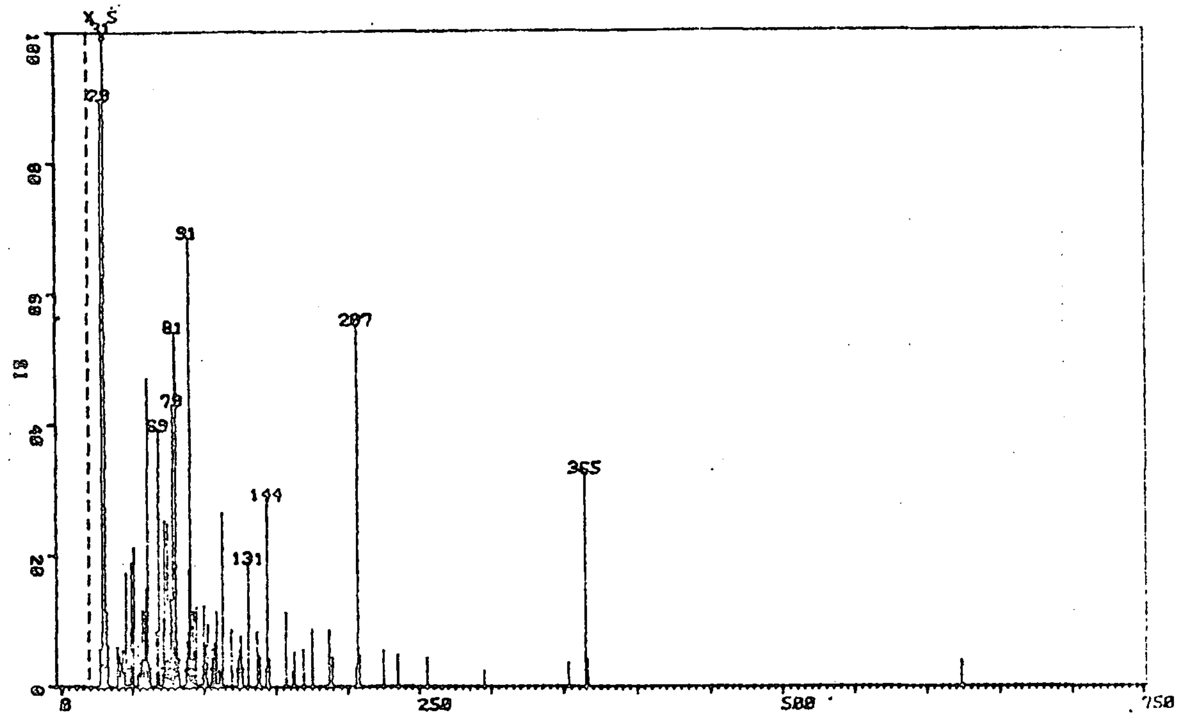
No. 42

Tri((1,2,3,3,4,4,5,5,6,6-decafluorocyclohexyl)methyl) borate (<u>65</u>).

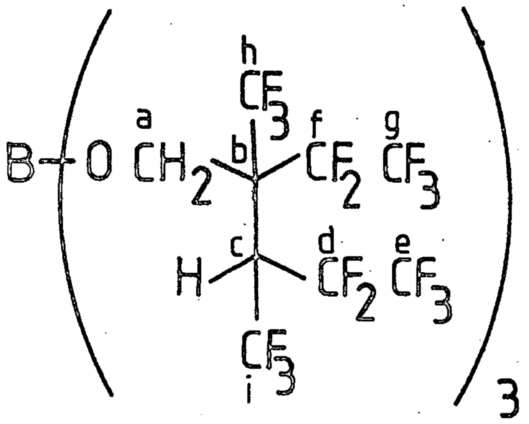


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
4.43	M(broad)	2	a
5.07	M(broad)	1	c
^{19}F			
115.0, 117.7, 118.7, 120.7, 121.3, 122.7, 123.8, 126.3, 127.3, 130.3, 131.7, 133.7, 135.7, 137.5, 138.8, 141.7, 142.7, 146.7.	Overlapping AB's	8	d, e, f, g
187.2	M	1	b (trans)
194.2	M		b (cis)
208.7	D of M, J_{FH}=43	1	c (trans)
231.3	D of M, J=43		c (cis)

M.Wt. 890 No.42

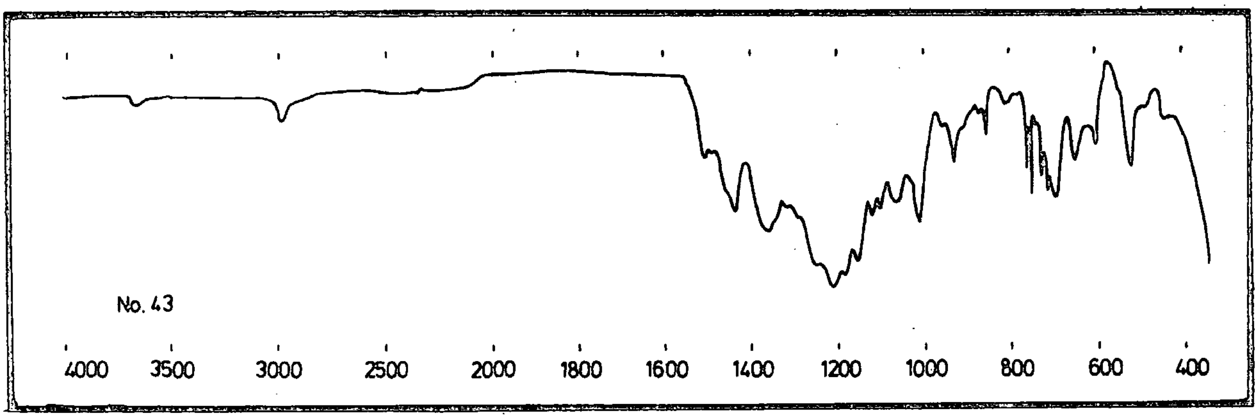


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.18	1.17	36	74.13	0.80	71	124.09	0.80
2	28.06	1.01	37	75.05	4.98	72	125.08	1.11
3	28.93	17.93	38	76.07	0.86	73	126.08	1.53
4	28.97	1.19	39	77.05	2.67	74	127.07	0.54
5	29.78	2.62	40	78.01	2.51	75	130.96	3.76
6	30.85	100.00	41	78.94	8.58	76	137.01	1.66
7	31.99	2.28	42	79.89	2.88	77	139.02	0.91
8	33.08	1.24	43	80.98	10.83	78	143.07	0.52
9	38.99	1.22	44	82.05	1.40	79	144.01	5.73
10	40.99	0.91	45	83.08	0.86	80	145.05	0.80
11	42.05	0.67	46	87.08	0.52	81	157.01	2.25
12	43.12	1.11	47	88.04	0.78	82	162.05	0.47
13	44.15	0.41	48	89.01	1.37	83	163.10	1.04
14	45.18	3.47	49	89.95	3.55	84	169.09	1.11
15	47.13	0.60	50	90.99	13.71	85	175.07	1.76
16	49.00	3.81	51	92.06	0.80	86	187.07	1.71
17	49.91	0.62	52	93.05	2.31	87	189.16	0.88
18	50.98	4.25	53	94.08	1.06	88	206.07	0.54
19	53.14	0.36	54	95.08	2.41	89	207.02	11.04
20	54.18	1.27	55	97.10	0.44	90	208.11	0.93
21	55.16	0.39	56	99.03	0.62	91	225.15	1.11
22	56.16	0.75	57	99.97	2.46	92	235.07	0.96
23	57.13	2.33	58	101.07	1.27	93	255.10	0.88
24	58.12	0.80	59	102.14	0.67	94	295.23	0.47
25	59.05	2.25	60	103.07	1.89	95	353.28	0.73
26	59.97	2.98	61	105.10	0.54	96	364.81	6.50
27	61.03	9.43	62	106.04	1.17	97	366.27	0.80
28	62.09	0.67	63	107.06	0.86	98	623.82	0.78
29	63.14	0.60	64	108.03	1.32			
30	67.15	1.68	65	108.96	2.31			
31	68.08	0.41	66	111.02	0.49			
32	68.96	7.83	67	112.02	0.39			
33	71.02	0.36	68	113.01	5.29			
34	72.07	2.07	69	118.99	1.74			
35	73.09	5.05	70	123.11	0.54			



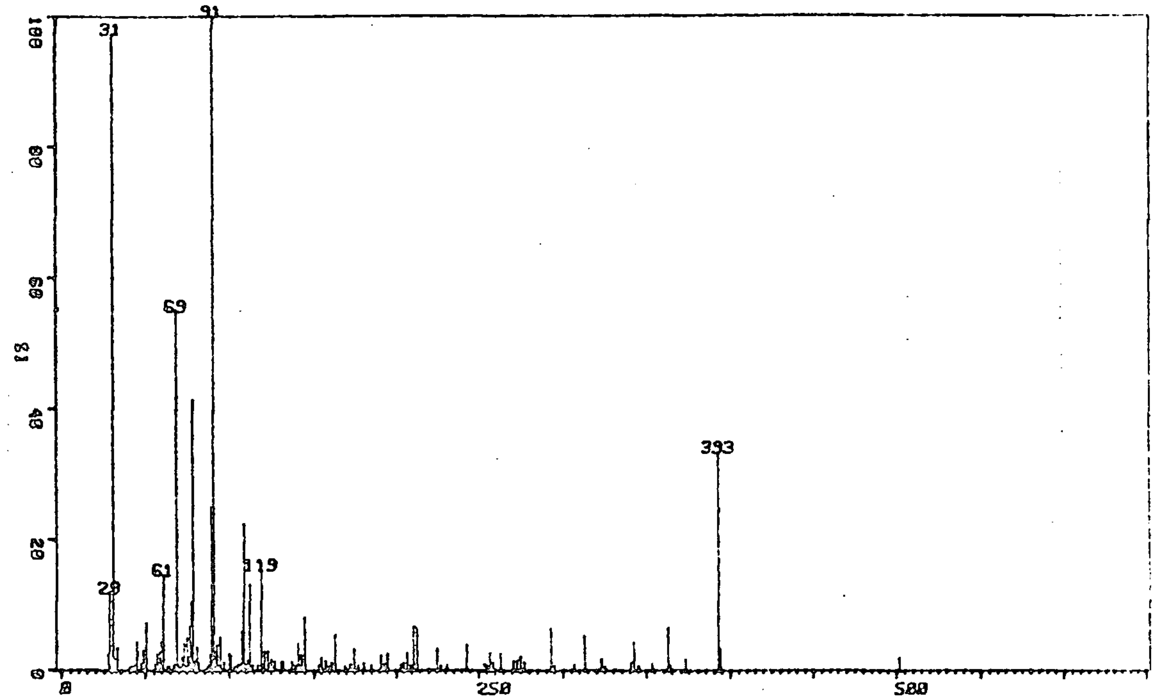
No. 43

Tri(2-pentafluoroethyl-4,4,5,5,5-pentafluoro-2,3-di(trifluoromethyl)-pentyl) borate (<u>66</u>).

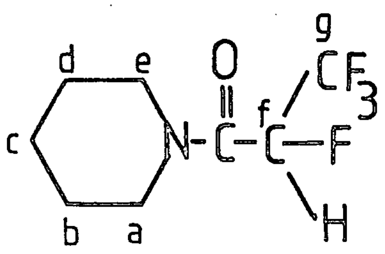


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
<u>^{1}H</u>			
4.1	M(very broad)	1	c
4.4	S(broad)	2	a
<u>^{19}F</u>			
57.7	M(broad)	3	h , i
61.8	M(broad)	3	
80.3	S	3	g , e
83.3	S	3	
109.3	M(broad)	4	d , f

M.Wt. 1304 No. 43

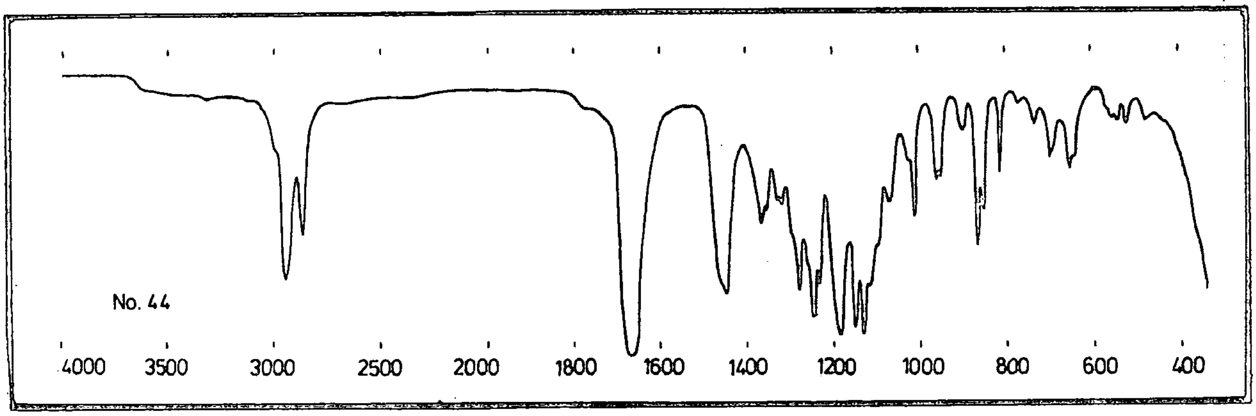


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.06	2.40	51	101.04	2.21	109	253.11	1.01
2	28.94	11.84	55	107.05	1.06	111	257.02	2.58
3	29.79	2.99	56	108.01	5.90	112	258.99	1.34
4	30.86	97.42	57	108.96	22.29	113	263.10	2.58
5	32.00	1.70	59	111.02	1.52	114	271.13	1.47
6	33.09	3.36	61	113.01	13.22	115	273.05	1.52
11	45.19	4.24	64	118.96	15.34	116	275.06	2.12
12	47.14	1.11	66	121.02	2.90	117	277.10	1.34
13	49.01	3.13	67	123.06	2.99	118	292.99	6.40
14	49.91	1.57	68	124.09	1.06	119	295.09	0.78
15	50.98	7.23	69	125.09	1.75	120	307.05	0.92
17	57.15	2.44	71	127.08	1.38	121	313.00	5.25
18	58.13	1.20	72	131.05	1.34	122	323.08	1.84
19	59.06	2.86	73	132.06	1.34	123	325.06	0.60
20	59.97	4.33	74	137.10	1.43	124	341.11	1.20
21	61.05	14.56	77	141.01	4.15	125	342.94	4.33
26	68.95	54.86	79	143.04	2.40	126	345.10	0.60
29	72.06	1.98	80	144.06	1.43	127	353.12	1.06
30	73.09	4.05	81	145.05	8.20	128	362.92	6.45
32	75.08	4.97	83	155.01	1.98	129	364.08	0.78
33	76.08	1.98	84	157.00	1.52	130	373.00	1.84
34	77.06	6.68	86	161.02	1.34	131	392.88	33.30
35	78.02	10.36	87	163.04	5.48	132	393.96	3.27
36	78.97	41.41	90	173.07	1.01	133	502.03	1.93
37	79.94	1.47	91	175.07	3.27			
38	80.99	3.55	93	180.99	1.15			
39	82.01	1.24	95	190.99	2.35			
42	89.00	2.44	96	193.09	1.06			
43	89.96	25.06	98	195.02	2.53			
44	91.00	100.00	100	205.02	1.15			
45	92.05	2.76	101	207.02	2.67			
46	93.06	3.92	103	210.98	6.68			
48	95.09	5.02	104	213.01	6.49			
49	97.05	1.24	105	225.03	3.22			
50	99.98	2.53	108	243.05	3.92			



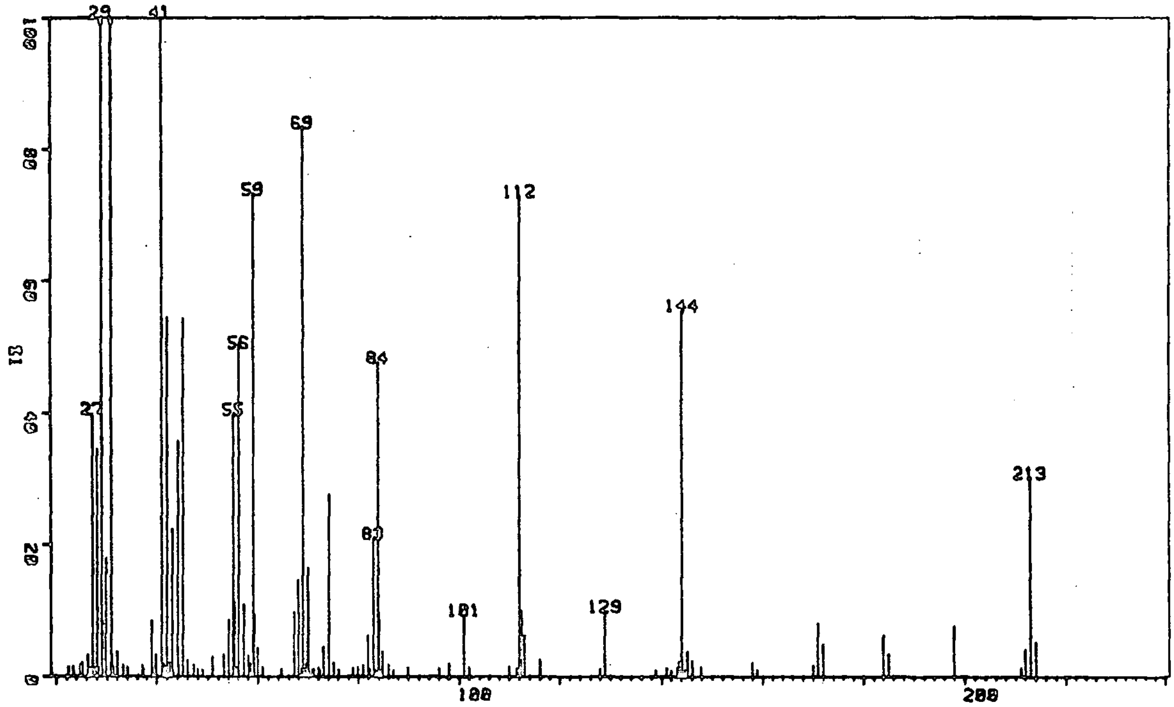
No. 44

N-(2,3,3,3-Tetrafluoropropanoyl)piperidine (74).

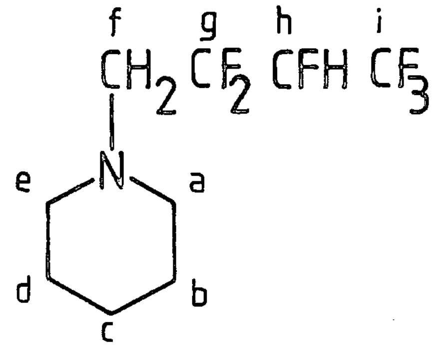


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
1.63	M	6	b, c, d
3.50	M	4	a , e
5.33	D of Q, J=47 and 6	1	f
^{19}F			
76.0	D of D, J=12 and 6	3	g
197.3	D of Q, J=43 and 12	1	f

M.Wt. 213 No. 44

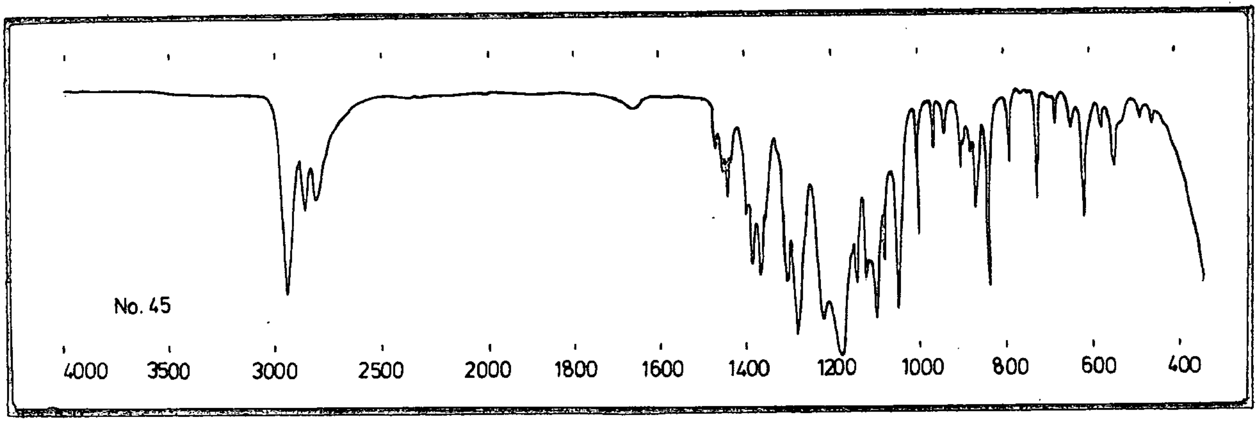


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	22.47	0.87	36	42.60	1.24	71	69.57	1.09	106	112.27	5.76
2	23.35	0.87	37	42.75	0.87	72	69.89	9.56	107	113.00	3.69
3	24.79	1.02	38	42.96	0.83	73	69.99	7.38	108	116.00	1.47
4	25.15	1.17	39	43.10	12.99	74	70.21	0.49	109	127.93	0.68
5	26.30	1.92	40	43.23	0.45	75	70.79	0.60	110	128.87	5.69
6	26.80	0.72	41	44.16	20.75	76	71.04	0.64	111	138.88	0.56
7	27.24	23.12	42	44.31	0.94	77	72.16	0.75	112	140.98	0.72
8	27.86	0.79	43	45.15	31.51	78	72.34	0.53	113	141.88	0.53
9	28.13	19.99	44	46.15	1.47	79	73.08	2.60	114	143.02	0.79
10	28.31	0.60	45	47.14	0.98	80	74.11	16.08	115	143.46	1.36
11	28.35	0.79	46	48.02	0.60	81	75.09	1.24	116	144.06	32.23
12	29.01	62.65	47	48.95	0.56	82	76.04	0.60	117	144.62	0.56
13	29.06	4.63	48	50.92	1.77	83	78.94	0.75	118	145.10	2.22
14	29.55	1.02	49	53.08	1.88	84	79.87	0.79	119	146.00	1.43
15	29.84	10.43	50	54.11	4.97	85	80.97	1.02	120	147.69	0.87
16	30.73	1.17	51	54.95	0.83	86	82.01	3.69	121	157.97	1.28
17	30.91	100.00	52	55.13	23.04	87	82.24	0.60	122	158.91	0.60
18	31.04	0.94	53	55.21	6.51	88	83.01	12.09	123	169.94	0.98
19	31.16	0.60	54	55.78	0.75	89	83.26	0.56	124	170.89	4.71
20	31.92	0.98	55	56.12	28.95	90	83.65	0.41	125	171.97	2.82
21	32.02	2.22	56	57.10	6.33	91	83.96	27.60	126	183.96	3.73
22	33.11	1.02	57	58.06	1.81	92	84.08	5.23	127	184.98	1.96
23	34.10	0.87	58	58.44	0.38	93	84.59	0.53	128	197.96	4.48
24	37.07	0.98	59	58.59	1.13	94	84.77	0.79	129	211.02	0.75
25	37.34	0.64	60	59.00	42.43	95	85.01	2.22	130	211.92	2.37
26	38.99	4.93	61	59.08	5.38	96	86.04	1.05	131	212.97	17.51
27	39.08	1.17	62	59.24	0.90	97	86.97	0.56	132	214.01	3.01
28	39.12	0.56	63	59.92	2.52	98	89.87	0.79			
29	39.72	0.94	64	60.83	0.79	99	96.06	0.72			
30	39.88	1.92	65	64.67	0.64	100	98.07	1.13			
31	40.96	58.09	66	67.14	5.65	101	100.94	5.38			
32	41.25	0.94	67	68.06	8.47	102	101.98	0.79			
33	41.32	1.09	68	68.66	0.64	103	109.95	0.87			
34	41.79	0.90	69	69.01	48.31	104	111.43	0.72			
35	42.05	31.63	70	69.45	0.68	105	112.02	42.32			



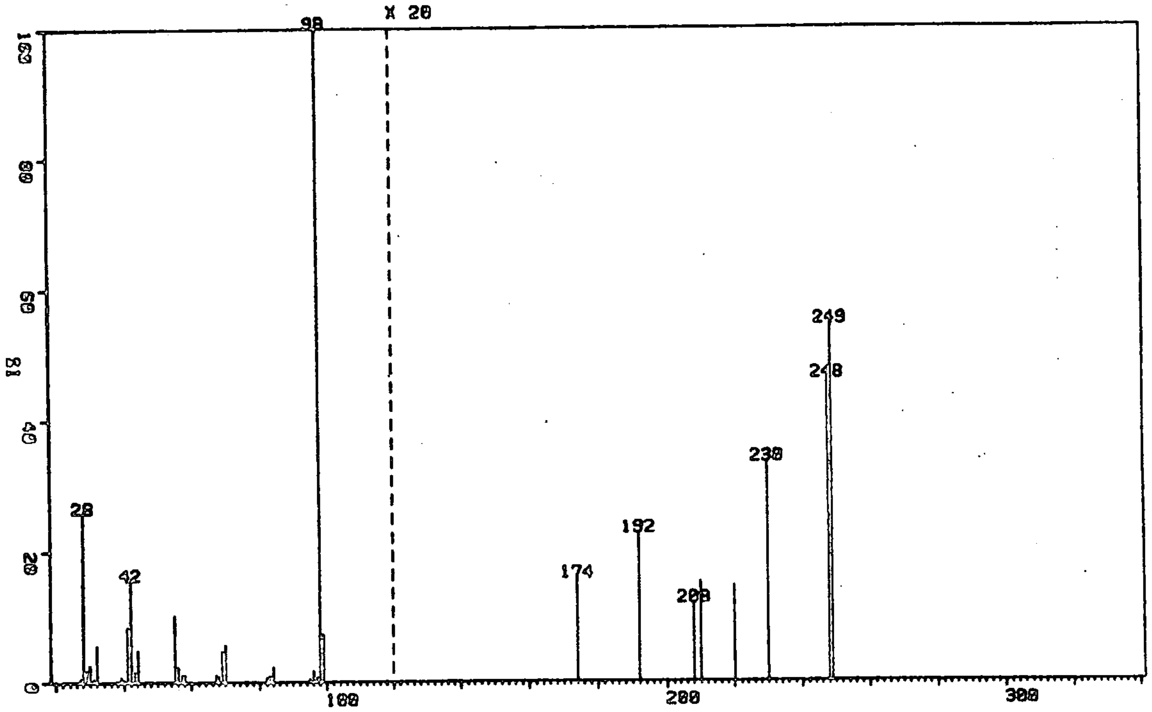
No. 45

N-(2,2,3,4,4,4-Hexafluorobutyl)piperidine (75).

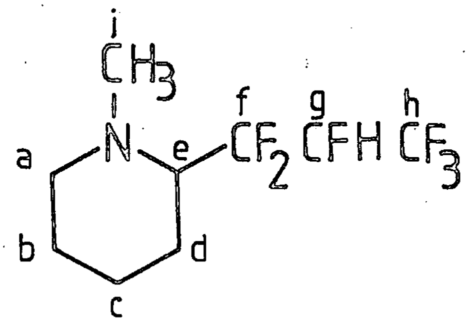


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
0.90	M	6	b, c, d
1.95	M	4	a , e
2.35	M	2	f
4.57	M(broad)	1	h
^{19}F			
75.0	M	3	i
115.7	M	2	g
213.0	D of M, J_{FH}=42	1	h

M.Wt. 249 No.45

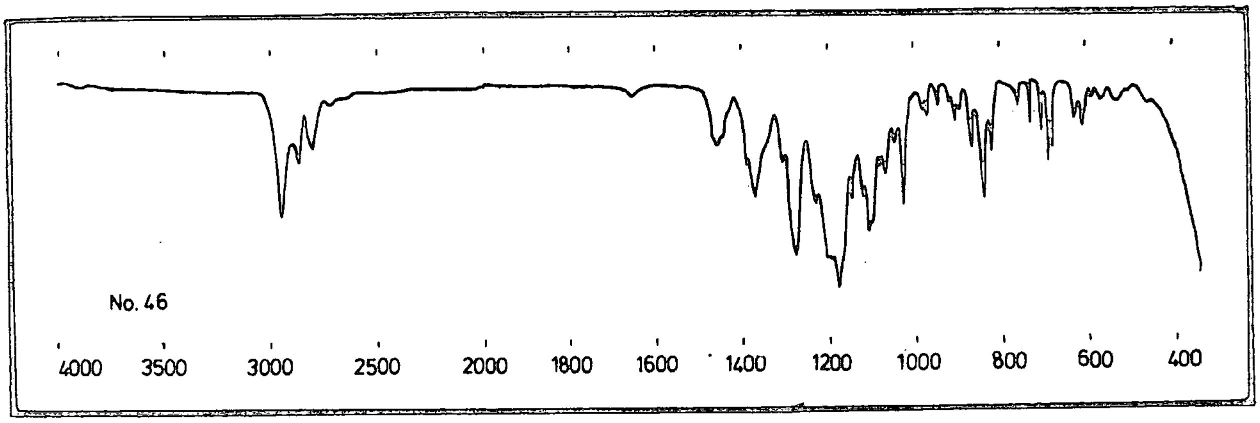


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.25	0.54	36	248.91	2.73
2	28.13	25.93			
3	29.03	1.68			
4	29.85	2.51			
5	30.94	0.44			
6	32.02	5.55			
7	39.01	0.73			
8	39.85	0.41			
9	40.99	8.38			
10	42.08	15.68			
11	43.14	1.56			
12	44.19	4.86			
13	55.16	10.12			
14	56.16	2.25			
15	57.15	1.11			
16	58.11	1.11			
17	67.13	1.08			
18	68.05	0.86			
19	69.01	4.67			
20	69.93	5.71			
21	82.03	0.67			
22	83.07	0.95			
23	84.10	2.32			
24	95.01	0.48			
25	96.08	1.75			
26	97.07	0.73			
27	98.03	100.00			
28	99.01	7.27			
29	173.97	0.79			
30	191.93	1.14			
31	207.95	0.60			
32	209.94	0.76			
33	219.91	0.73			
34	229.94	1.68			
35	247.86	2.32			



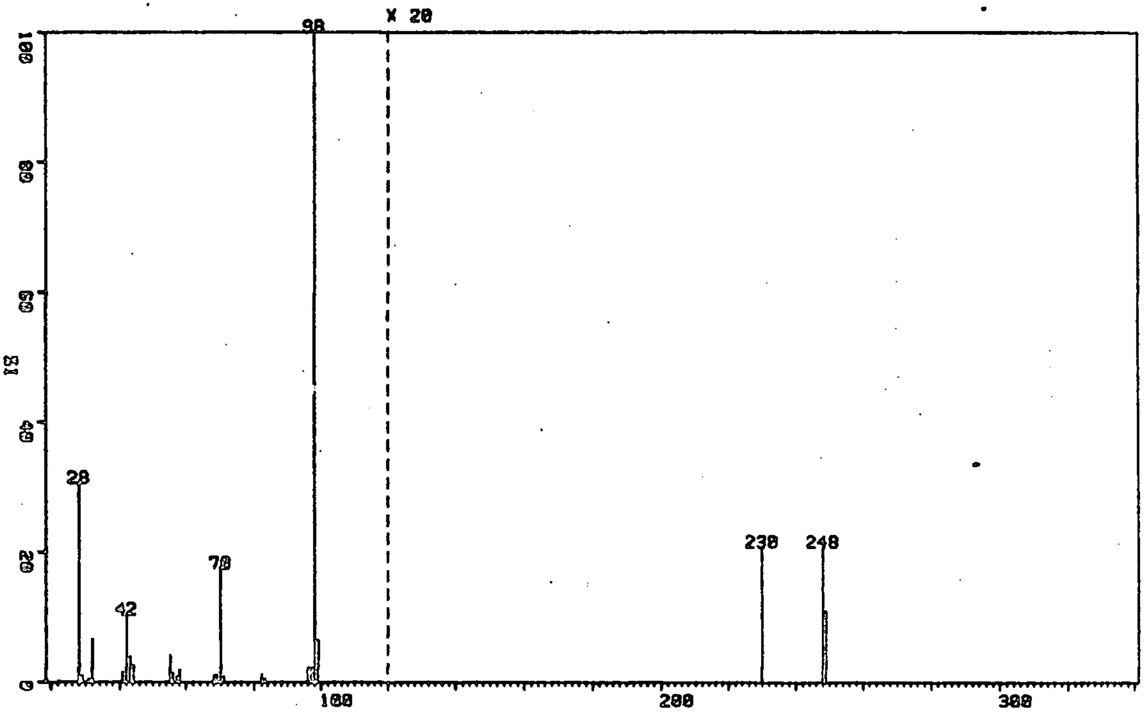
No. 46

N-Methyl-2-(1,1,2,3,3,3-hexafluoropropyl)piperidine (76).

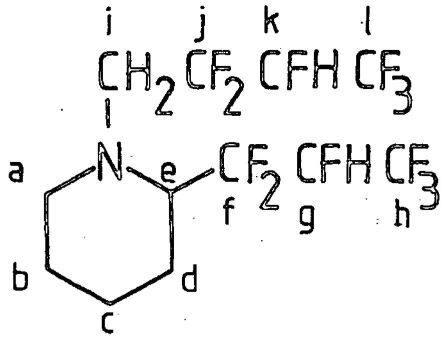


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
1.37	M	6	b, c, d
2.00	S	3	i
2.20	S		
2.48	M	3	a , e
4.97	D of M, J=43	1	g
^{19}F			
75.0	M	3	h
106.2, 115.8	AB, J_{FF}=271	2	f
118.0	M		
211.0	D of M, J=42	1	g
212.0	D of M, J=42		

M.Wt. 249 No. 46

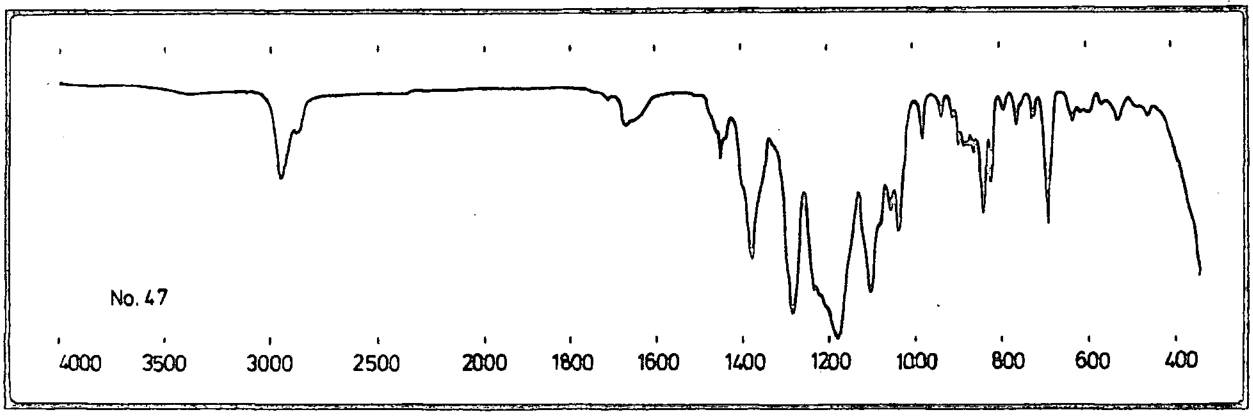


PEAK NO.	MASS	%HT. BASE
1	28.13	30.70
2	29.02	0.96
3	30.93	0.54
4	32.02	6.61
5	40.99	1.55
6	42.07	10.46
7	43.12	3.89
8	44.18	2.63
9	55.16	4.14
10	56.16	1.42
11	57.14	0.92
12	58.10	1.80
13	68.09	1.09
14	69.04	1.13
15	69.97	17.52
16	71.04	0.88
17	82.05	1.25
18	83.10	0.59
19	96.11	2.34
20	97.08	2.22
21	98.06	100.00
22	99.03	6.57
23	229.93	1.05
24	247.89	1.05
25	248.94	0.54



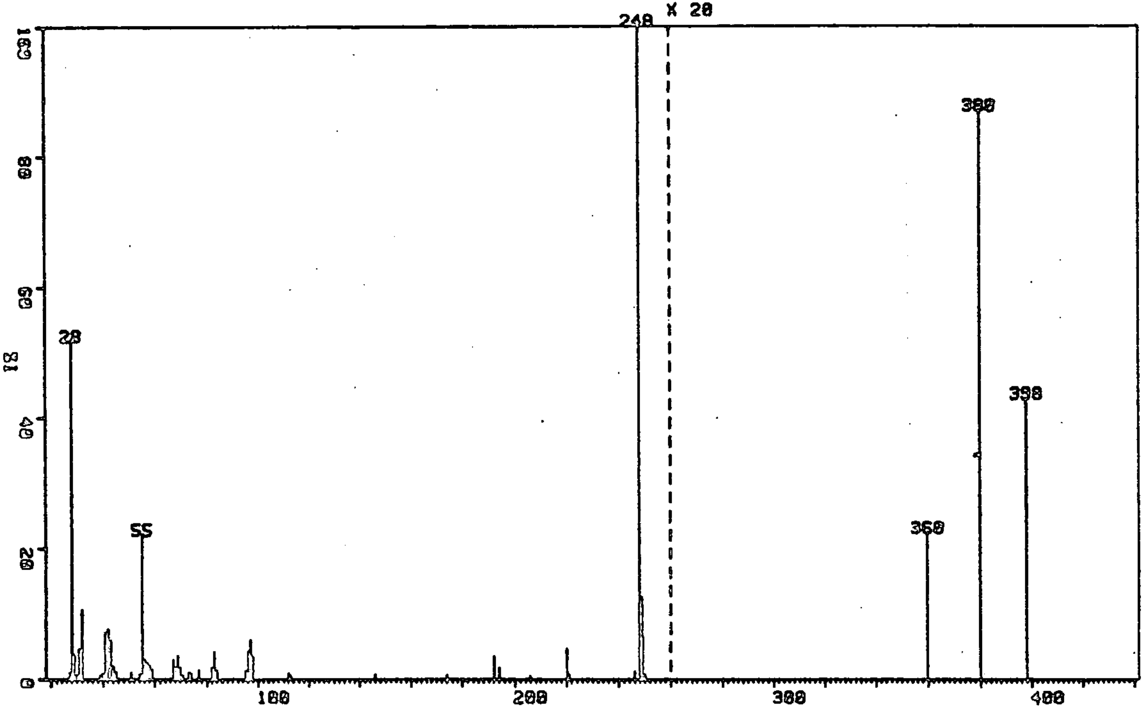
No. 47

N-(2,2,3,4,4,4-Hexafluorobutyl)-2-(1,1,2,3,3,3-hexafluoropropyl)-piperidine (77).



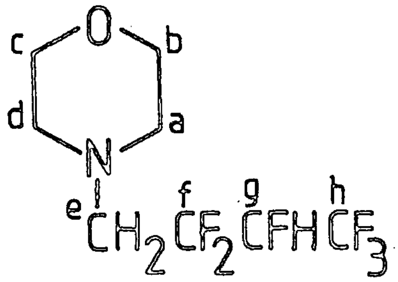
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
1.57	M(broad)	6	b, c, d
2.92	M(broad)	5	a, e, i
4.87	D of M(broad), J=44	2	g , k
^{19}F			
69.8	M(broad)	3	h , l
111.3	M(broad)	2	f , j
206.3	M(broad)	1	g , k

M.Wt. 399 No. 47

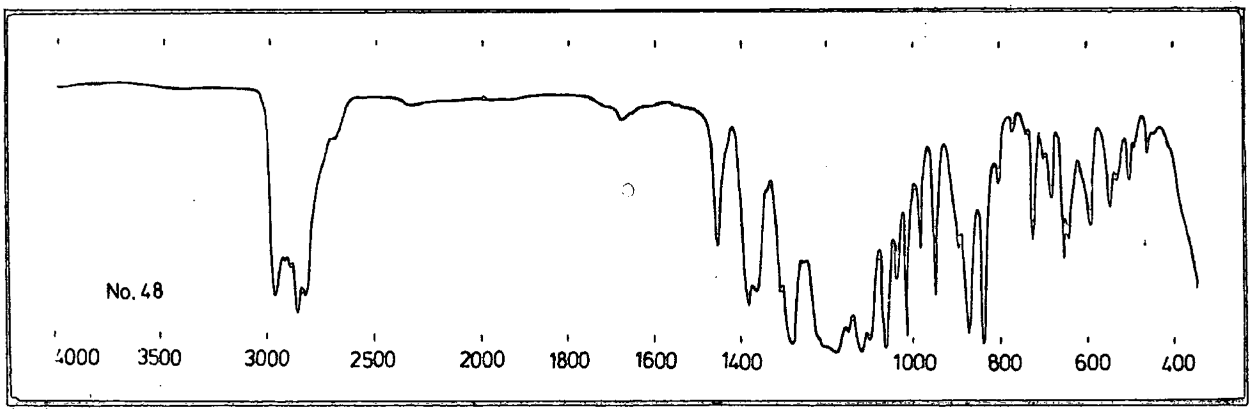


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.25	1.03	36	111.98	1.03
2	28.13	51.73	37	112.99	0.68
3	29.02	3.71	38	146.01	0.78
4	29.86	0.83	39	173.98	0.73
5	30.93	4.69	40	191.93	3.47
6	32.02	10.65	41	193.98	1.81
7	39.01	0.64	42	205.97	0.54
8	39.85	0.88	43	219.87	4.59
9	40.99	7.18	44	220.95	0.73
10	42.08	7.57	45	246.06	1.22
11	43.12	6.06	46	247.93	100.00
12	44.18	1.95	47	248.75	12.55
13	45.18	1.17	48	249.26	6.50
14	50.95	1.12	49	249.93	0.83
15	54.14	0.93	50	250.36	0.59
16	55.16	22.03	51	359.91	1.12
17	56.16	3.03	52	379.85	4.35
18	57.14	2.59	53	397.93	2.15
19	58.09	2.10			
20	59.02	1.51			
21	67.12	2.98			
22	68.05	1.91			
23	68.99	3.52			
24	69.95	1.81			
25	71.02	0.64			
26	73.07	1.07			
27	74.11	0.93			
28	77.01	1.47			
29	81.99	1.91			
30	83.03	4.15			
31	84.05	1.42			
32	95.01	1.32			
33	96.06	4.35			
34	97.05	6.11			
35	98.04	3.37			

No. 48

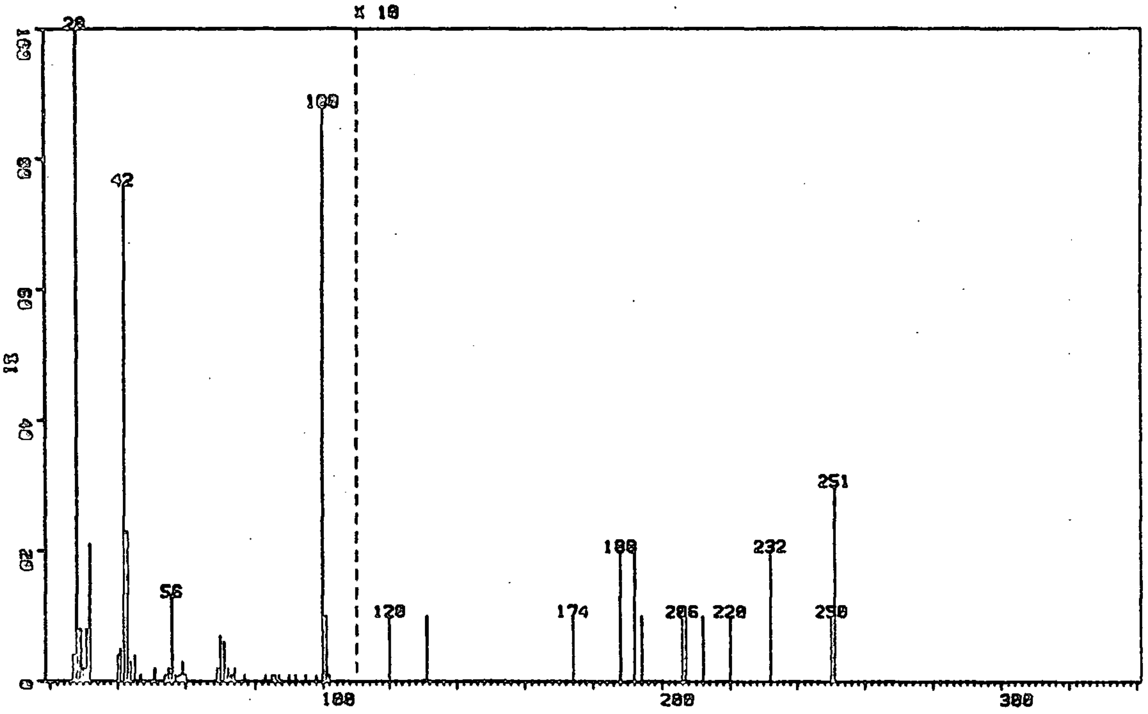


N-(2,2,3,4,4,4-Hexafluorobutyl)morpholine (78).

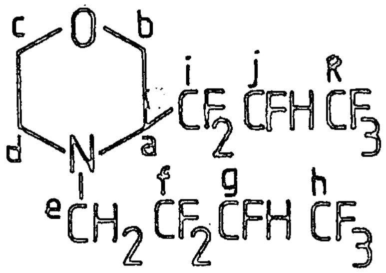


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
2.56	M	6	a, d, e
3.64	M	4	b, c
5.16	D of M, $J_{HF}=44$	1	g
^{19}F			
73.6	M (D of Q)	3	h
114.4	M	2	f
212.8	D of M, $J_{FH}=44$	1	g

M.Wt. 251 No. 48

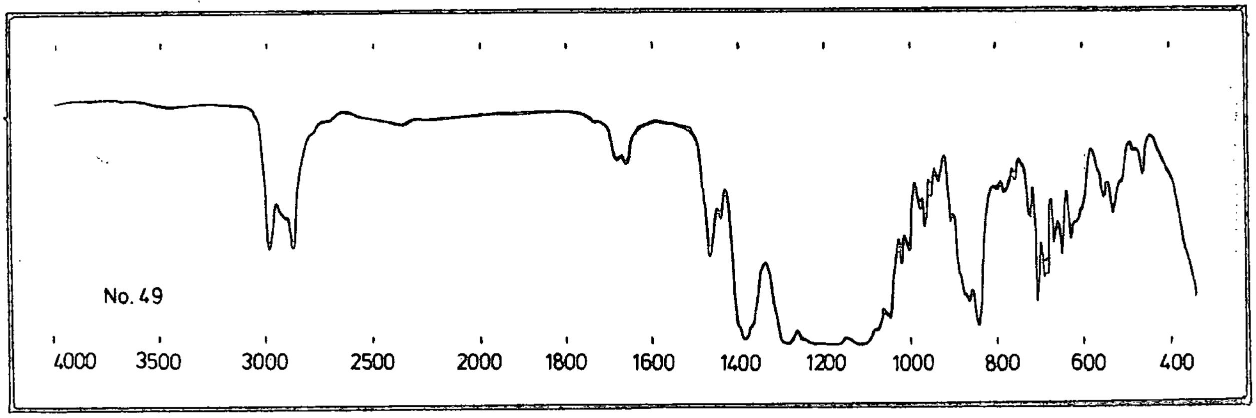


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.00	4.00*	36	98.00	1.00*
2	28.00	100.00*	37	100.00	88.00*
3	29.00	8.00*	38	101.00	10.00*
4	30.00	2.00*	39	102.00	1.00*
5	31.00	8.00*	40	120.00	1.00*
6	32.00	21.00*	41	131.00	1.00*
7	40.00	4.00*	42	174.00	1.00*
8	41.00	5.00*	43	188.00	2.00*
9	42.00	76.00*	44	192.00	2.00*
10	43.00	23.00*	45	194.00	1.00*
11	44.00	3.00*	46	206.00	1.00*
12	45.00	4.00*	47	207.00	1.00*
13	47.00	1.00*	48	212.00	1.00*
14	51.00	2.00*	49	220.00	1.00*
15	54.00	1.00*	50	232.00	2.00*
16	55.00	2.00*	51	250.00	1.00*
17	56.00	13.00*	52	251.00	3.00*
18	57.00	1.00*			
19	58.00	1.00*			
20	59.00	3.00*			
21	60.00	1.00*			
22	69.00	2.00*			
23	70.00	7.00*			
24	71.00	6.00*			
25	72.00	2.00*			
26	73.00	1.00*			
27	74.00	2.00*			
28	77.00	1.00*			
29	83.00	1.00*			
30	85.00	1.00*			
31	86.00	1.00*			
32	87.00	1.00*			
33	90.00	1.00*			
34	92.00	1.00*			
35	95.00	1.00			



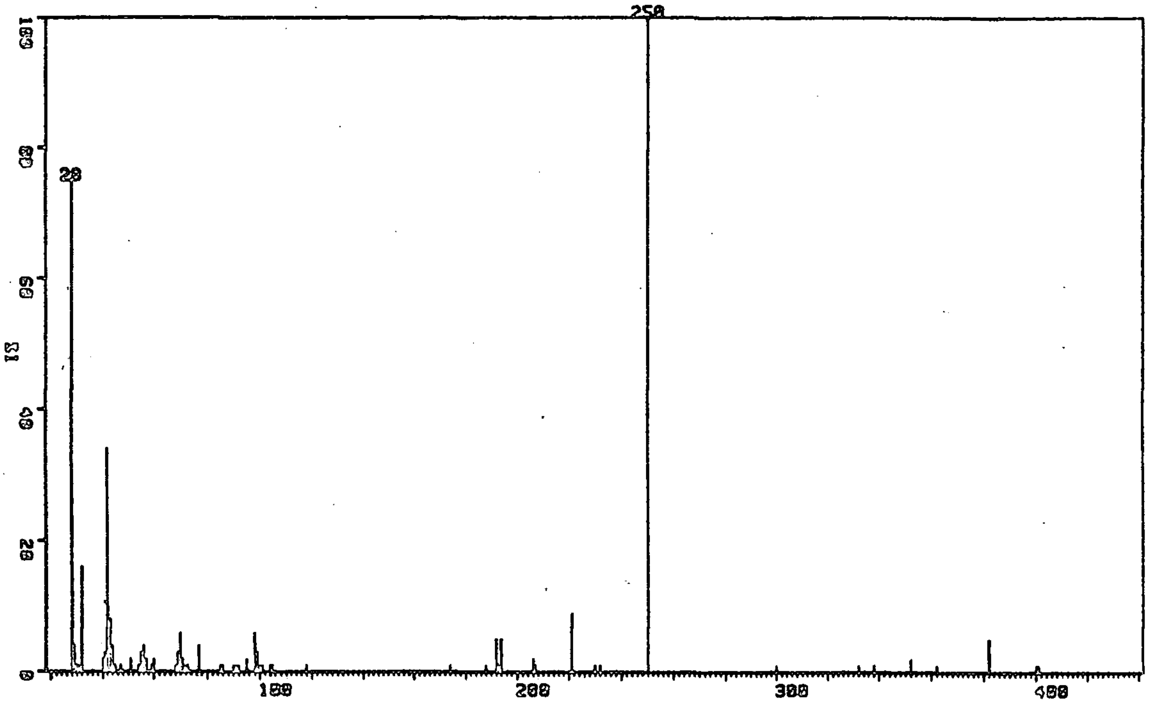
No. 49

N-(2,2,3,4,4,4-Hexafluorobutyl)-2-(1,1,2,3,3,3-hexafluoropropyl)-morpholine (79).



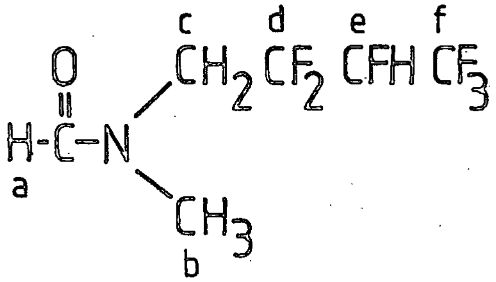
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
2.64	M	2	d
3.66	M	7	a, b, c, e
5.06	D of M, J_{HF}=44	2	g , j
^{19}F			
73.7	M	3	h , k
114.8	M(broad)	2	f , i
210.8	M(broad)	1	g , j

M.Wt. 401 No.49

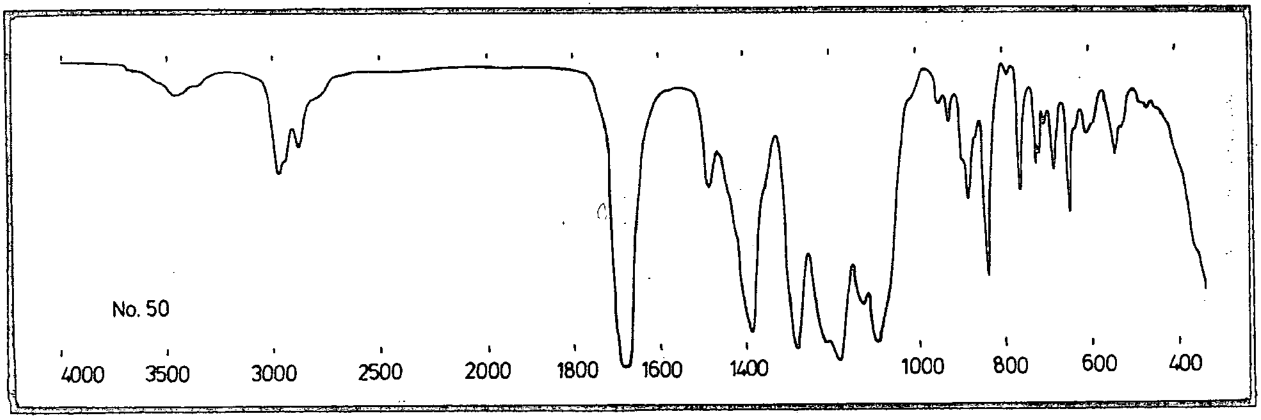


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.00	75.00*	36	101.00	1.00*
2	29.00	4.00*	37	104.00	1.00*
3	30.00	1.00*	38	105.00	1.00*
4	31.00	1.00*	39	118.00	1.00*
5	32.00	16.00*	40	174.00	1.00*
6	40.00	2.00*	41	188.00	1.00*
7	41.00	3.00*	42	192.00	5.00*
8	42.00	34.00*	43	193.00	1.00*
9	43.00	8.00*	44	194.00	5.00*
10	44.00	4.00*	45	206.00	2.00*
11	45.00	1.00*	46	207.00	1.00*
12	47.00	1.00*	47	221.00	9.00*
13	51.00	2.00*	48	230.00	1.00*
14	54.00	1.00*	49	232.00	1.00*
15	55.00	3.00*	50	250.00	100.00*
16	56.00	4.00*	51	300.00	1.00*
17	57.00	2.00*	52	332.00	1.00*
18	59.00	1.00*	53	338.00	1.00*
19	60.00	2.00*	54	352.00	2.00*
20	68.00	1.00*	55	362.00	1.00*
21	69.00	3.00*	56	382.00	5.00*
22	70.00	6.00*	57	400.00	1.00*
23	71.00	2.00*	58	401.00	1.00*
24	72.00	1.00*			
25	73.00	1.00*			
26	77.00	4.00*			
27	85.00	1.00*			
28	86.00	1.00*			
29	90.00	1.00*			
30	91.00	1.00*			
31	92.00	1.00*			
32	95.00	2.00*			
33	98.00	6.00*			
34	99.00	3.00*			
35	100.00	1.00			

No. 50

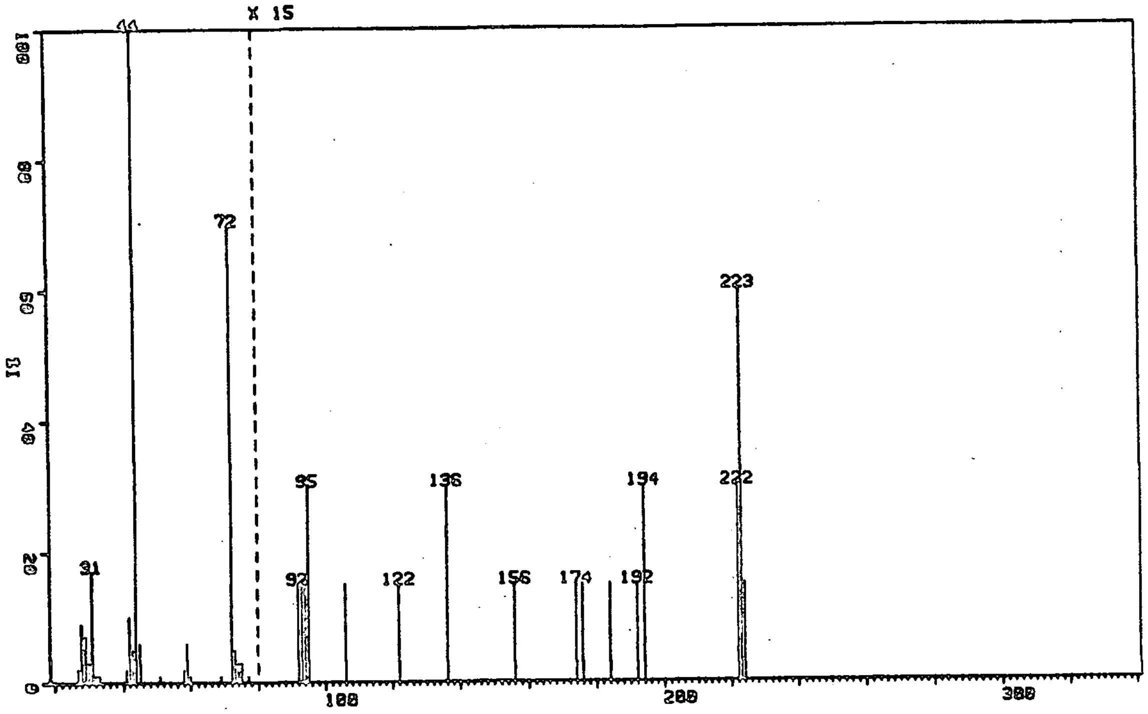


N-(2,2,3,4,4,4-Hexafluorobutyl)-N-methylformamide (81).



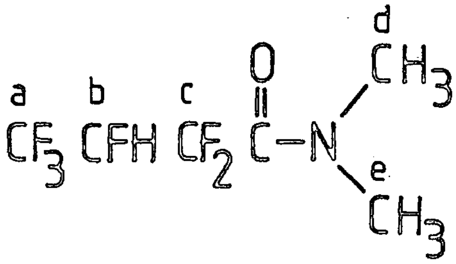
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
2.70	S	3	b
2.83	S		
3.72	M	2	c
5.13	D of M, J_{HF}=43, J=6	1	e
7.90	M	1	a
^{19}F			
76.5	M	3	f
114.6, 119.2	AB, J=267	2	d
114.7, 116.7	AB, J=256		
213.7	D of M, J=42 and 9	1	e
214.5	D of M, J=42 and 9		

M.Wt. 223 No.50

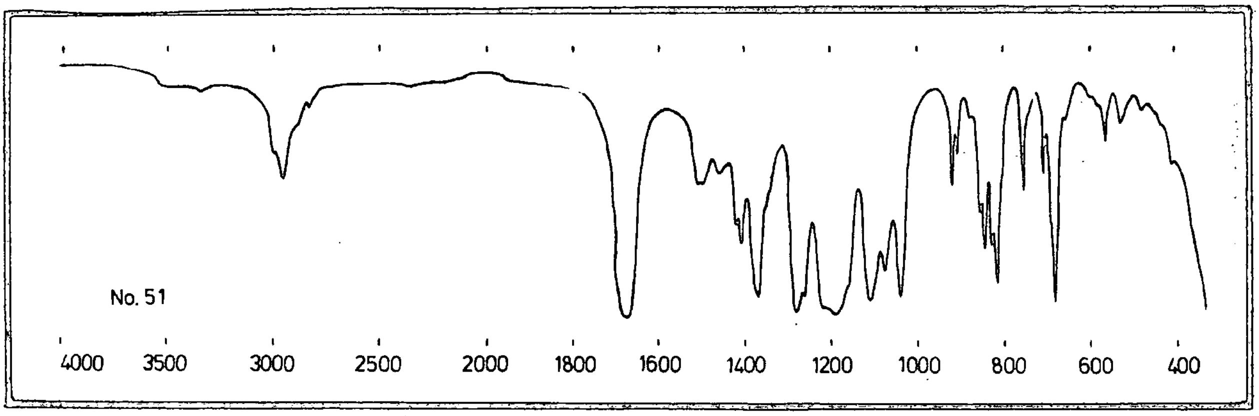


PEAK NO.	MASS	%HT. BASE
1	27.25	2.43
2	28.13	8.67
3	29.01	6.64
4	29.85	3.36
5	30.92	17.44
6	32.02	1.06
7	33.12	0.66
8	40.97	1.66
9	42.06	10.07
10	43.12	5.02
11	44.17	100.00
12	45.17	5.95
13	50.93	1.00
14	58.05	1.76
15	59.02	6.18
16	59.93	1.10
17	68.96	1.46
18	72.02	69.50
19	73.05	4.82
20	74.09	3.16
21	75.07	2.66
22	77.01	1.10
23	92.00	1.13
24	93.04	1.30
25	94.08	0.53
26	95.02	1.69
27	106.04	1.00
28	122.02	1.16
29	136.03	1.53
30	156.00	1.36
31	173.97	1.43
32	175.99	1.40
33	183.99	1.03
34	191.92	1.46
35	193.97	1.96
36	221.92	2.23
37	222.91	4.35
38	223.96	0.66

No. 51

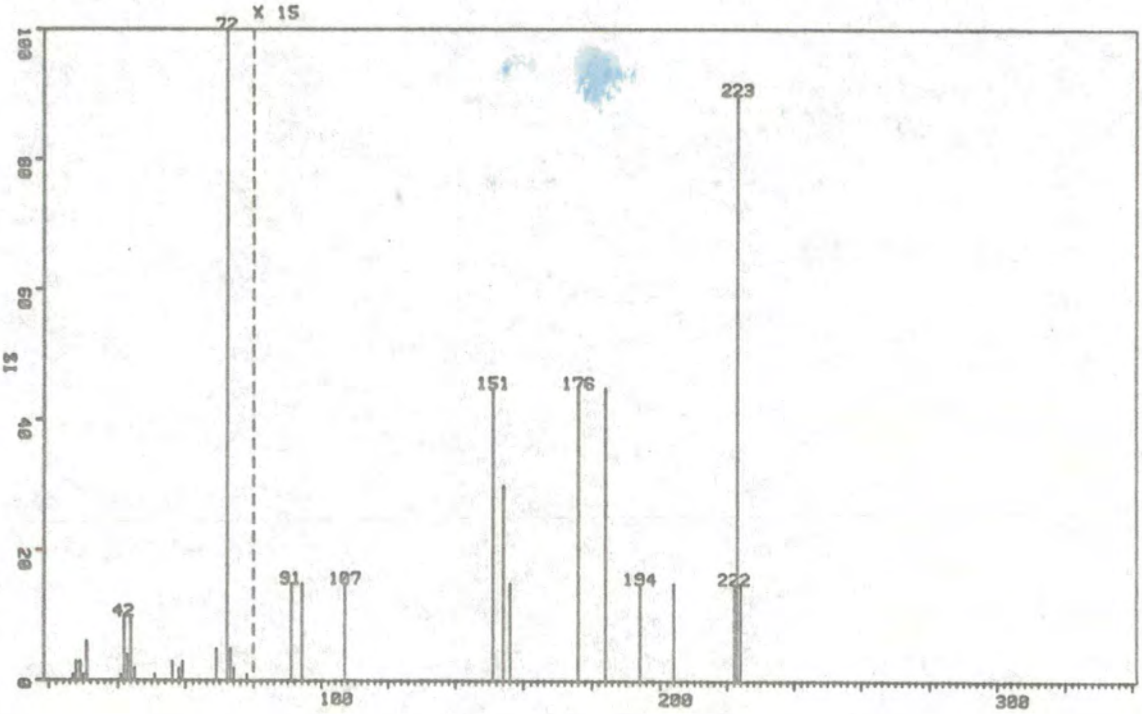


N,N-Dimethyl-2,2,3,4,4,4-hexafluorobutanamide (82).



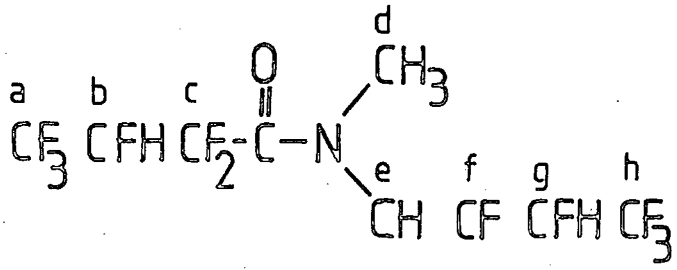
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
2.97	S	6	d, e
3.14	M		
5.40	D of M, J_{HF}=44	1	b
^{19}F			
73.0	M	3	a
112.7, 114.7	AB, J=113	2	c
212.5	D of M, J=42 and 10	1	b

M.Wt. 223 No. 51

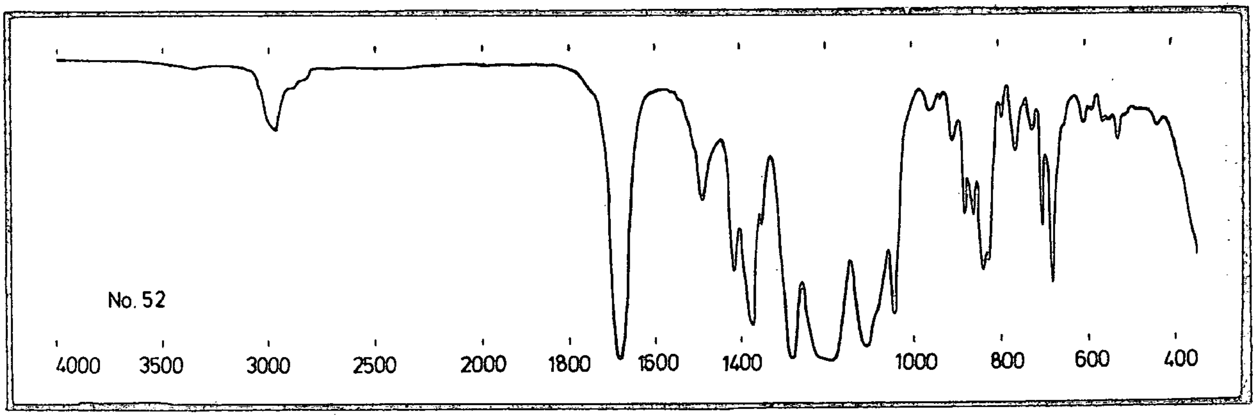


PEAK NO.	MASS	%HT. BASE
1	27.00	1.00*
2	28.00	3.00*
3	29.00	3.00*
4	30.00	1.00*
5	31.00	6.00*
6	41.00	1.00*
7	42.00	10.00*
8	43.00	4.00*
9	44.00	10.00*
10	45.00	2.00*
11	51.00	1.00*
12	56.00	3.00*
13	58.00	2.00*
14	59.00	3.00*
15	69.00	5.00*
16	72.00	100.00*
17	73.00	5.00*
18	74.00	2.00*
19	78.00	1.00*
20	91.00	1.00*
21	94.00	1.00*
22	107.00	1.00*
23	151.00	3.00*
24	154.00	2.00*
25	156.00	1.00*
26	176.00	3.00*
27	184.00	3.00*
28	194.00	1.00*
29	204.00	1.00*
30	222.00	1.00*
31	223.00	6.00*
32	224.00	1.00*

No. 52

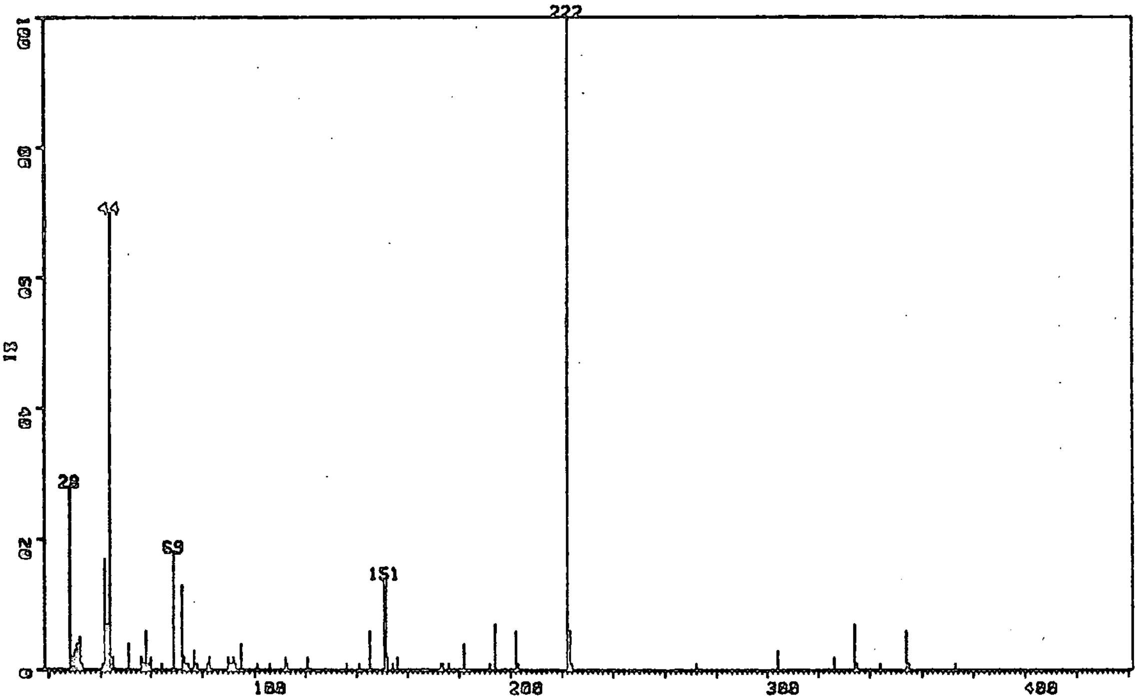


N-(2,2,3,4,4,4-Hexafluorobutyl)-N-methyl-2,2,3,4,4,4-hexafluorobutanamide (83).

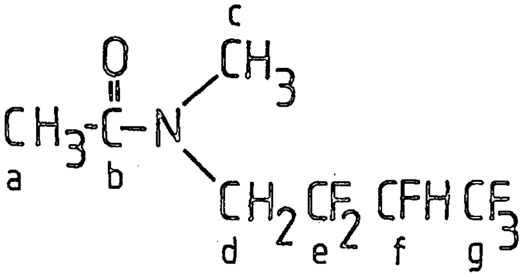


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
3.10	M	3	d
3.33	M		
4.00	M	2	e
5.40	D of M, J=42	2	b , g
^{19}F			
73.8	M	3	a , h
74.3	M		
1113, 112.5	AB, J=292	2	c , f
113.3, 115.3	AB, J=301		
210.3	D of Sx, J=45 and 11	1	b , g
212.5	D of M, J=45		

M.Wt. 373 No.52

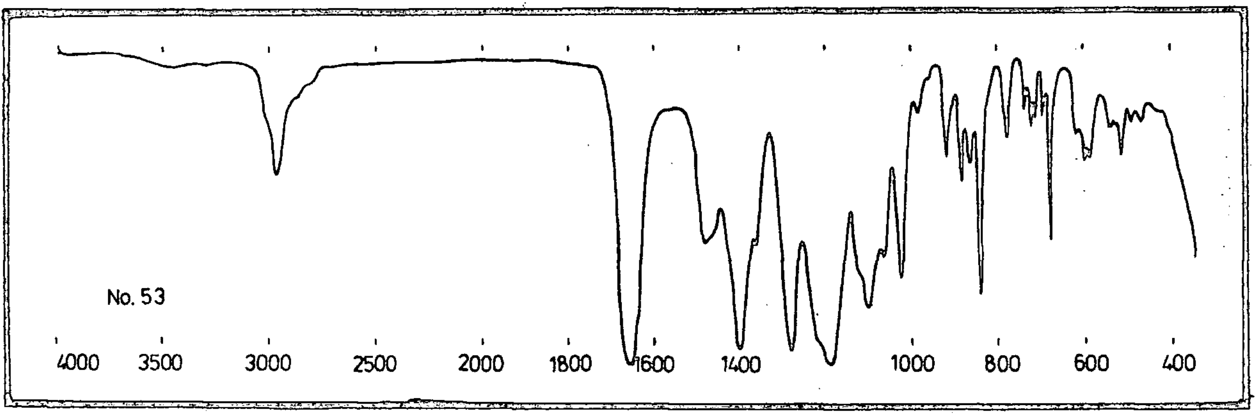


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE			
1	28.13	27.86	28	89.90	1.98	54	222.04	100.00
2	29.01	1.66	29	90.93	0.84	55	223.05	6.46
3	29.85	2.53	30	91.99	1.66	56	224.07	1.14
4	30.93	3.96	31	93.04	0.81	57	272.08	1.07
5	32.02	5.19	32	95.04	4.35	58	304.03	2.69
6	33.13	1.27	33	100.98	1.01	59	326.02	2.24
7	40.99	0.52	34	106.09	1.20	60	333.99	6.88
8	42.07	17.18	35	112.07	1.53	61	335.11	0.71
9	43.14	6.53	36	113.04	1.07	62	344.00	0.58
10	44.18	69.71	37	120.99	1.53	63	353.98	6.27
11	45.19	2.08	38	136.05	1.20	64	355.03	0.55
12	50.94	3.73	39	140.99	0.62	65	372.99	0.75
13	56.13	1.66	40	145.04	5.91			
14	57.11	0.91	41	150.95	14.16			
15	58.07	5.55	42	152.01	1.62			
16	59.04	1.30	43	154.05	0.75			
17	59.94	1.75	44	156.04	1.53			
18	64.11	0.91	45	173.05	0.84			
19	68.95	17.76	46	174.05	1.10			
20	72.02	12.69	47	176.07	1.14			
21	73.06	1.62	48	182.04	3.93			
22	74.06	0.84	49	183.07	0.49			
23	75.06	0.45	50	192.05	1.27			
24	77.01	3.18	51	194.08	6.62			
25	77.96	1.20	52	202.02	5.52			
26	81.93	0.58	53	203.08	0.55			
27	82.98	1.59						



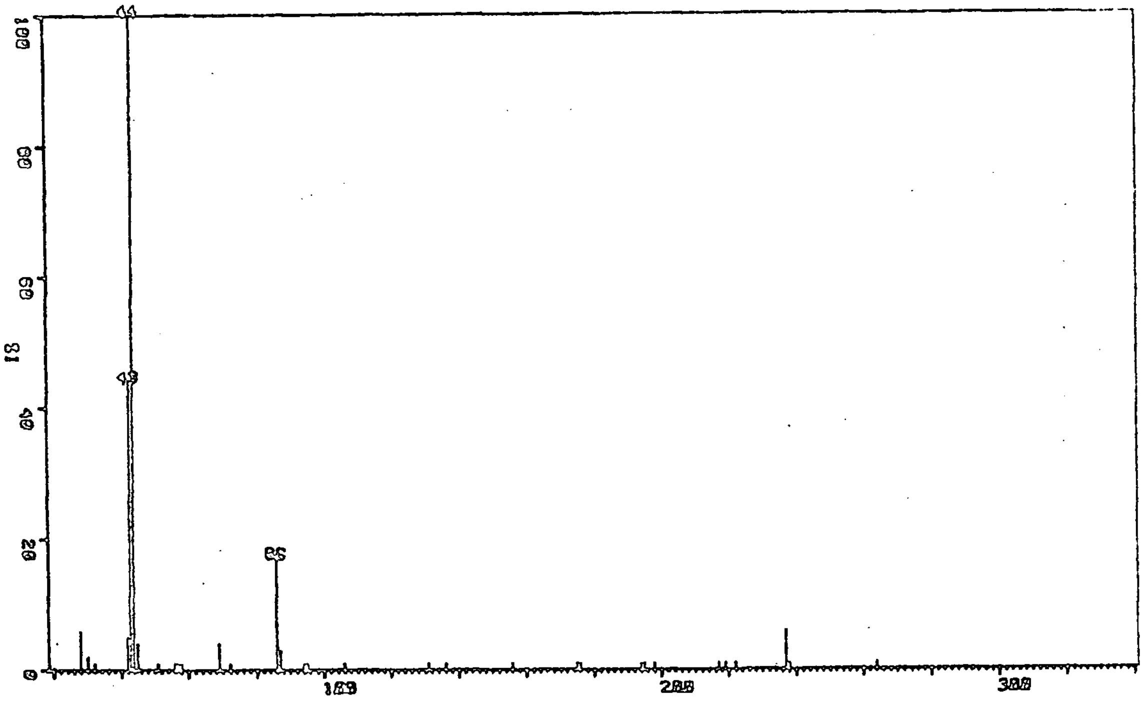
No. 53

N-(2,2,3,4,4,4-Hexafluorobutyl)-N-methylacetamide (84).



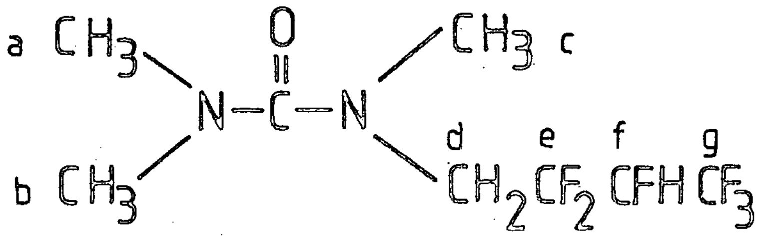
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
1.83	S	3	a
2.73	S	3	c
2.90	S		
3.73	T, J=15	2	d
3.83	T, J=15		
5.10	D of M, J=43	1	f
^{19}F			
76.2	M	3	g
116.3	M	2	e
173.0	D of M, J=43	1	f
^{13}C - broad band proton decoupled.			
20.9	S	-	a
37.5	S	-	c
49.1	T, J=25	-	d
84.7	D of Q, J=194 and 31	-	f
117.3	T of D, J=250 and 23	-	e
120.6	Q of D, J=280 and 24	-	g
171.9	S	-	b

M.Wt. 237 No. 53

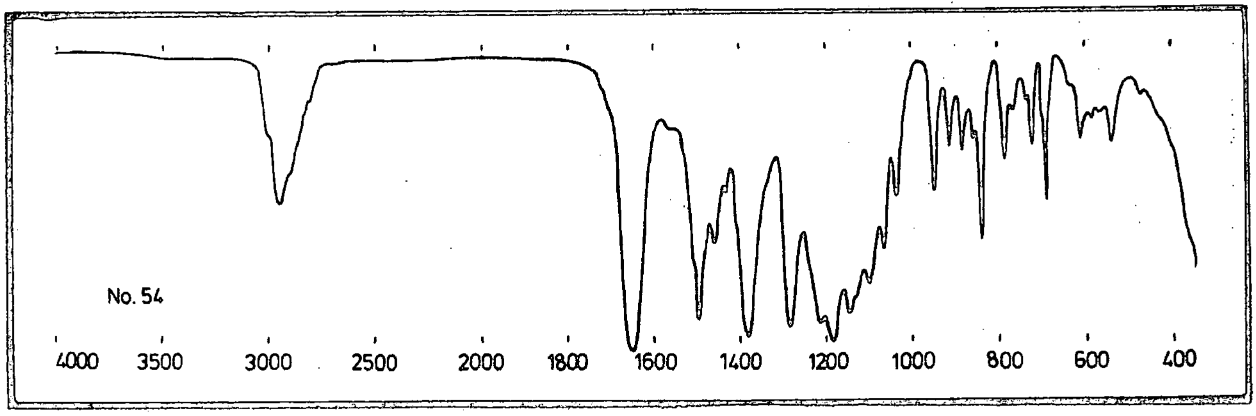


PEAK NO.	MASS	%HT. BASE
1	28.13	5.80
2	29.86	1.70
3	32.02	1.21
4	42.07	4.56
5	43.11	44.48
6	44.18	100.00
7	45.19	3.87
8	50.94	0.49
9	56.15	0.36
10	57.14	0.79
11	58.07	0.85
12	68.97	3.57
13	72.05	0.95
14	86.07	17.54
15	87.06	2.52
16	94.08	1.05
17	95.05	0.59
18	106.06	1.02
19	130.96	0.95
20	136.05	0.88
21	156.03	0.75
22	175.03	0.75
23	176.02	1.41
24	194.01	1.34
25	195.01	1.34
26	197.98	1.15
27	216.98	1.21
28	218.88	1.21
29	221.99	1.08
30	237.00	5.87
31	238.02	0.62
32	263·98	0·49

No. 54

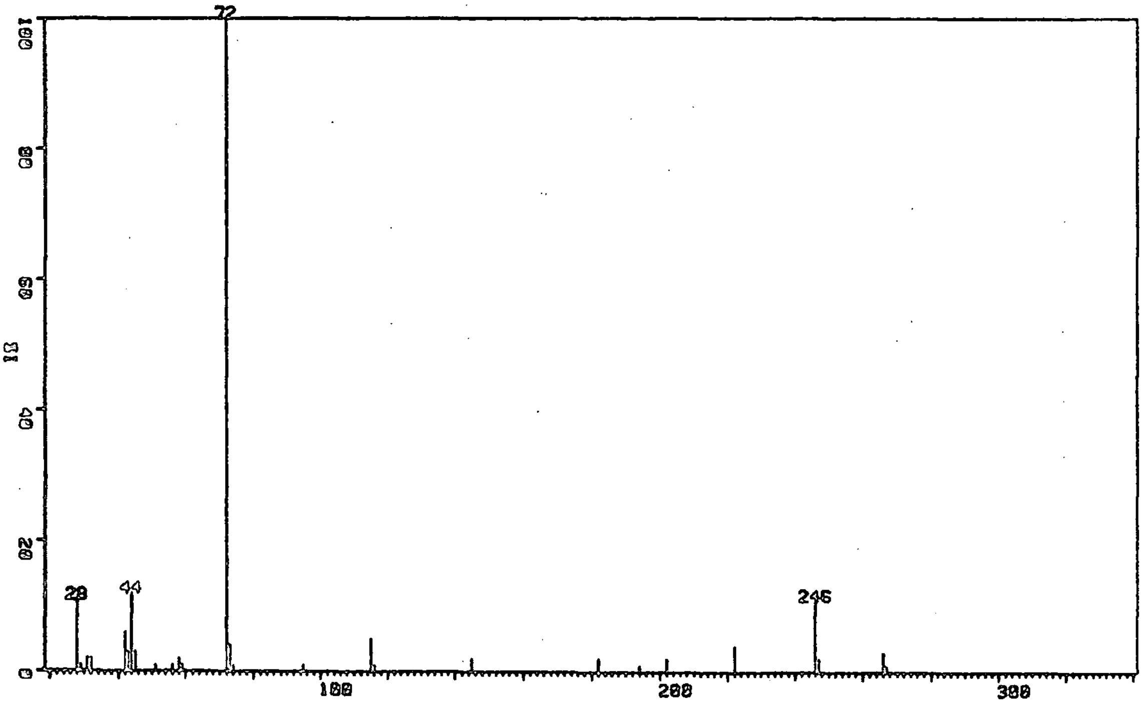


N-(2,2,3,4,4,4-Hexafluorobutyl)-N,N',N'-trimethylurea (85).



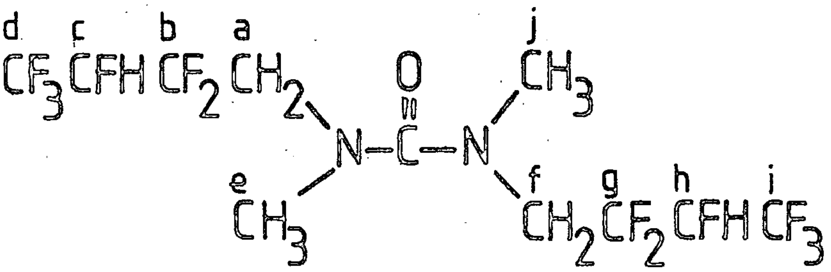
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
2.77	S	6	a , b
2.95	S	3	c
3.78	M	2	d
5.10	D of M, J=43 and 6	1	f
^{19}F			
74.8	M	3	g
114.0, 115.3	AB, J=263	2	e
212.3	D of M, J=42 and 9	1	f

M.Wt. 266 No.54

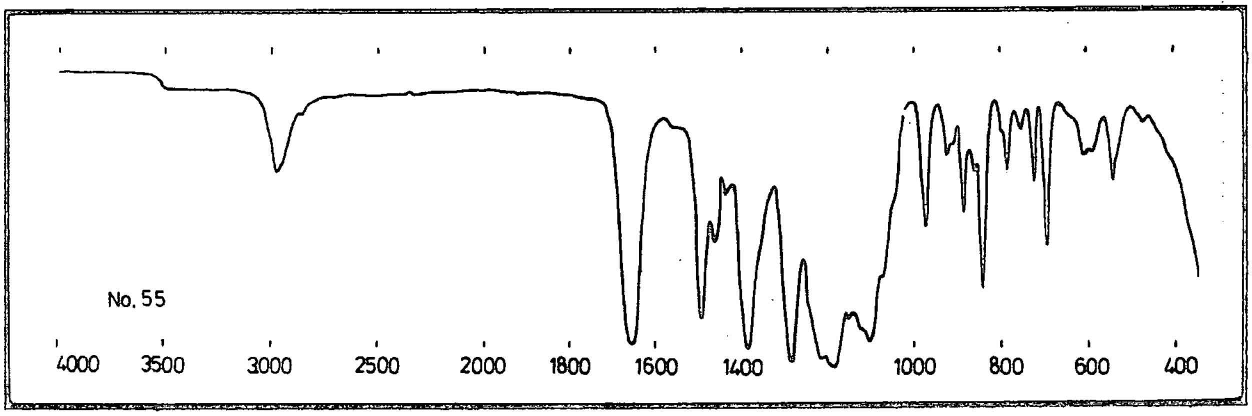


PEAK NO.	MASS	%HT. BASE
1	27.26	0.54
2	28.13	10.71
3	29.02	1.01
4	29.86	0.29
5	30.94	2.41
6	32.02	2.07
7	40.99	0.29
8	42.07	5.52
9	43.13	2.83
10	44.18	12.31
11	45.20	3.32
12	50.94	0.52
13	56.13	1.30
14	58.08	1.76
15	59.04	1.11
16	59.94	0.41
17	72.06	100.00
18	73.09	3.89
19	74.12	0.80
20	77.00	0.44
21	82.98	0.34
22	95.04	0.88
23	113.04	0.36
24	115.10	5.47
25	116.09	1.17
26	144.99	1.92
27	181.98	1.89
28	194.04	1.06
29	201.99	2.26
30	221.97	4.46
31	246.04	10.96
32	247.06	1.79
33	266.06	3.40
34	267.08	0.52

No.55

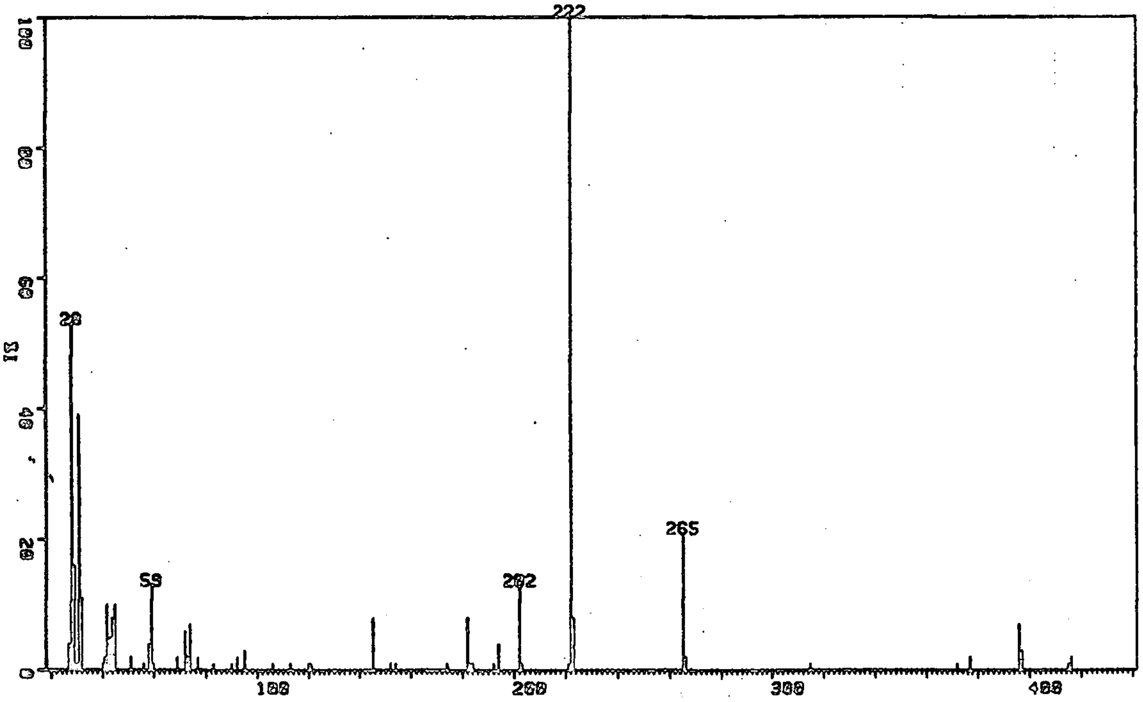


N,N'-Di(2,2,3,4,4,4-hexafluorobutyl)-N,N'-dimethylurea (87).

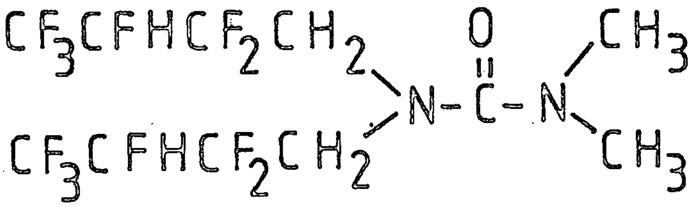


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
2.80	S	3	e , j
3.68	T, J=16	2	a , f
4.73	D of M, J_{HF}=44, J=6	1	c , h
^{19}F			
75.0	M	3	d , i
113.0, 115.8	AB, J_{FF}=275	2	b , f
212.2	D of M, J_{FH}=42, J=9	1	c , h

M.Wt. 416 No. 55



PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE			
1	27.25	4.39	28	95.01	2.72	54	377.02	2.42
2	28.13	53.41	29	106.00	0.45	55	395.98	6.93
3	29.02	16.08	30	113.01	0.78	56	396.88	2.57
4	29.87	0.63	31	119.94	0.87	57	415.00	0.57
5	30.93	38.55	32	120.98	0.87	58	415.95	2.00
6	32.02	11.45	33	140.93	0.45			
7	39.85	0.90	34	144.97	7.50			
8	40.99	2.18	35	151.99	0.72			
9	42.08	9.77	36	154.00	1.17			
10	43.14	4.78	37	174.04	0.90			
11	44.19	7.65	38	182.01	8.25			
12	45.18	10.13	39	183.00	1.17			
13	50.95	1.61	40	183.62	0.54			
14	56.13	0.78	41	185.16	0.33			
15	58.08	3.50	42	192.03	0.60			
16	59.03	12.52	43	194.02	3.77			
17	59.94	1.23	44	201.96	13.30			
18	68.98	1.61	45	202.99	1.05			
19	72.06	6.16	46	220.81	0.57			
20	73.11	2.00	47	222.02	100.00			
21	74.11	6.60	48	222.89	7.98			
22	75.09	0.45	49	223.40	5.77			
23	77.01	1.85	50	265.11	21.25			
24	83.00	0.75	51	266.10	1.64			
25	89.90	1.43	52	315.13	1.23			
26	91.98	1.58	53	371.92	1.40			
27	93.02	0.48						



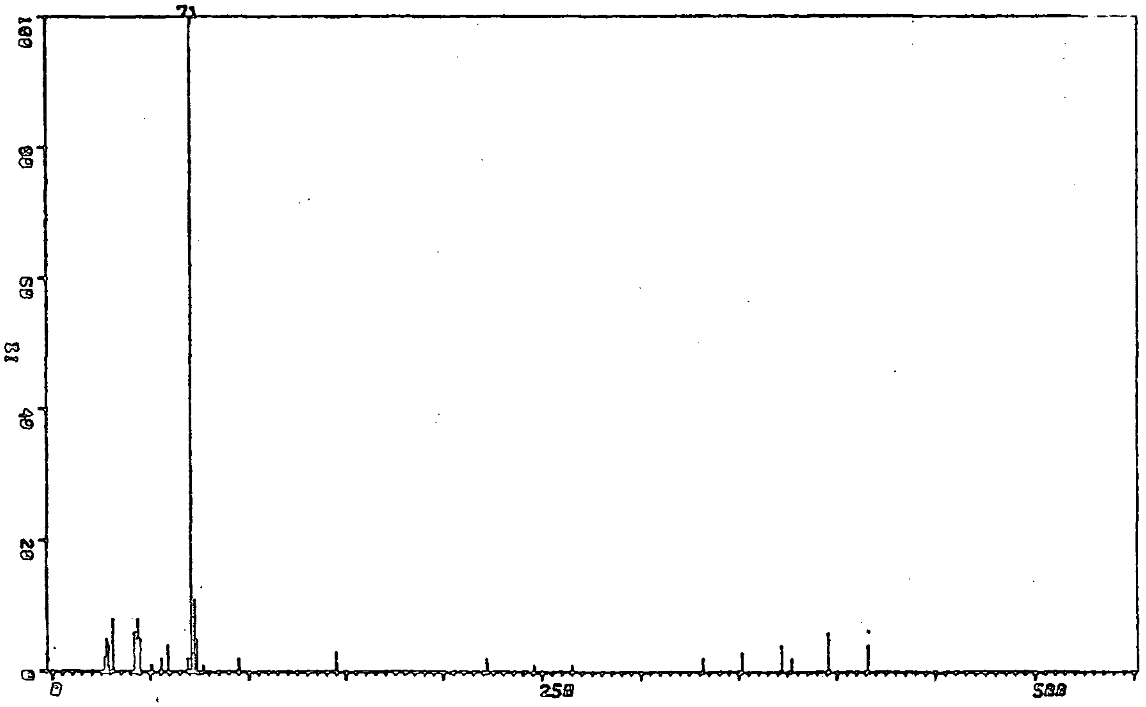
No.56

N,N-Di(2,2,3,4,4,4-hexafluorobutyl)-N', N'-dimethylurea (86).

No Spectrum.

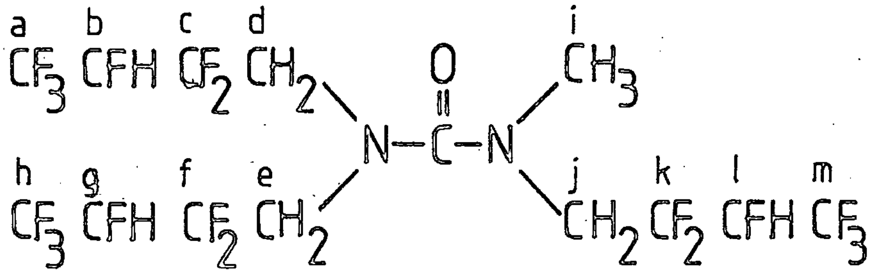
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
	No Spectrum.		

M.Wt. 416 No. 56

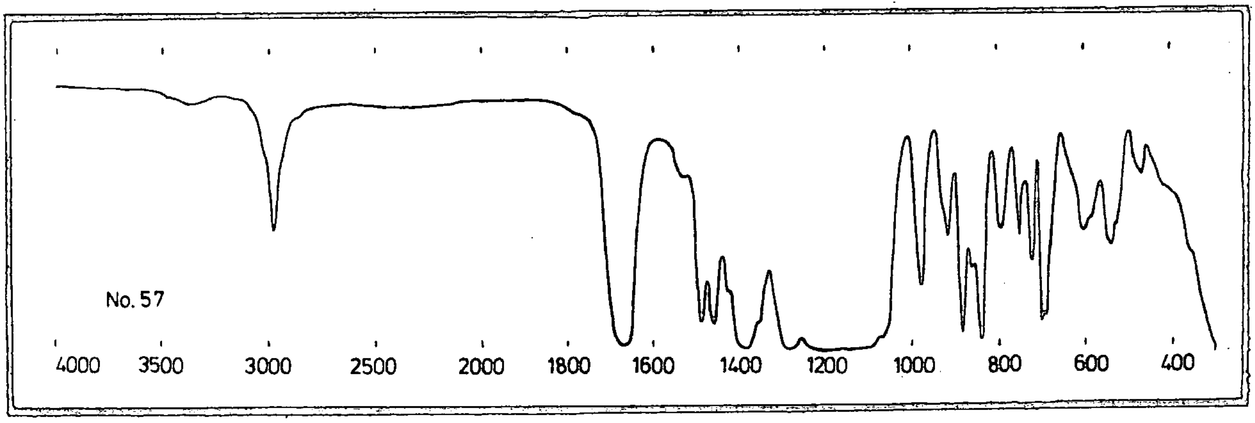


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	25.28	0.29	36	72.81	11.11	71	251.66	0.27
2	27.15	1.68	37	74.23	5.40	72	263.20	0.44
3	28.04	4.57	38	76.17	0.27	73	264.25	0.24
4	28.94	4.22	39	77.10	1.27	74	265.27	1.32
5	30.84	8.47	40	83.04	0.81	75	266.21	0.63
6	31.95	0.71	41	89.96	0.27	76	267.25	0.24
7	40.88	0.27	42	95.09	2.10	77	270.17	0.49
8	40.98	0.61	43	101.07	0.29	78	311.90	0.78
9	41.83	0.39	44	113.20	0.56	79	315.15	0.68
10	42.06	5.54	45	115.19	0.68	80	329.46	0.27
11	42.33	0.27	46	118.96	0.39	81	330.52	0.24
12	42.40	0.27	47	120.02	0.22	82	332.16	1.81
13	42.45	0.29	48	125.12	0.24	83	335.08	0.46
14	42.50	0.27	49	141.06	0.27	84	344.11	0.44
15	43.12	4.47	50	145.05	2.98	85	346.24	0.24
16	44.17	8.33	51	146.15	0.24	86	348.05	0.27
17	44.47	0.27	52	151.10	0.34	87	352.12	2.64
18	45.18	4.62	53	154.17	0.32	88	354.24	0.22
19	45.34	0.34	54	164.00	0.29	89	355.82	0.27
20	45.45	0.27	55	169.13	0.44	90	372.19	4.18
21	46.20	0.27	56	170.23	0.27	91	377.15	2.49
22	50.96	1.42	57	174.23	0.37	92	379.74	0.34
23	56.14	1.64	58	182.21	0.44	93	391.81	0.27
24	57.16	0.34	59	190.17	0.39	94	393.38	0.27
25	58.09	0.90	60	192.17	0.66	95	396.38	5.79
26	59.04	3.98	61	194.13	0.66	96	416.23	4.18
27	59.97	0.49	62	202.10	0.46			
28	63.22	0.29	63	220.18	0.29			
29	64.14	0.29	64	222.17	1.86			
30	67.90	0.27	65	223.27	0.27			
31	68.11	0.27	66	240.18	0.27			
32	68.55	0.29	67	245.37	0.42			
33	68.78	0.27	68	246.19	1.27			
34	69.04	2.12	69	247.28	0.27			
35	70.66	100.00	70	251.21	0.29			

No. 57

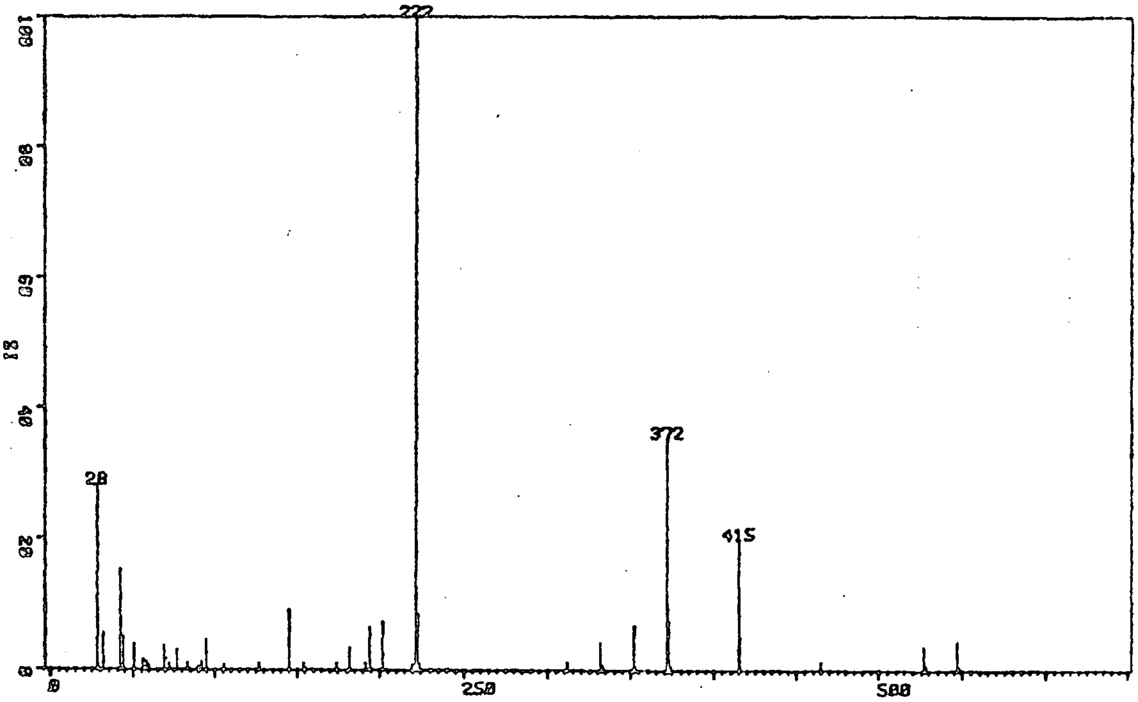


N,N,N'-Tri(2,2,3,4,4,4-hexafluorobutyl)-N'-methylurea (88).

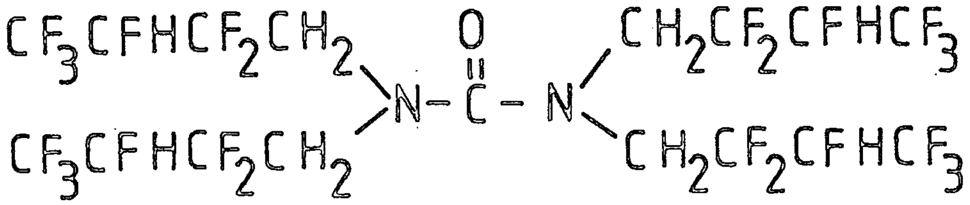


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
3.03	S	1	i
3.93	M	2	d, e, j
4.73	D of M, J=44	1	b, g, l

M.Wt. 566 No. 57



PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	28.28	36	372.89	7.46
2	32.02	5.58	37	374.16	0.61
3	42.08	15.29	38	415.15	20.03
4	43.15	4.69	39	415.86	5.02
5	44.19	4.97	40	465.15	1.31
6	50.97	3.89	41	527.06	3.71
7	56.15	1.59	42	528.14	0.75
8	58.11	1.31	43	546.76	4.36
9	59.96	0.66	44	548.15	0.52
10	69.01	3.66			
11	72.08	0.98			
12	77.09	3.05			
13	83.06	1.03			
14	89.97	0.61			
15	92.04	1.31			
16	95.11	4.60			
17	106.08	0.84			
18	127.08	1.08			
19	145.09	9.15			
20	154.13	1.03			
21	174.11	1.17			
22	182.01	3.56			
23	192.03	1.08			
24	194.08	6.47			
25	202.03	7.32			
26	220.06	0.94			
27	222.02	100.00			
28	222.96	8.40			
29	224.09	0.94			
30	312.12	1.27			
31	332.16	4.32			
32	333.12	0.70			
33	352.05	6.75			
34	353.11	0.61			
35	372.02	35.51			



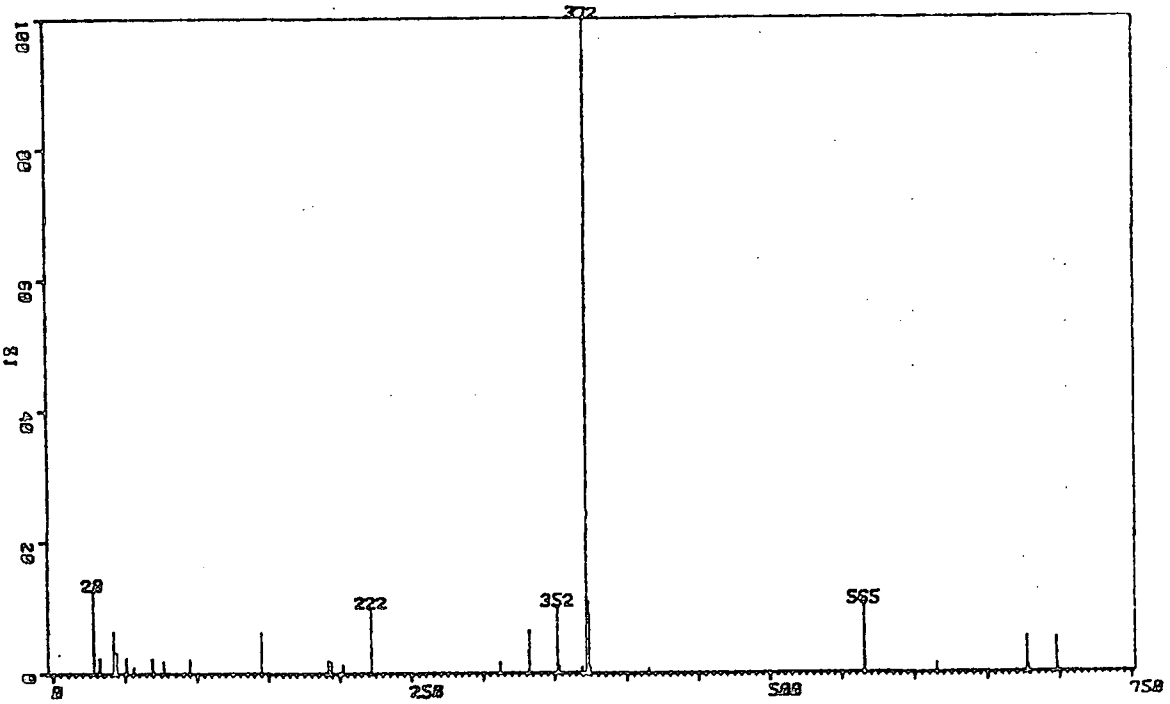
<u>No.58</u>

N,N,N',N'-Tetra(2,2,3,4,4,4-hexafluorobutyl)urea. (<u>89</u>).

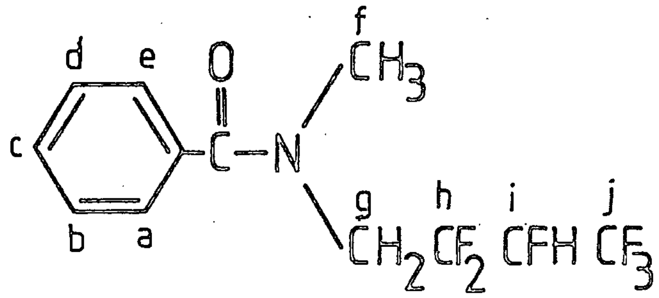
No Spectrum.

SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
	No Spectrum.		

M.Wt. 716 No. 58

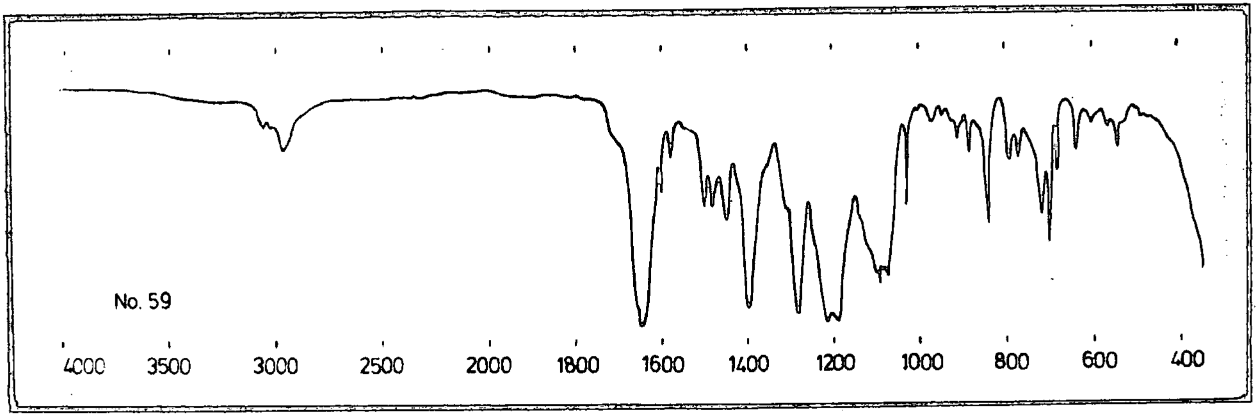


PEAK NO.	MASS	%HT. BASE
1	28.13	12.70
2	32.02	2.35
3	42.08	6.30
4	44.18	3.10
5	50.96	2.45
6	56.15	0.90
7	68.99	2.25
8	77.07	1.80
9	95.06	2.00
10	145.05	6.35
11	192.05	1.90
12	194.07	1.75
13	202.05	1.25
14	222.07	9.95
15	312.05	1.65
16	332.44	6.50
17	352.06	10.25
18	353.06	1.00
19	369.09	0.95
20	372.05	100.00
21	372.92	10.75
22	373.54	8.90
23	374.72	0.80
24	415.31	0.70
25	565.46	10.55
26	615.48	1.45
27	677.55	5.30
28	678.54	0.95
29	697.92	5.15



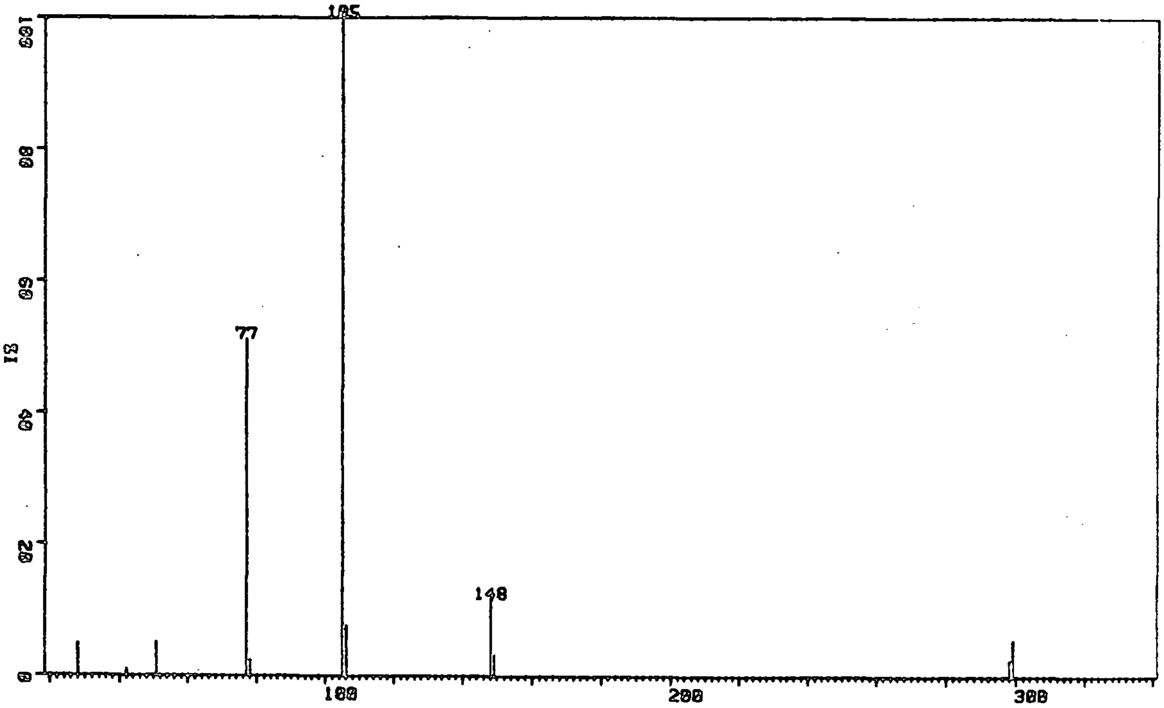
No.59

N-(2,2,3,4,4,4-Hexafluorobutyl)-N-methylbenzamide (90).



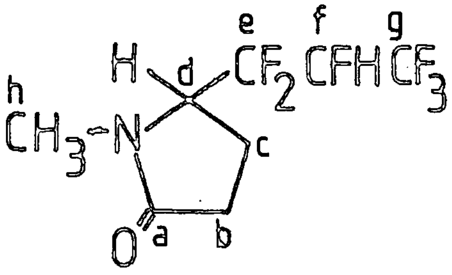
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
2.85	S	3	f
2.93	S		
3.93	T, J=15	2	g
4.97	D of M, J=43	1	i
7.20	S	5	a, b, c, d, e.
^{19}F			
74.7	M	3	j
113.5	M	2	h
211.3	D of M, J=38 and 8	1	i

M.Wt. 299 No. 59

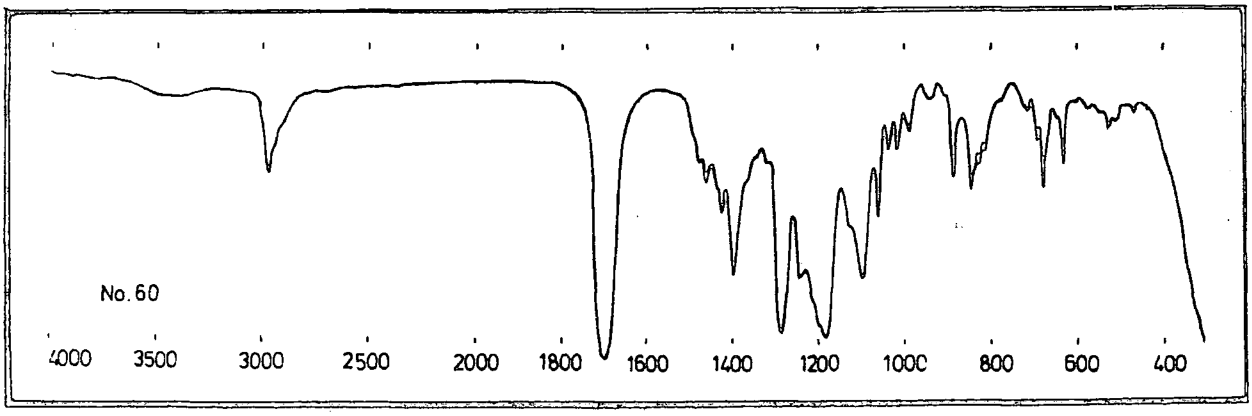


PEAK NO.	MASS	%HT. BASE
1	28.12	4.79
2	42.07	0.95
3	50.97	5.10
4	77.04	51.21
5	78.01	2.42
6	105.07	100.00
7	106.07	7.67
8	148.10	11.79
9	149.08	3.17
10	298.22	2.56
11	299.16	5.54

No. 60

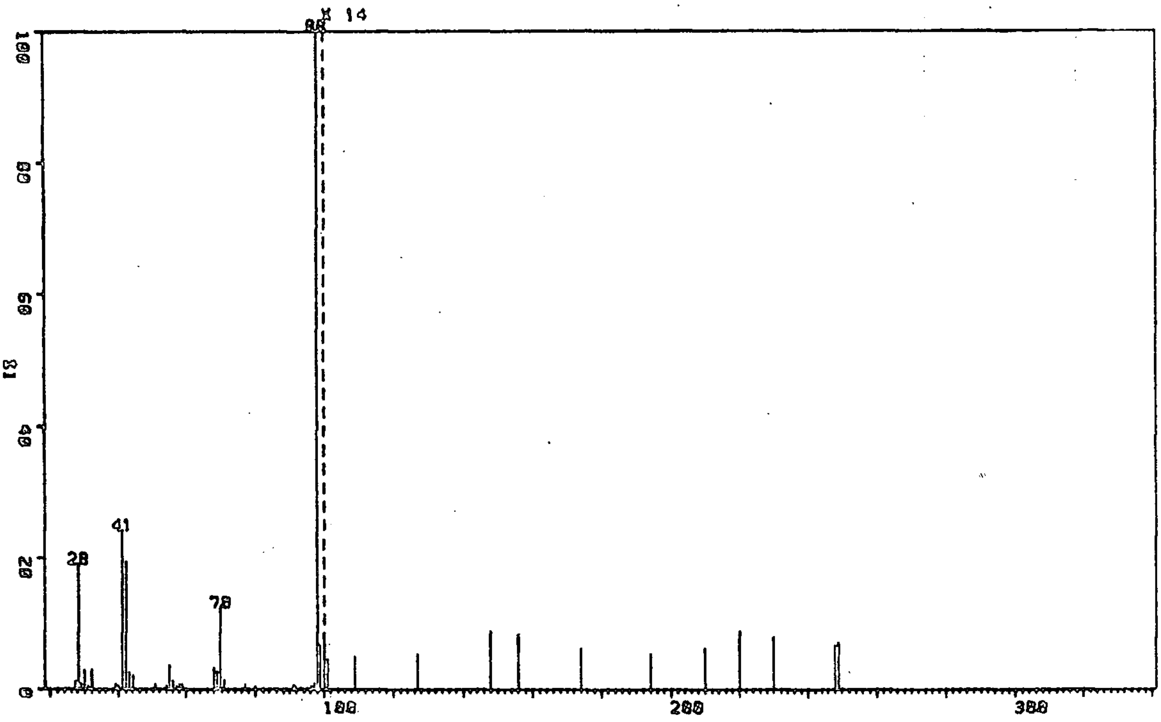


N-Methyl-5-(1,1,2,3,3,3-hexafluoropropyl)pyrrolidin-2-one (91).

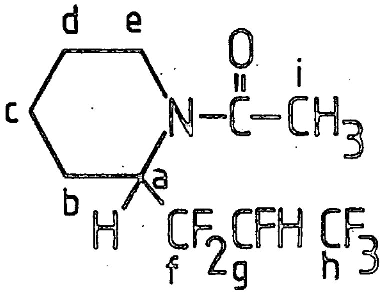


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
2.30	M	4	b, c
2.92	S	3	h
3.97	M(broad)	1	d
5.00	D of M, J_{HF}=44	1	f
^{19}F			
74.2	M	3	g
115.0, 117.7	AB, J_{FF}=282	2	e
117.1, 120.7	AB, J_{FF}=271		
211.2	D of M, J_{FH}=44	1	f
^{13}C - broad band proton decoupled.			
19.5	S	-	c
29.1	S	-	h
30.8	S	-	b
62.0	T, J_{CF}=25	-	d
85.3	D of M, J_{CF}=206 and26	-	f
118.7	T of D, J_{CF}=251 and 22	-	e
121.0	Q of D, J_{CF}=276 and 29	-	g

M.Wt. 249 No. 60

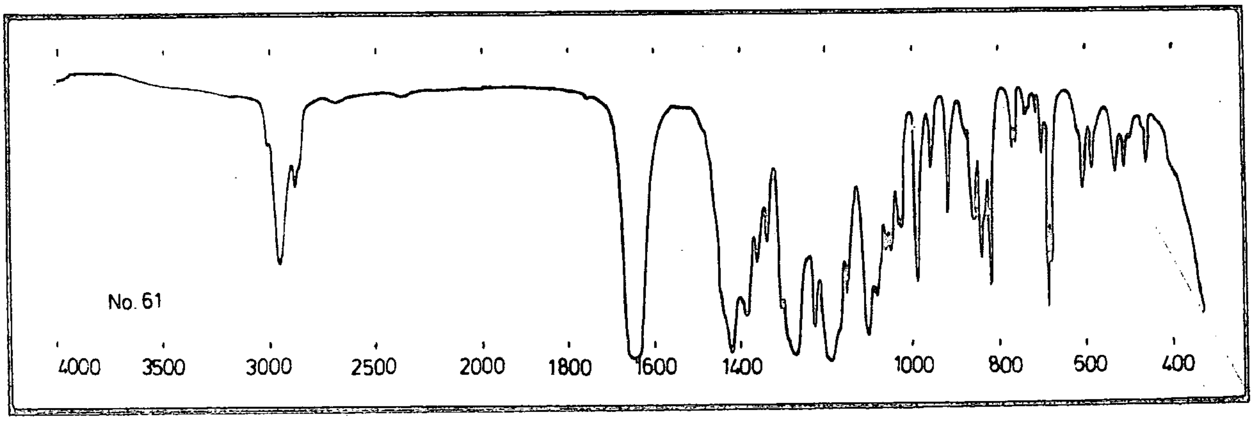


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.26	1.18	36	100.00	0.51
2	28.14	19.13	37	101.01	0.33
3	29.02	0.87	38	109.01	0.36
4	29.86	2.92	39	127.06	0.39
5	30.94	0.42	40	148.05	0.63
6	32.03	2.98	41	156.06	0.60
7	39.00	0.84	42	174.05	0.45
8	39.84	0.48	43	194.01	0.39
9	39.90	0.36	44	209.95	0.45
10	40.98	24.19	45	219.98	0.63
11	42.07	19.37	46	229.98	0.57
12	43.14	2.62	47	247.97	0.48
13	44.17	2.08	48	248.95	0.51
14	50.94	0.69			
15	54.13	0.45			
16	55.12	3.62			
17	56.13	1.24			
18	57.11	0.39			
19	58.06	0.72			
20	59.01	0.57			
21	68.06	3.28			
22	68.99	2.74			
23	69.96	12.44			
24	70.99	1.42			
25	77.01	0.69			
26	79.89	0.45			
27	88.95	0.27			
28	90.94	0.69			
29	91.98	0.36			
30	93.03	0.33			
31	95.03	0.33			
32	96.05	0.48			
33	97.04	0.93			
34	98.02	100.00			
35	98.79	6.72			



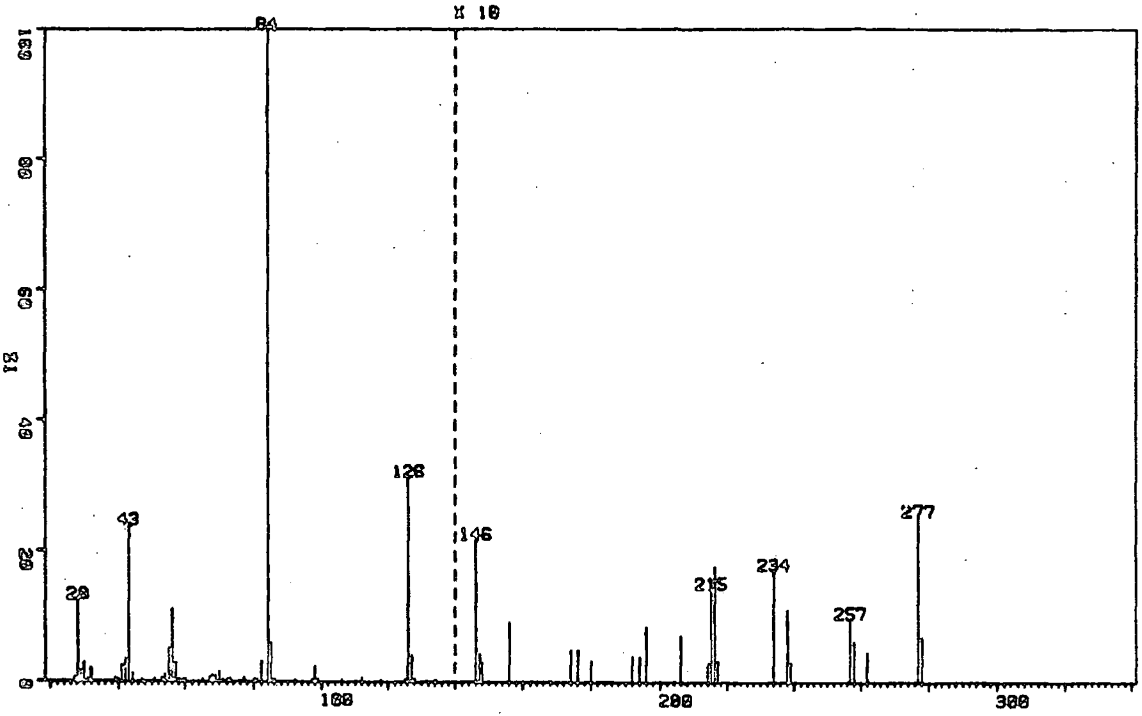
No.61

N-Acetyl-2-(1,1,2,3,3,3-hexafluoropropyl)piperidine (92).

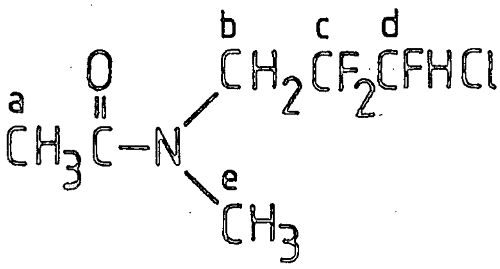


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
1.52	M(broad)	6	b, c, d
1.85	S	3	i
3.2	M(broad)	2	e
5.2	M(broad)	2	a , g
^{19}F			
74.8	M	3	h
110.6, 118.4	AB, J_{FF}=271	2	f
211.0	D of M, J_{FH}=38, J=8	1	g

M.Wt. 277 No. 61

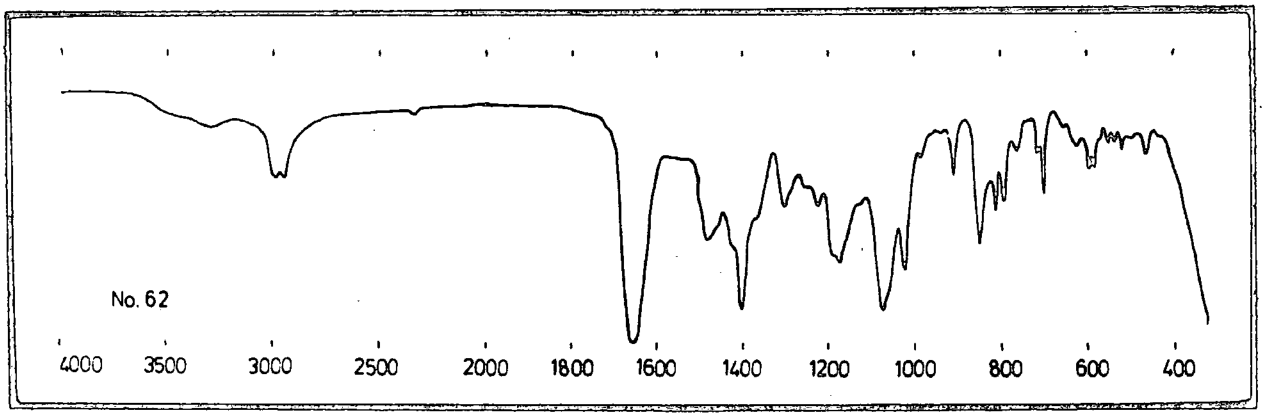


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.26	0.68	36	84.04	100.00	71	256.98	0.98
2	28.14	12.60	37	84.80	5.96	72	258.04	0.62
3	29.03	1.60	38	85.57	0.33	73	261.99	0.46
4	29.87	2.90	39	86.07	0.49	74	277.02	2.54
5	30.95	0.36	40	92.01	0.33	75	278.03	0.68
6	32.03	2.02	41	97.16	0.42			
7	39.01	0.55	42	98.10	2.41			
8	39.85	0.33	43	99.03	0.55			
9	41.00	2.51	44	106.11	0.33			
10	42.08	3.48	45	112.09	0.68			
11	43.12	23.93	46	118.09	0.33			
12	44.17	1.24	47	125.15	0.33			
13	47.13	0.33	48	125.50	0.36			
14	50.95	0.36	49	126.15	31.36			
15	53.11	0.52	50	127.07	4.01			
16	54.15	1.07	51	128.09	0.49			
17	55.18	5.08	52	134.13	0.33			
18	56.16	11.04	53	146.09	2.18			
19	56.42	0.36	54	147.11	0.42			
20	57.15	2.83	55	148.05	0.29			
21	58.10	0.36	56	156.06	0.91			
22	59.05	0.36	57	174.07	0.49			
23	59.96	0.55	58	176.05	0.49			
24	65.14	0.39	59	179.99	0.33			
25	67.12	0.85	60	192.00	0.39			
26	68.05	1.01	61	194.05	0.39			
27	68.99	0.94	62	196.06	0.85			
28	69.93	1.53	63	206.02	0.72			
29	70.98	0.36	64	214.02	0.29			
30	72.04	0.39	65	215.03	1.43			
31	73.06	0.49	66	216.00	1.76			
32	77.02	0.68	67	217.04	0.33			
33	79.91	0.49	68	234.03	1.73			
34	80.97	0.36	69	238.03	1.11			
35	82.01	3.16	70	239.05	0.29			



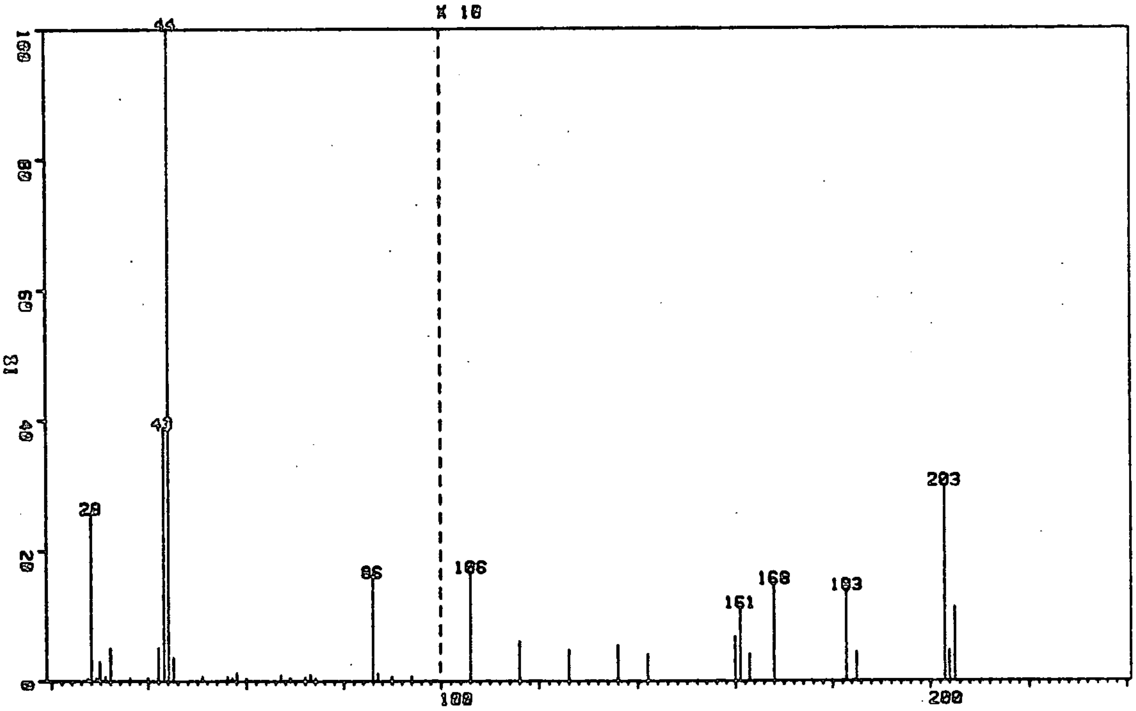
No. 62

N-Methyl-N-(3-chloro-2,2,3-trifluoropropyl)acetamide (93).



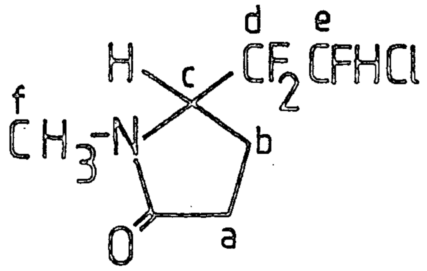
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
2.17	S	3	a
3.07	S	3	e
3.18	S		
4.05	T, J=15	2	b
6.30	D of M, J_{HF}=48	1	d
^{19}F			
112.7, 116.1	AB, J_{FF}=254	2	c
153.2	D of M, J_{FH}=47, J=11	1	d

M.Wt. 203·5 No. 62

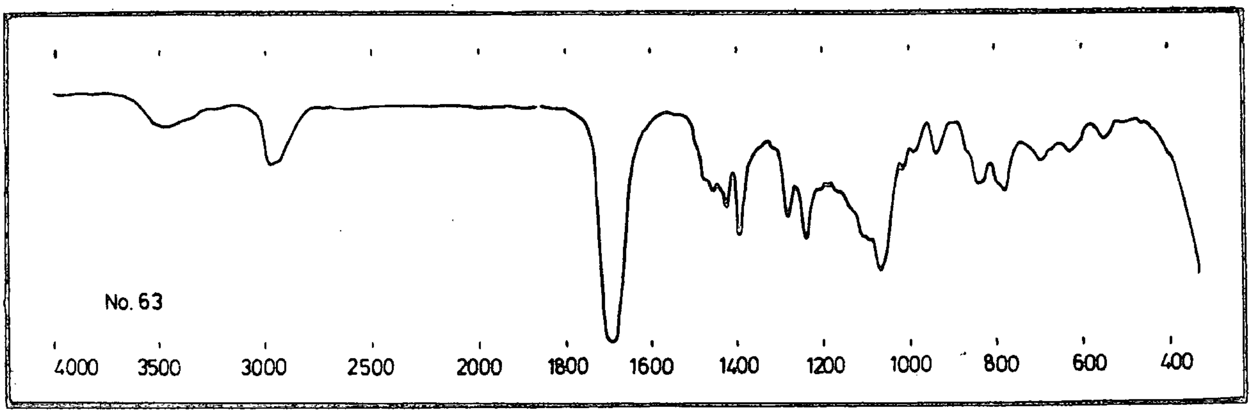


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.25	0.37	36	182.94	1.40
2	28.13	25.67	37	184.98	0.44
3	29.01	0.41	38	202.95	3.00
4	29.86	2.89	39	203.98	0.48
5	30.95	0.65	40	204.94	1.12
6	32.01	4.94			
7	36.16	0.48			
8	39.83	0.51			
9	42.07	5.04			
10	43.12	38.75			
11	44.18	100.00			
12	45.20	3.58			
13	50.95	0.78			
14	56.15	0.68			
15	57.14	0.48			
16	58.07	1.23			
17	59.94	0.44			
18	67.04	0.99			
19	68.95	0.44			
20	72.03	0.65			
21	73.07	1.06			
22	74.09	0.37			
23	86.04	15.87			
24	87.05	1.16			
25	89.90	0.65			
26	94.06	0.72			
27	106.05	1.67			
28	116.03	0.61			
29	126.03	0.48			
30	136.00	0.54			
31	141.94	0.41			
32	159.87	0.68			
33	160.94	1.12			
34	162.96	0.41			
35	167.99	1.50			

No. 63

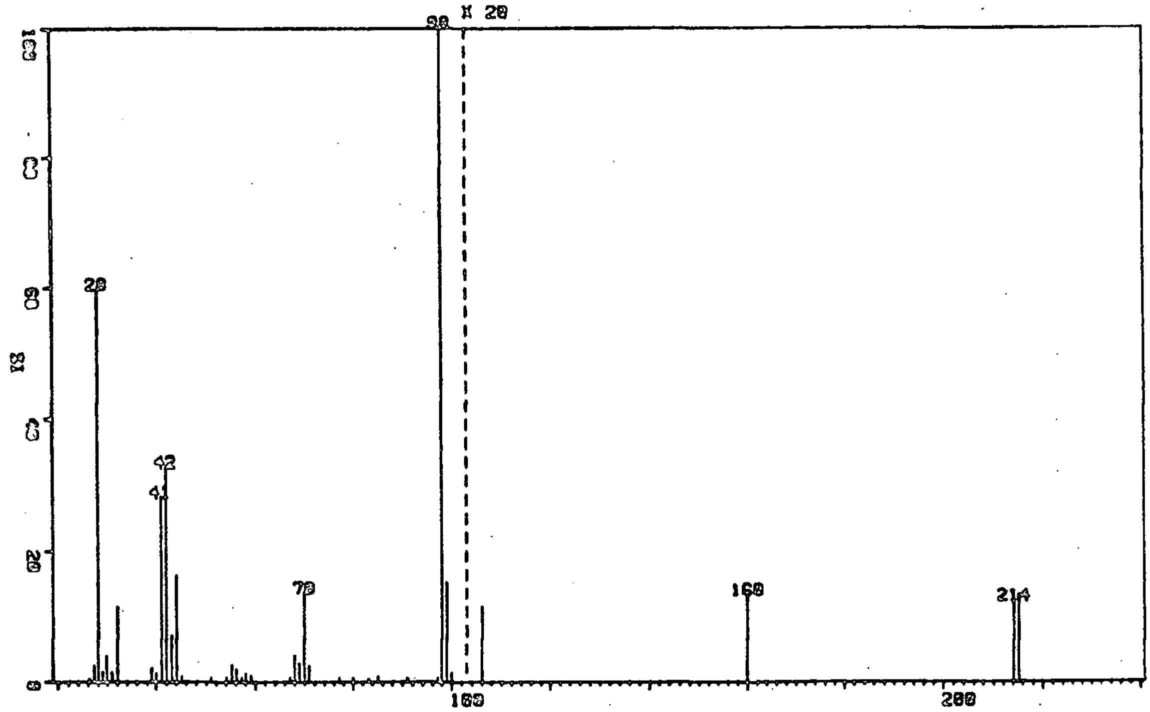


N-Methyl-5-(2-chloro-1,1,2-trifluoroethyl)pyrrolidin-2-one (97).



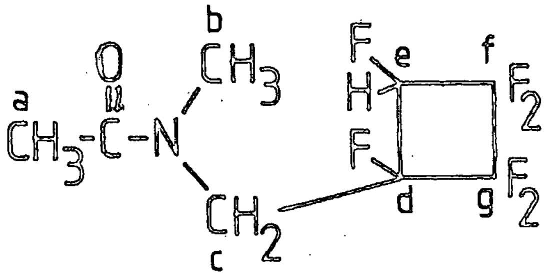
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
2.25	M	4	a , b
2.88	S	3	f
4.03	M	1	c
6.67	D of M, J_{HF}=47	1	e
^{19}F			
117.6, 125.7	AB, J=265	2	d
119.0	M		
153.3	D of T, J_{FH}=47, J_{FF}=12	1	e
154.8	D of T, J_{FH}=47, J_{FF}=12		

M.Wt. 215·5 No.63

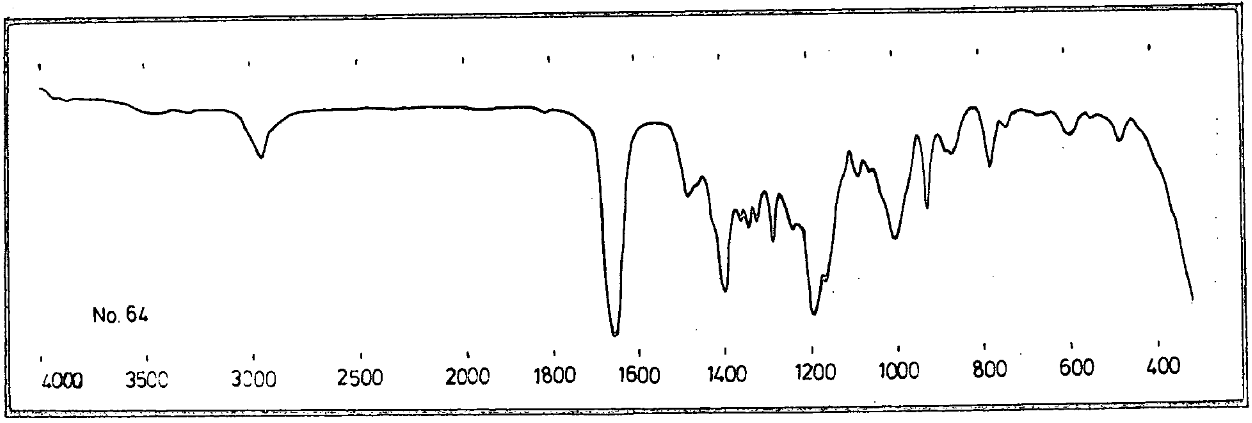


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	26.31	0.49	36	106.11	0.58
2	27.25	2.45	37	160.05	0.67
3	28.13	59.72	38	214.13	0.62
4	29.02	1.56	39	215.14	0.67
5	29.86	3.96			
6	30.94	1.47			
7	32.02	11.39			
8	39.01	2.09			
9	39.87	1.38			
10	41.00	28.26			
11	42.08	32.75			
12	43.15	7.12			
13	44.19	16.24			
14	45.20	0.93			
15	50.97	0.67			
16	54.16	0.76			
17	55.17	2.63			
18	56.16	1.96			
19	57.14	0.76			
20	58.09	1.38			
21	59.04	1.02			
22	67.09	0.85			
23	68.12	3.96			
24	69.02	2.85			
25	69.98	13.57			
26	71.02	2.54			
27	77.10	0.67			
28	79.98	0.58			
29	83.12	0.49			
30	85.13	0.93			
31	91.00	0.67			
32	97.10	0.67			
33	98.04	100.00			
34	99.03	15.18			
35	100.00	1.38			

No. 64

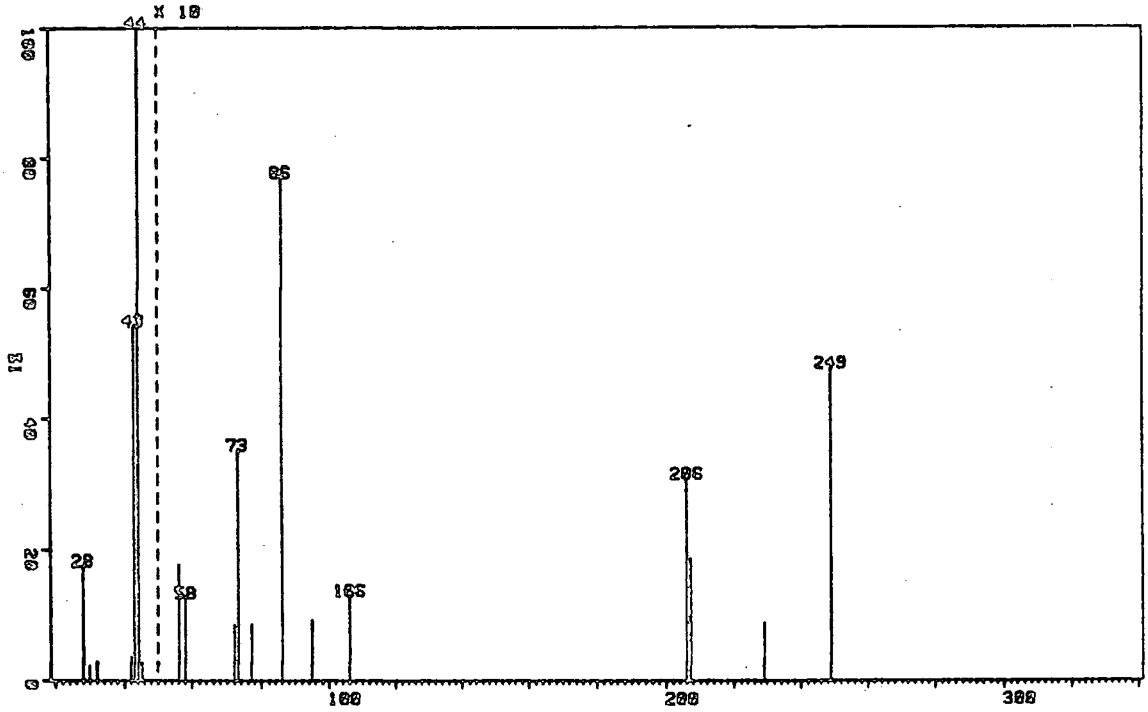


N-(1,2,3,3,4,4-Hexafluorocyclobutyl)methyl-N-methylacetamide (96).



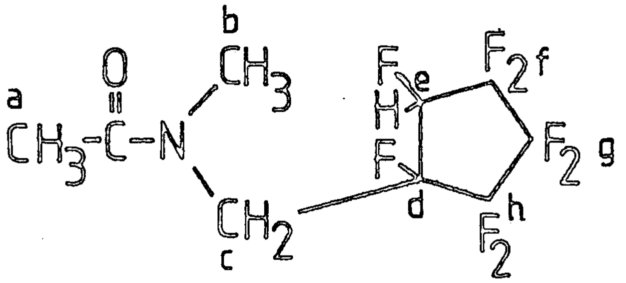
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
2.03	S	3	a
3.05	M	3	b
3.82	S	2	c
4.17	S		
5.33	D of M, J_{HF}=48	1	e
^{19}F			
Series of peaks between 116.0 and 138.2	Overlapping AB's	4	f , g
175.2	M	1	d (trans)
194.5	M		d (cis)
216.0	D of M, J_{FH}=48	1	e (trans)
219.0	D of M, J_{FH}=48		e (cis)

M.Wt. 249 No. 64

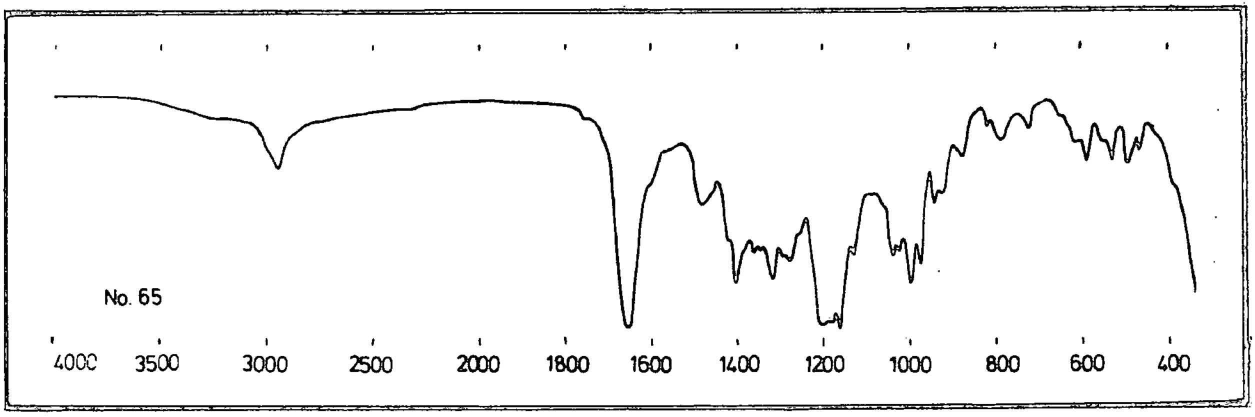


PEAK NO.	MASS	%HT. BASE
1	28.13	17.52
2	29.86	2.33
3	32.02	2.89
4	42.08	3.59
5	43.12	54.26
6	44.19	100.00
7	45.21	2.78
8	56.17	1.78
9	58.09	1.26
10	72.09	0.85
11	73.13	3.52
12	77.08	0.85
13	86.11	7.70
14	95.05	0.93
15	106.08	1.30
16	206.09	3.07
17	207.08	1.85
18	229.07	0.89
19	249.04	4.78

No. 65

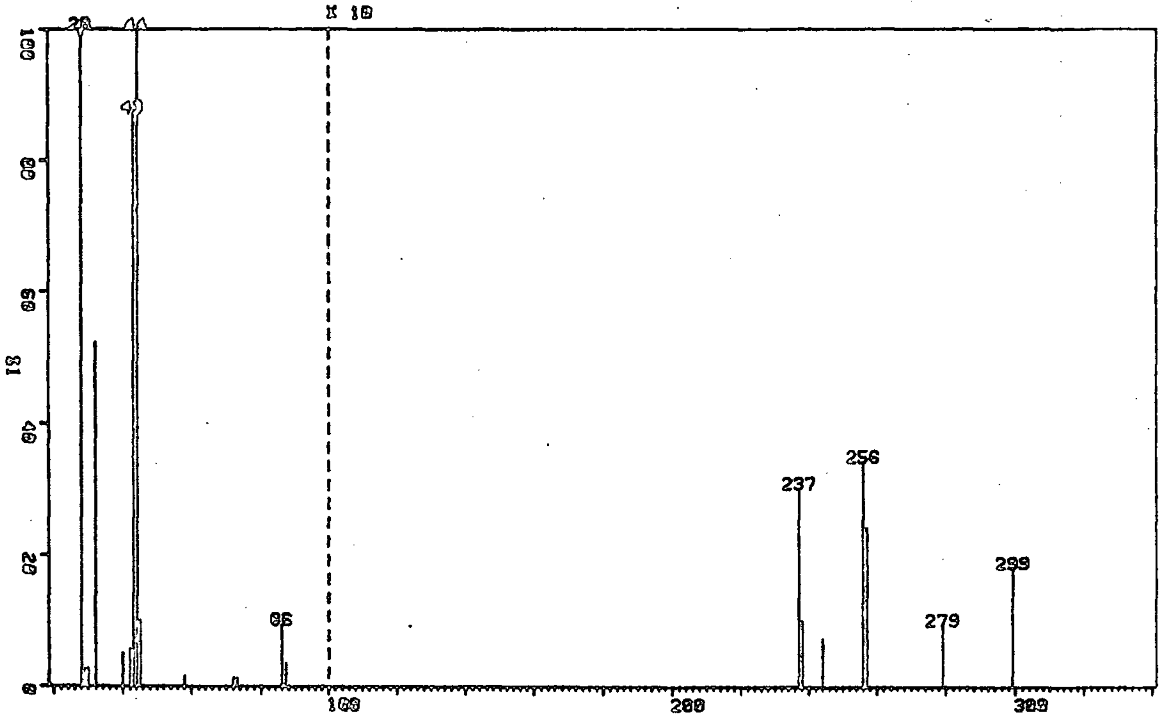


N-(1,2,3,3,4,4,5,5-Octafluorocyclopentyl)methyl-N-methylacetamide (95).

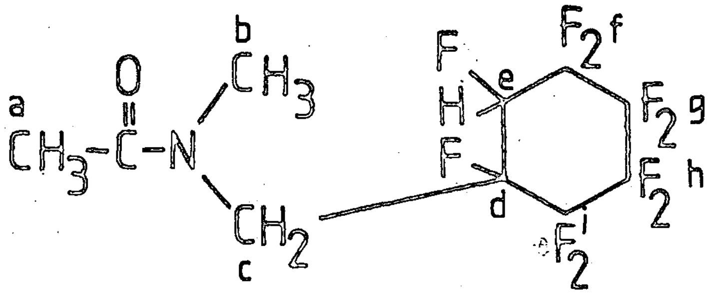


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
2.04	S	3	a
3.12	S	3	b
4.26, 4.55, 4.90, 5.18.	M(broad)	3	c , e
^{19}F			
Series of peaks between 107.8 and 141.0.	Overlapping AB's	6	f, g, h
182.3	M	1	d (trans)
187.7	M		d (cis)
207.2	D of M, J_{FH}=47	1	e (trans)
225.3	D of M, J_{FH}=47		e (cis)

M.Wt. 299 No. 65

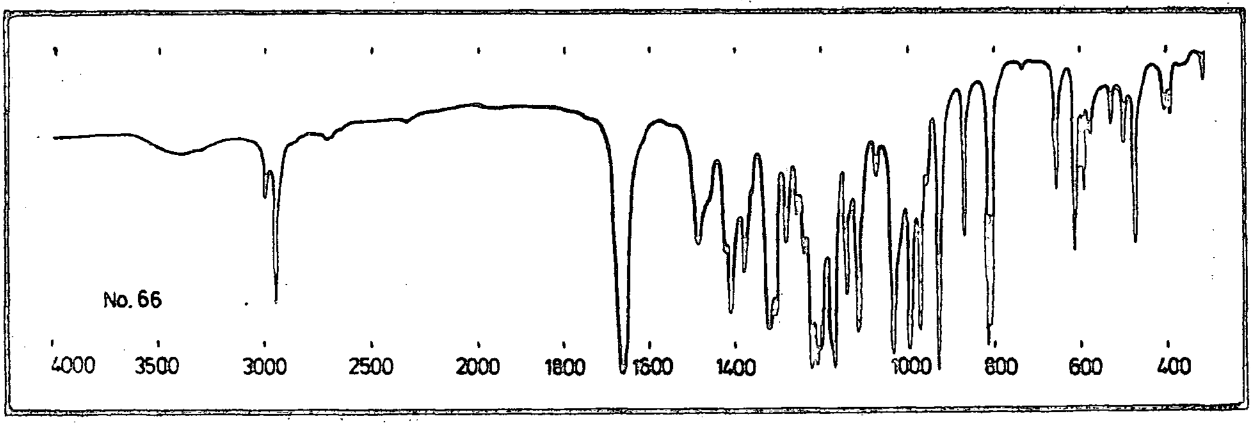


PEAK NO.	MASS	%HT. BASE
1	28.13	100.00
2	29.00	0.98
3	29.85	1.03
4	32.02	19.64
5	39.84	1.92
6	42.07	2.15
7	43.11	32.84
8	44.18	37.61
9	45.19	3.74
10	58.08	0.58
11	72.08	0.50
12	73.12	0.50
13	86.09	3.56
14	87.08	1.34
15	237.02	1.14
16	238.04	0.38
17	244.00	0.28
18	256.00	1.29
19	257.02	0.91
20	279.00	0.35
21	299.03	0.68



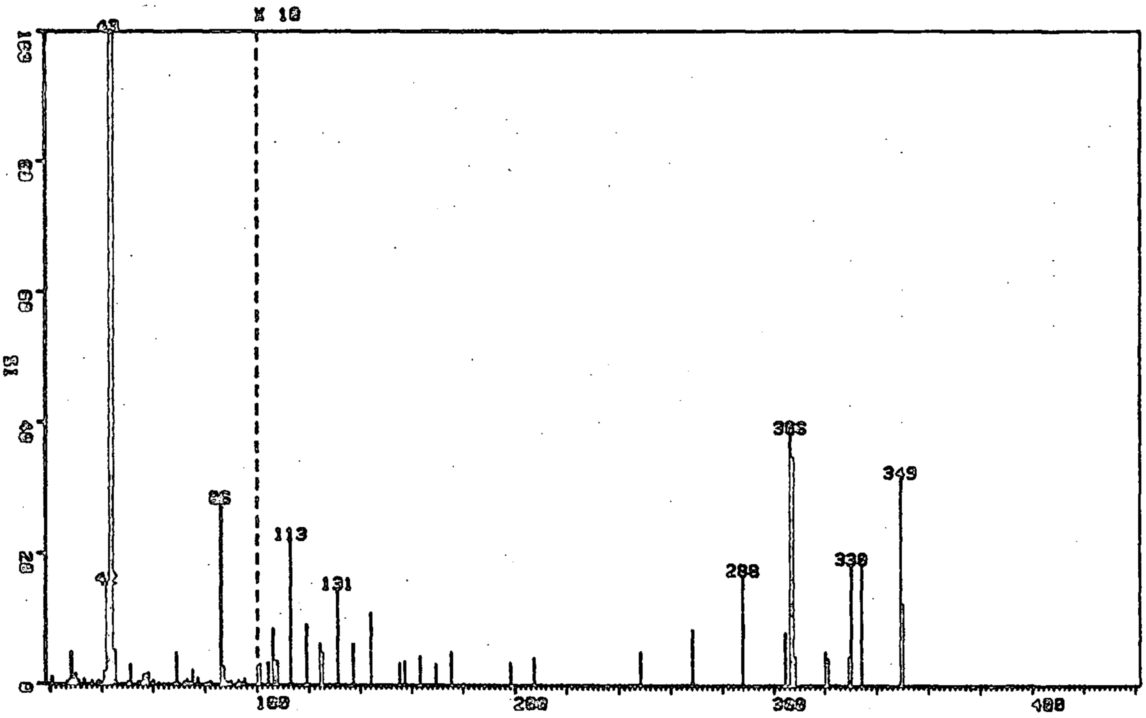
No. 66

N-(1,2,3,3,4,4,5,5,6,6-Decafluorocyclohexyl)methyl-N-methylacetamide (94).

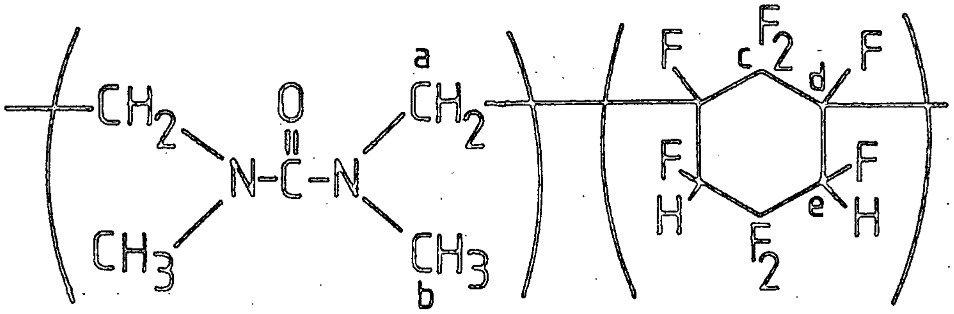


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
2.15	S	3	a
3.17	S	3	b
3.63	T, J=15	3	c , e
4.68	D of D, J=32 and 3		
4.95	D of D, J=32 and 3		
5.1	M(broad)		
^{19}F			
115.2, 120.5, 121.8, 127.0, 128.0, 135.5, 138.7, 140.7, 142.8, 143.5, 147.8	Overlapping AB's	8	f, g, h, i
186.2	M	1	d (trans)
188.0	M		d (cis)
208.8	M	1	e (cis)
232.3	D of M		e (trans)

M.Wt. 349 No. 66

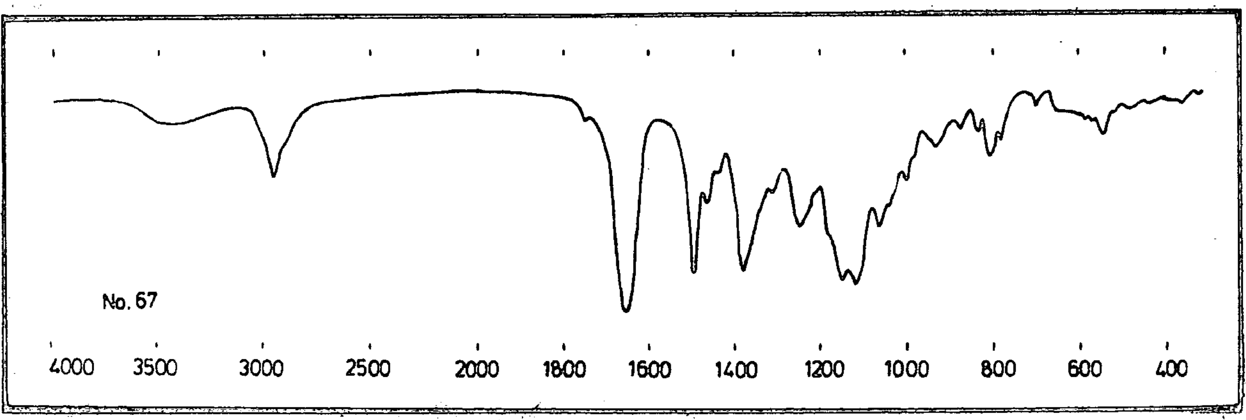


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	20.55	1.07	36	82.02	0.42	71	308.20	0.44
2	26.54	0.29	37	86.10	27.74	72	320.28	0.51
3	27.42	0.71	38	87.10	2.78	73	321.22	0.42
4	28.26	4.86	39	88.05	0.44	74	329.26	0.44
5	29.13	0.71	40	89.02	0.32	75	330.16	1.86
6	29.95	1.59	41	89.99	0.54	76	334.12	1.83
7	30.99	0.78	42	93.03	0.71	77	349.04	3.17
8	33.14	0.81	43	94.10	0.32	78	350.05	1.25
9	36.13	0.56	44	95.07	0.98			
10	38.04	0.29	45	99.97	1.05			
11	38.98	0.61	46	101.07	0.32			
12	39.89	0.42	47	104.13	0.34			
13	40.93	2.00	48	106.11	0.85			
14	42.01	15.41	49	107.10	0.37			
15	43.04	100.00	50	108.05	0.37			
16	44.10	100.00	51	113.03	2.22			
17	45.14	5.27	52	119.03	0.93			
18	49.93	0.29	53	124.11	0.63			
19	50.97	3.00	54	125.07	0.49			
20	54.17	0.42	55	130.96	1.47			
21	55.19	0.39	56	137.07	0.63			
22	56.16	1.44	57	144.06	1.10			
23	57.14	1.64	58	155.07	0.34			
24	58.10	1.78	59	157.11	0.37			
25	59.09	0.27	60	163.11	0.44			
26	60.01	0.66	61	169.11	0.32			
27	62.12	0.22	62	175.15	0.51			
28	69.03	4.81	63	198.09	0.34			
29	70.01	0.24	64	207.12	0.42			
30	72.13	0.42	65	248.19	0.51			
31	73.16	0.81	66	268.11	0.85			
32	74.11	0.29	67	287.73	1.68			
33	75.08	2.17	68	304.15	0.81			
34	77.07	1.05	69	306.10	3.86			
35	80.98	0.34	70	307.10	3.49			



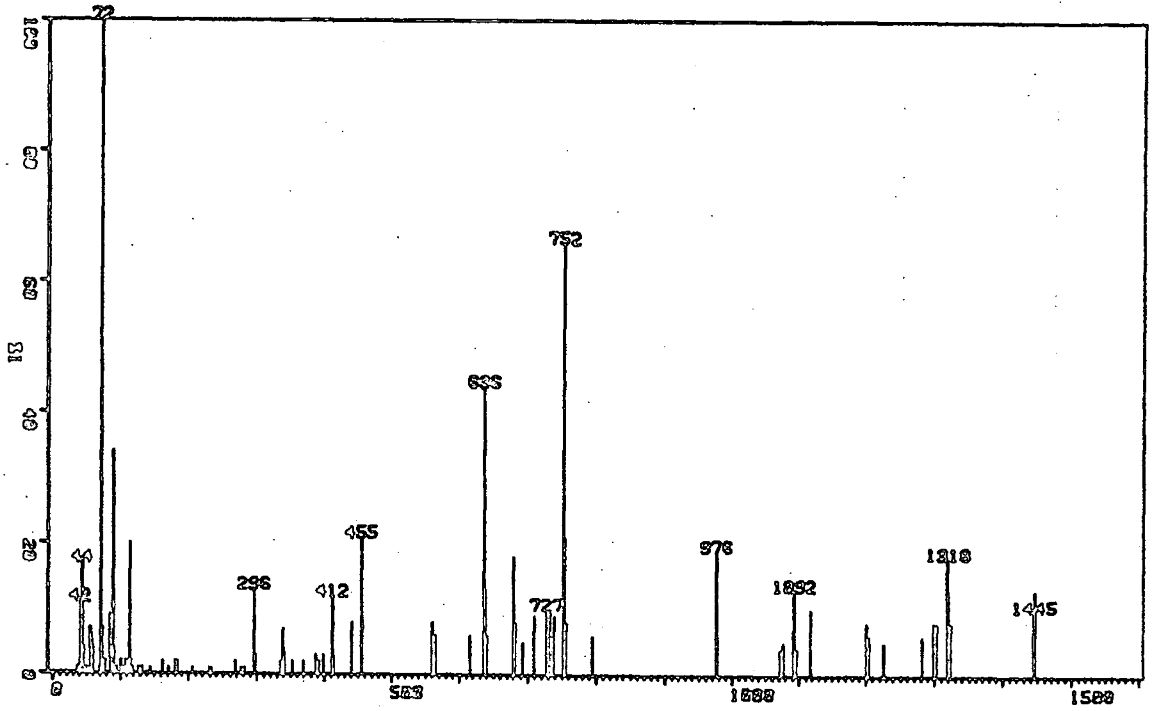
No. 67

N,N,N',N'-Tetramethylurea / Perfluorocyclohexa-1,4-diene polymer (98).



SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
2.22	S	1.5	b
2.87	S	7.9	
3.03	S		
Series of peaks between 3.73 and 5.43	M(broad)	5.6	a, e
^{19}F			
Series of peaks between 110.0 and 131.7	M(broad)	2	c
Series of peaks between 178.3 and 191.0	M(broad)	1	d
Series of peaks between 222.3 and 230.0	M(broad)	1	e

No.67

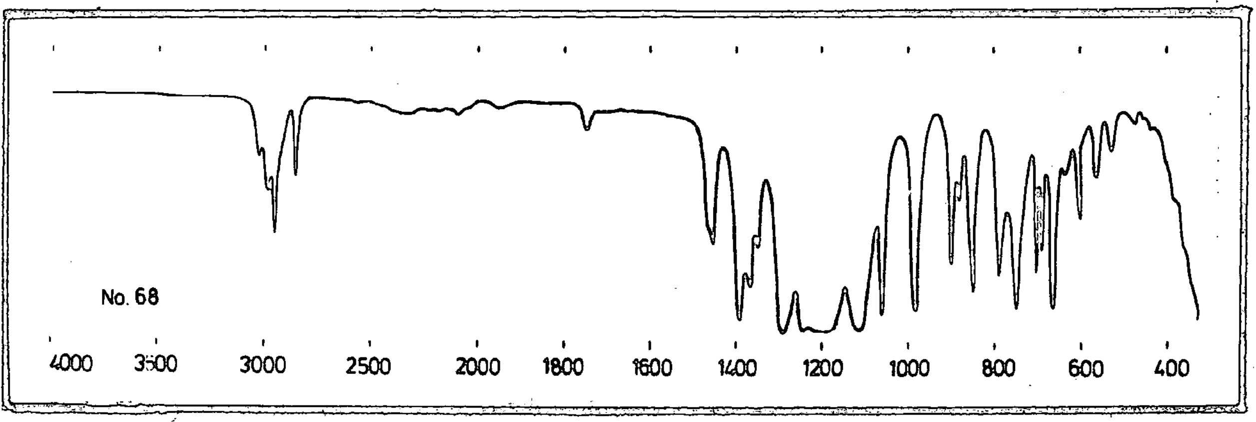


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	36.00	1.00*	36	172.00	1.00*	71	709.00	9.00*
2	38.00	1.00*	37	181.00	2.00*	72	727.00	10.00*
3	39.00	1.00*	38	184.00	2.00*	73	732.00	10.00*
4	40.00	1.00*	39	205.00	1.00*	74	736.00	6.00*
5	41.00	2.00*	40	230.00	1.00*	75	738.00	9.00*
6	42.00	11.00*	41	233.00	1.00*	76	752.00	66.00*
7	43.00	8.00*	42	268.00	2.00*	77	753.00	21.00*
8	44.00	17.00*	43	276.00	1.00*	78	754.00	5.00*
9	45.00	4.00*	44	282.00	1.00*	79	756.00	8.00*
10	51.00	1.00*	45	296.00	13.00*	80	795.00	6.00*
11	55.00	1.00*	46	297.00	3.00*	81	976.00	19.00*
12	56.00	7.00*	47	335.00	2.00*	82	977.00	6.00*
13	57.00	6.00*	48	339.00	7.00*	83	1072.00	4.00*
14	58.00	5.00*	49	340.00	4.00*	84	1076.00	5.00*
15	60.00	4.00*	50	341.00	2.00*	85	1092.00	13.00*
16	69.00	1.00*	51	353.00	2.00*	86	1093.00	5.00*
17	72.00	100.00*	52	369.00	2.00*	87	1096.00	4.00*
18	73.00	7.00*	53	387.00	3.00*	88	1117.00	10.00*
19	77.00	2.00*	54	392.00	2.00*	89	1201.00	8.00* x100
20	85.00	9.00*	55	398.00	3.00*	90	1205.00	6.00*
21	90.00	34.00*	56	412.00	12.00*	91	1226.00	5.00*
22	91.00	4.00*	57	413.00	3.00*	92	1282.00	6.00*
23	95.00	1.00*	58	441.00	8.00*	93	1298.00	8.00*
24	101.00	2.00*	59	455.00	21.00*	94	1302.00	5.00*
25	102.00	2.00*	60	456.00	8.00*	95	1303.00	8.00*
26	104.00	1.00*	61	559.00	8.00* x10	96	1318.00	18.00*
27	108.00	2.00*	62	564.00	6.00*	97	1319.00	13.00*
28	113.00	2.00*	63	616.00	6.00*	98	1323.00	8.00*
29	115.00	20.00*	64	636.00	44.00*	99	1445.00	10.00*
30	116.00	2.00*	65	637.00	13.00*	100	1446.00	13.00*
31	119.00	1.00*	66	641.00	6.00*			
32	127.00	1.00*	67	679.00	18.00*			
33	133.00	1.00*	68	680.00	8.00*			
34	145.00	1.00*	69	681.00	8.00*			
35	163.00	2.00	70	693.00	5.00			

$\overset{a}{CF_3}\,\overset{b}{CFH}\,\overset{c}{CF_2}\,\overset{d}{CHCl}\,O\,\overset{e}{CH_3}$

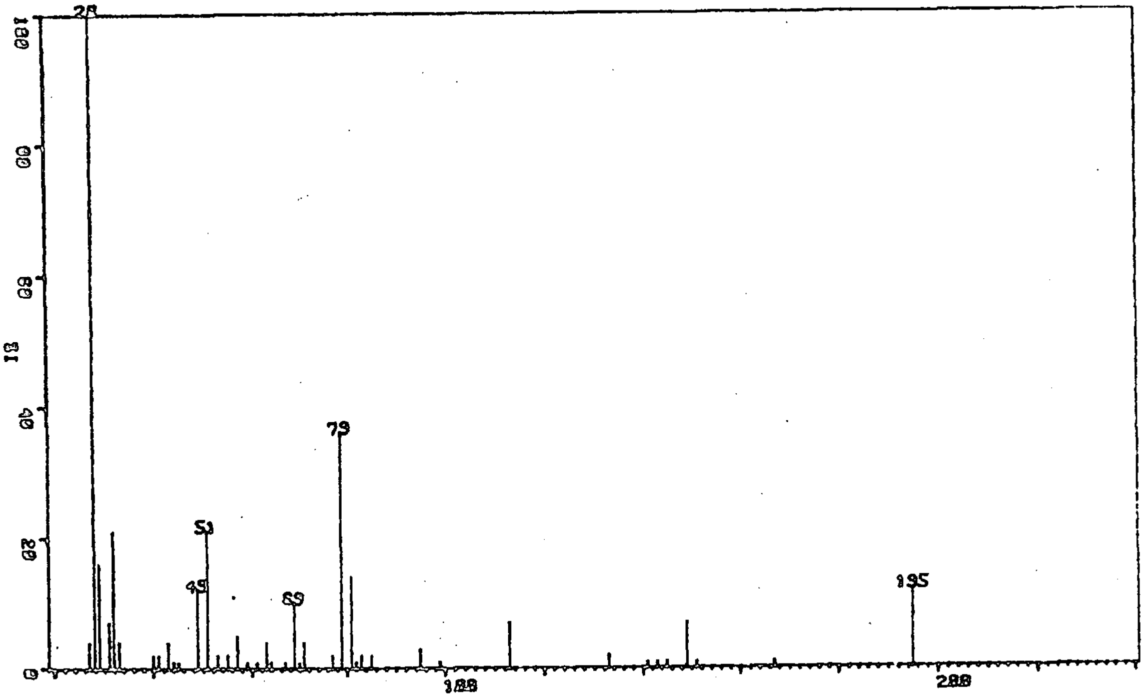
No. 68

1-Chloro-2,2,3,4,4,4-hexafluorobutyl methyl ether (126).



SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
3.78	S	3	e
5.77	T	1	d
^{19}F			
74.2	M (D of Q, J=6 and 12)	3	a
74.6	D of Q, J=7 and 11		
122.4	P(broad), J=10	2	c
124.0, 124.7	M		
214.9	D of M, J_{HF}=44	1	b
216.0	D of M, J_{HF}=44, J=12		

M.Wt. 230·5 No. 68

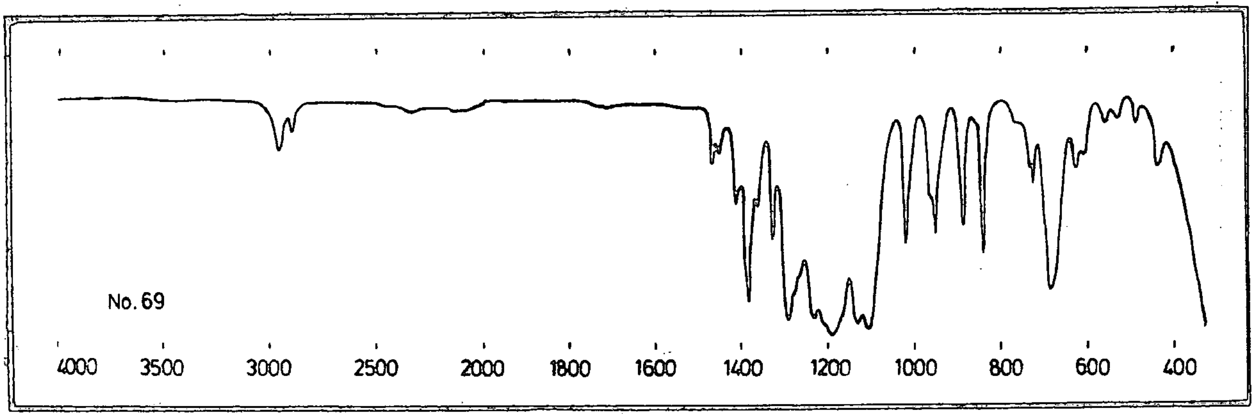


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.00	4.00%	36	143.00	1.00%
2	28.00	100.00%	37	145.00	1.00%
3	29.00	16.00%	38	149.00	7.00%
4	31.00	7.00%	39	151.00	1.00%
5	32.00	21.00%	40	167.00	1.00%
6	33.00	4.00%	41	195.00	12.00%
7	40.00	2.00%			
8	41.00	2.00%			
9	43.00	4.00%			
10	44.00	1.00%			
11	45.00	1.00%			
12	49.00	12.00%			
13	51.00	21.00%			
14	53.00	2.00%			
15	55.00	2.00%			
16	57.00	5.00%			
17	59.00	1.00%			
18	61.00	1.00%			
19	63.00	4.00%			
20	64.00	1.00%			
21	67.00	1.00%			
22	69.00	10.00%			
23	70.00	1.00%			
24	71.00	4.00%			
25	77.00	2.00%			
26	79.00	36.00%			
27	81.00	14.00%			
28	82.00	1.00%			
29	83.00	2.00%			
30	85.00	2.00%			
31	95.00	3.00%			
32	99.00	1.00%			
33	113.00	7.00%			
34	133.00	2.00%			
35	141.00	1.00			

$\overset{e}{CF_3}\,\overset{d}{CFH}\,\overset{c}{CF_2}\,\overset{b}{CH_2}\,O\,\overset{a}{CH_2}Cl$

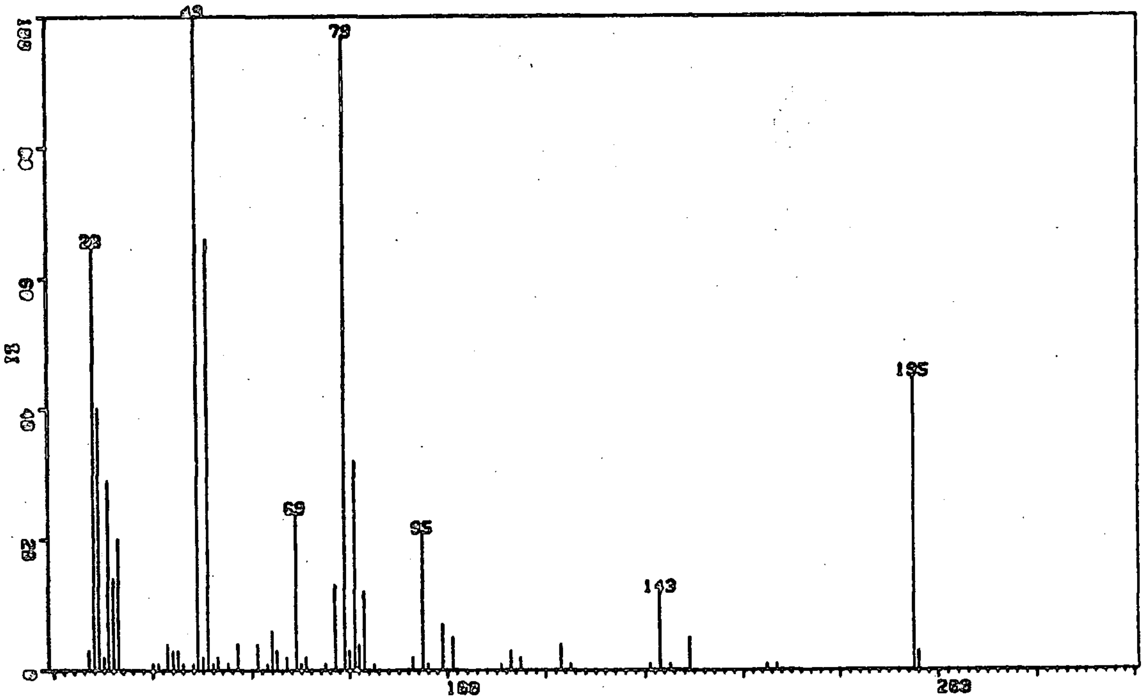
No.69

2,2,3,4,4,4-Hexafluorobutyl chloromethyl ether (127).



SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
4.13	M, J=10	2	b
5.10	D of M, J_{HF}=44	1	d
5.63	S	2	a
^{19}F			
75.0	D of Q, J=7 and 10.5	3	e
117.3, 122.0	AB, J_{FF}=221	2	c
214.3	D of M, J_{FH}=44	1	d

M.Wt. 230·5 No.69

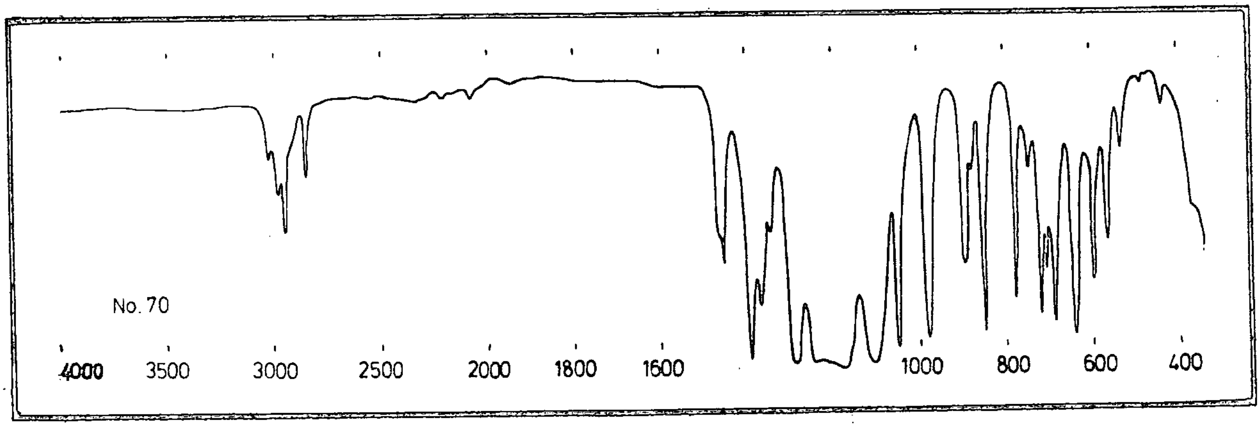


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.00	3.00*	36	83.00	12.00*
2	28.00	65.00*	37	85.00	1.00*
3	29.00	40.00*	38	93.00	2.00*
4	30.00	2.00*	39	95.00	21.00*
5	31.00	29.00*	40	96.00	1.00*
6	32.00	14.00*	41	99.00	7.00*
7	33.00	20.00*	42	101.00	5.00*
8	40.00	1.00*	43	111.00	1.00*
9	41.00	1.00*	44	113.00	3.00*
10	43.00	4.00*	45	115.00	2.00*
11	44.00	3.00*	46	123.00	4.00*
12	45.00	3.00*	47	125.00	1.00*
13	46.00	1.00*	48	141.00	1.00*
14	48.00	1.00*	49	143.00	12.00*
15	49.00	100.00*	50	145.00	1.00*
16	50.00	2.00*	51	149.00	5.00*
17	51.00	66.00*	52	165.00	1.00*
18	52.00	1.00*	53	167.00	1.00*
19	53.00	2.00*	54	195.00	45.00*
20	55.00	1.00*	55	196.00	3.00*
21	57.00	4.00*			
22	61.00	4.00*			
23	63.00	1.00*			
24	64.00	6.00*			
25	65.00	3.00*			
26	67.00	2.00*			
27	69.00	24.00*			
28	70.00	1.00*			
29	71.00	2.00*			
30	75.00	1.00*			
31	77.00	13.00*			
32	79.00	97.00*			
33	80.00	3.00*			
34	81.00	32.00*			
35	82.00	4.00			

$\overset{e}{CF_3}\ \overset{d}{CFH}\ \overset{c}{CF_2}\ \overset{b}{CHBr}\ O\ \overset{a}{CH_3}$

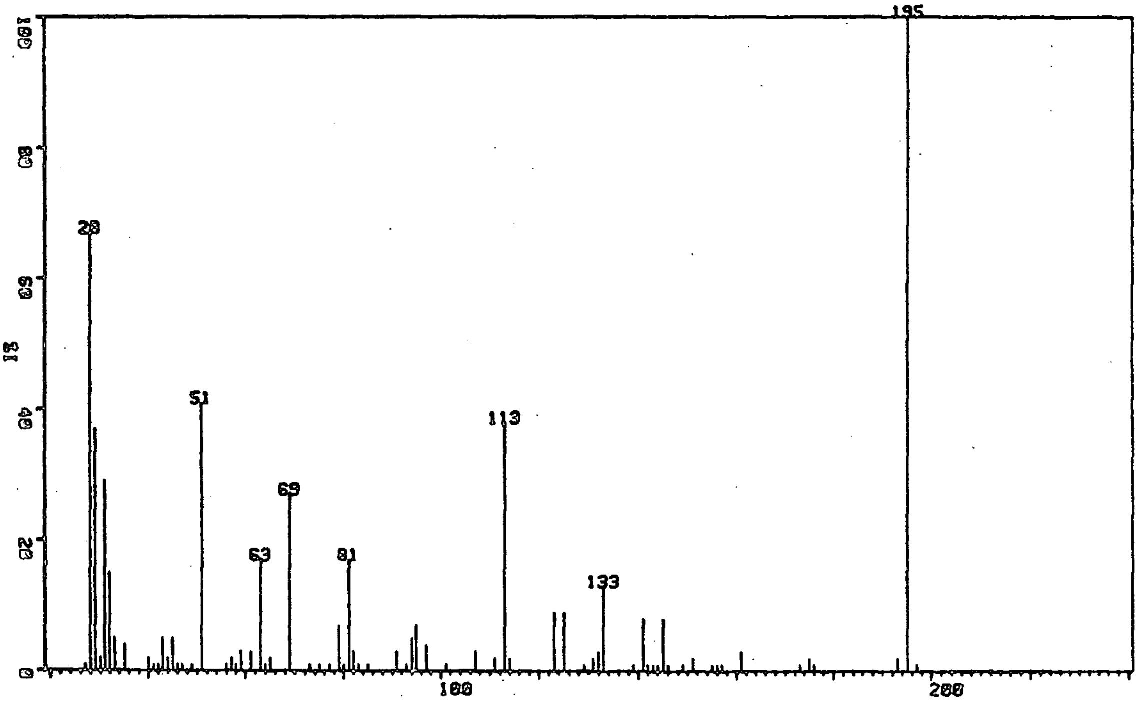
No.70

1-Bromo-2,2,3,4,4,4-hexafluorobutyl methyl ether (130).

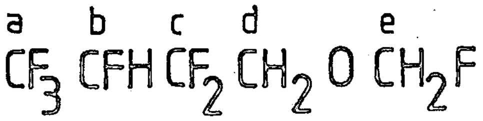


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
3.63	S	3	a
5.27	D of M, J_{HF}=44, J=6	1	d
6.00	T, J_{HF}=9	1	b
6.07	T, J_{HF}=9		
^{19}F			
76.1	D of Q, J=7 and 11	3	e
76.7	D of Q of M, J=7 and 11		
120.1	Sp of M, J=11	2	c
122.1	Sp of M, J=11		
215.3	D of M, J_{FH}=44	1	d
217.3	D of M, J_{FH}=44		

M.Wt. 275 No.70



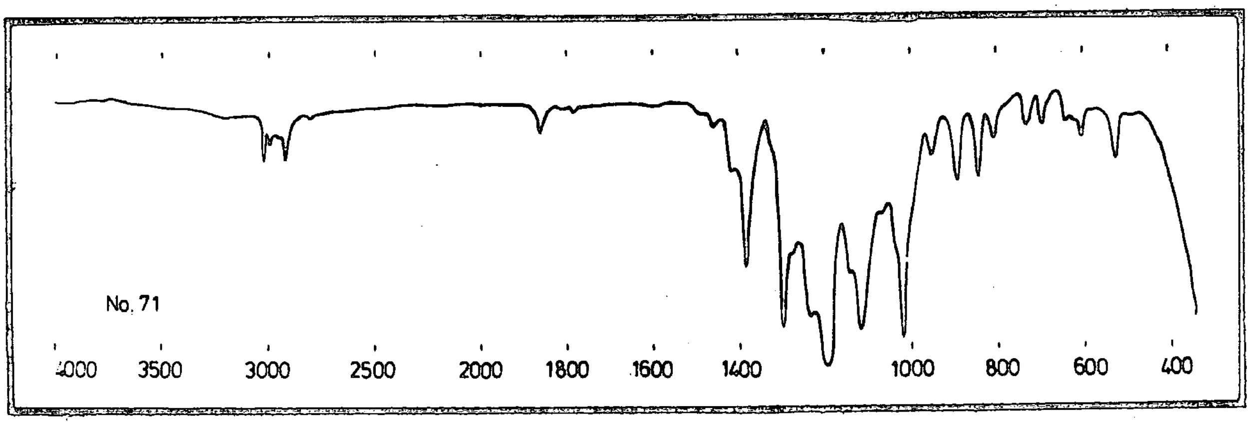
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.00	1.00*	36	85.00	1.00*	71	197.00	1.00*
2	28.00	67.00*	37	91.00	3.00*			
3	29.00	37.00*	38	93.00	1.00*			
4	30.00	2.00*	39	94.00	5.00*			
5	31.00	29.00*	40	95.00	7.00*			
6	32.00	15.00*	41	97.00	4.00*			
7	33.00	5.00*	42	101.00	1.00*			
8	35.00	4.00*	43	107.00	3.00*			
9	40.00	2.00*	44	111.00	2.00*			
10	41.00	1.00*	45	113.00	38.00*			
11	42.00	1.00*	46	114.00	2.00*			
12	43.00	5.00*	47	123.00	9.00*			
13	44.00	2.00*	48	125.00	9.00*			
14	45.00	5.00*	49	129.00	1.00*			
15	46.00	1.00*	50	131.00	2.00*			
16	47.00	1.00*	51	132.00	3.00*			
17	49.00	1.00*	52	133.00	13.00*			
18	51.00	41.00*	53	139.00	1.00*			
19	56.00	1.00*	54	141.00	8.00*			
20	57.00	2.00*	55	142.00	1.00*			
21	58.00	1.00*	56	143.00	1.00*			
22	59.00	3.00*	57	144.00	1.00*			
23	61.00	3.00*	58	145.00	8.00*			
24	63.00	17.00*	59	146.00	1.00*			
25	64.00	1.00*	60	149.00	1.00*			
26	65.00	2.00*	61	151.00	2.00*			
27	69.00	27.00*	62	155.00	1.00*			
28	73.00	1.00*	63	156.00	1.00*			
29	75.00	1.00*	64	157.00	1.00*			
30	77.00	1.00*	65	161.00	3.00*			
31	79.00	7.00*	66	173.00	1.00*			
32	80.00	1.00*	67	175.00	2.00*			
33	81.00	17.00*	68	176.00	1.00*			
34	82.00	3.00*	69	193.00	2.00*			
35	83.00	1.00	70	195.00	100.00*			



$\overset{a}{CF_3}\,\overset{b}{CFH}\,\overset{c}{CF_2}\,\overset{d}{CH_2}\,O\,\overset{e}{CH_2F}$

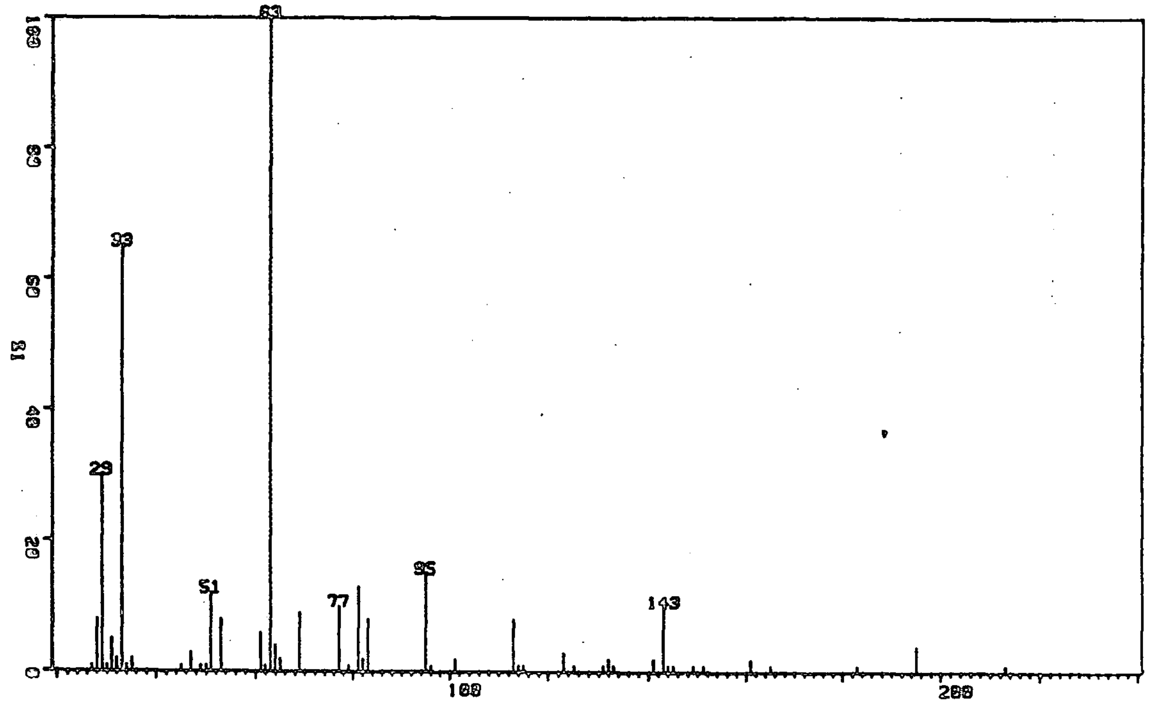
No.71

2,2,3,4,4,4-Hexafluorobutyl fluoromethyl ether (134).



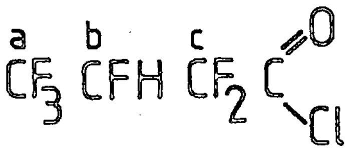
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
3.17	M	2	d
4.36	D, J=55	2	e
4.80	M	1	b
^{19}F			
76.2	M	3	a
118.9, 123.0	AB, J=277	2	c
155.7	T, J=54	1	e
215.7	D of M, J=44	1	b

M.Wt. 214 No.71



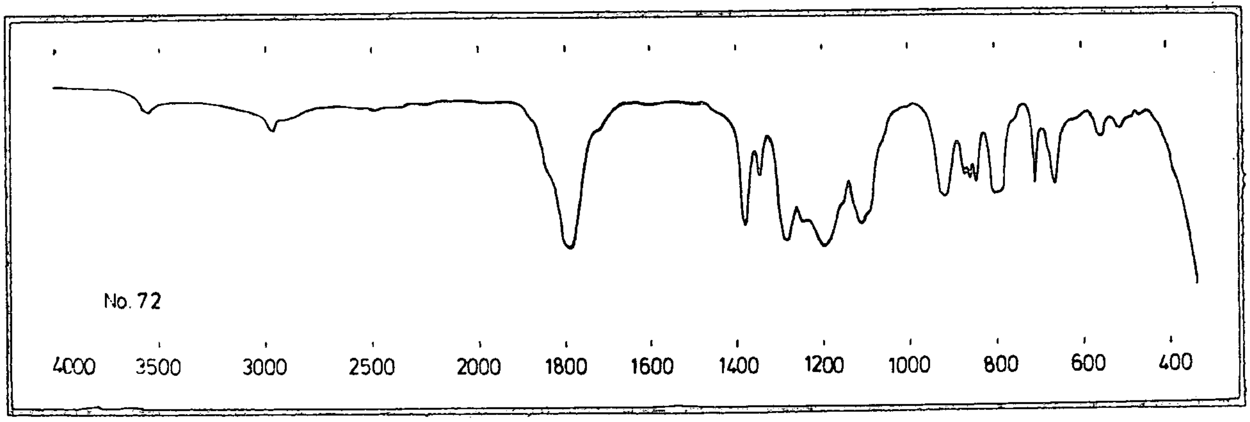
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.00	1.00*	36	131.00	1.00*
2	28.00	8.00*	37	132.00	2.00*
3	29.00	30.00*	38	133.00	1.00*
4	30.00	1.00*	39	141.00	2.00*
5	31.00	5.00*	40	143.00	10.00*
6	32.00	2.00*	41	144.00	1.00*
7	33.00	65.00*	42	145.00	1.00*
8	34.00	1.00*	43	149.00	1.00*
9	35.00	2.00*	44	151.00	1.00*
10	45.00	1.00*	45	161.00	2.00*
11	47.00	3.00*	46	165.00	1.00*
12	49.00	1.00*	47	183.00	1.00*
13	50.00	1.00*	48	195.00	4.00*
14	51.00	12.00*	49	213.00	1.00*
15	53.00	8.00*			
16	61.00	6.00*			
17	61.00	4.00*			
18	62.00	1.00*			
19	63.00	100.00*			
20	64.00	4.00*			
21	65.00	2.00*			
22	69.00	9.00*			
23	77.00	10.00*			
24	79.00	1.00*			
25	81.00	13.00*			
26	82.00	2.00*			
27	83.00	8.00*			
28	95.00	15.00*			
29	96.00	1.00*			
30	101.00	2.00*			
31	113.00	8.00*			
32	114.00	1.00*			
33	115.00	1.00*			
34	123.00	3.00*			
35	125.00	1.00			

No.72



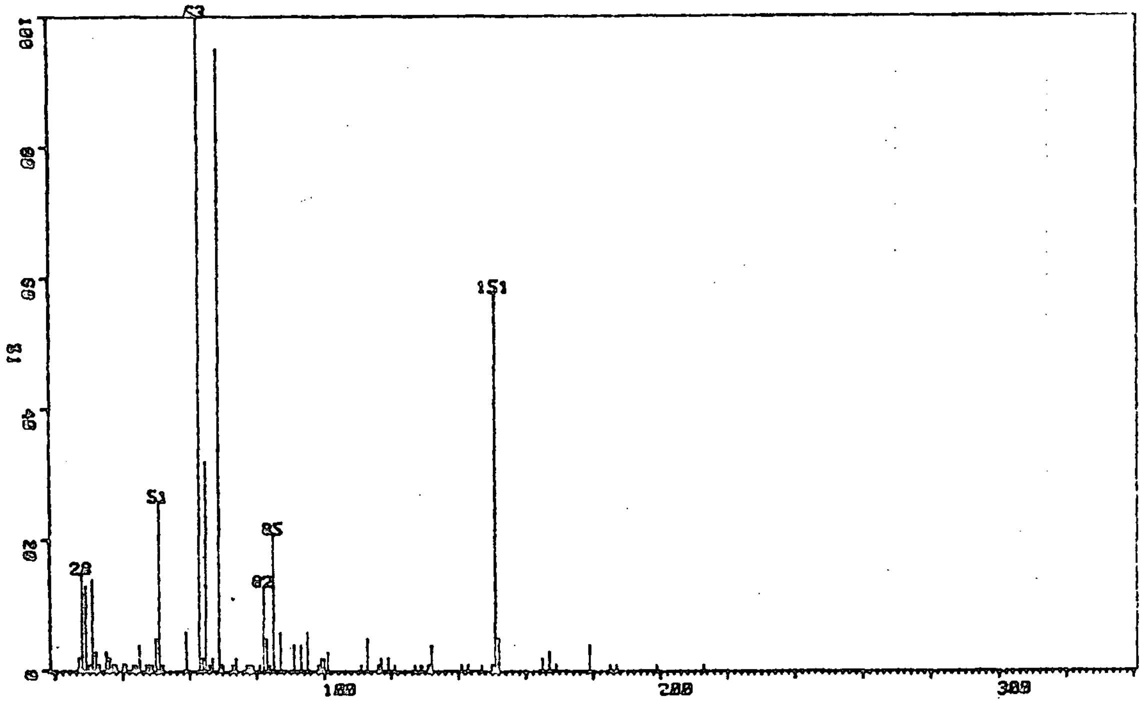
$\overset{a}{CF_3}\overset{b}{CFH}\overset{c}{CF_2}C(=O)Cl$

2,2,3,4,4,4-Hexafluorobutanoyl chloride (<u>138</u>).

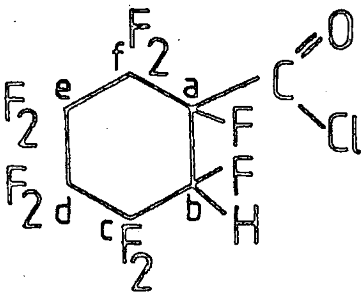


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
<u>^1H</u>			
5.08	D of M, J_{HF}=44, J=6	–	b
<u>^{19}F</u>			
76.0	M	3	a
112.3	AB, J=278 (M)	2	c
117.1	AB, J=278 (T of Q, J=13 and 9)		
214.2	D of Sx, J=42 and 11	1	b

M.Wt. 214·5 No.72

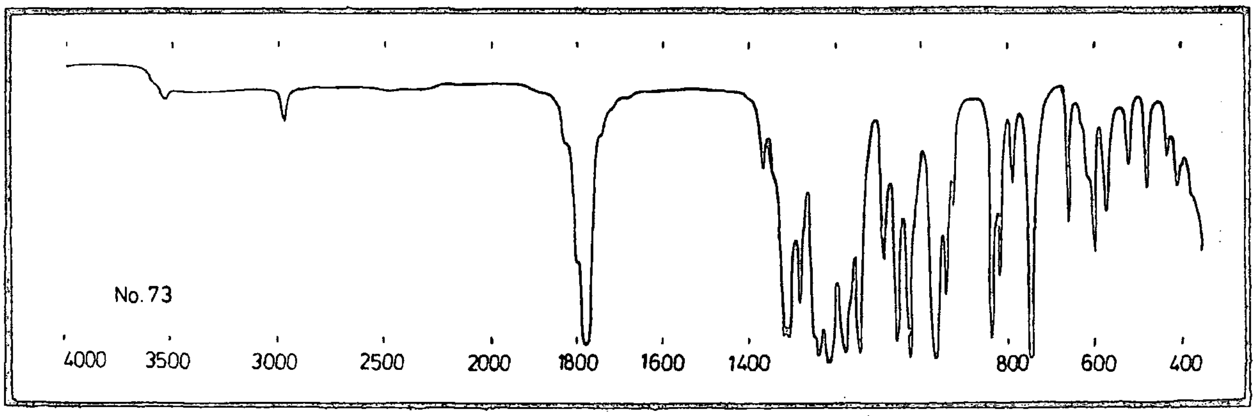


PEAK NO.	MASS	%HT. BASE
1	27.25	1.65
2	28.13	14.65
3	29.00	12.57
4	29.84	1.26
5	30.93	13.51
6	30.98	5.41
7	32.03	2.82
8	33.13	1.04
9	35.16	3.14
10	36.16	1.88
11	37.12	1.04
12	38.05	1.07
13	39.84	0.42
14	40.99	1.10
15	43.12	1.07
16	44.13	1.17
17	45.18	4.18
18	47.08	1.07
19	48.03	0.78
20	48.96	1.33
21	49.88	4.96
22	50.95	25.60
23	52.04	0.49
24	59.02	5.61
25	63.02	100.00
26	63.19	6.71
27	64.03	1.59
28	65.02	31.69
29	66.01	0.62
30	67.01	1.59
31	68.93	95.37
32	69.09	6.03
33	69.88	1.00
34	73.11	0.58
35	74.10	2.43
36	77.01	1.46
37	77.94	1.17
38	78.88	1.07
39	80.90	0.49
40	81.95	12.86
41	82.09	5.48
42	82.95	4.67
43	83.94	0.55
44	84.99	21.03
45	85.97	0.36
46	86.96	6.45
47	90.92	3.60
48	92.99	4.37
49	95.03	5.77
50	96.02	0.36
51	97.96	0.87
52	98.91	2.43
53	99.88	1.72
54	100.94	2.72
55	102.96	0.42
56	110.94	0.75
57	113.03	5.25
58	114.04	0.36
59	116.01	0.52
60	116.95	1.78
61	118.92	1.72
62	120.88	0.65
63	127.03	0.87
64	128.05	0.42
65	128.98	1.13
66	131.03	1.39
67	132.06	3.99
68	133.09	0.49
69	141.03	0.87
70	143.01	0.36
71	147.05	0.81
72	149.00	0.45
73	149.99	0.55
74	151.03	57.65
75	151.70	4.89
76	165.09	2.30
77	167.07	3.14
78	169.03	1.10
79	179.03	3.53
80	185.05	0.91
81	187.02	0.36
82	199.01	0.39
83	213.04	0.36



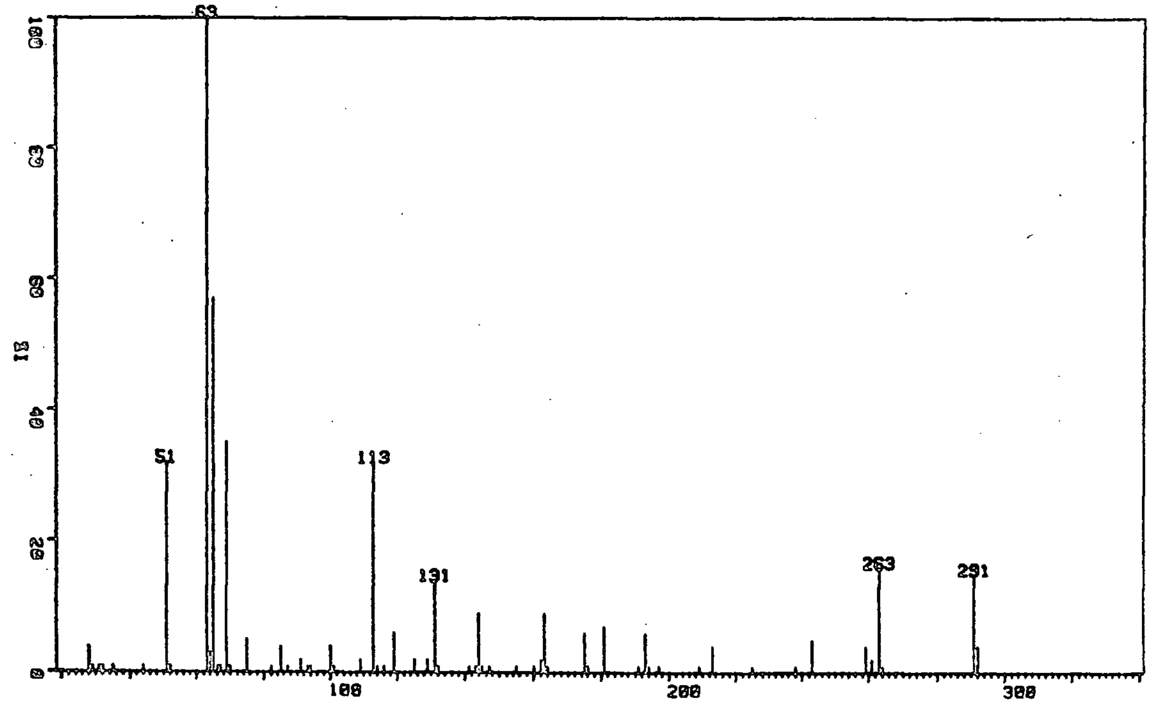
No.73

1,2,3,3,4,4,5,5,6,6-Decafluorocyclohexylmethanoyl chloride (139).

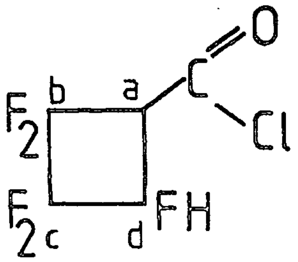


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
5.32	M, J=10	-	b
^{19}F			
118.1, 122.3, 123.1, 127.5, 130.3, 133.2, 138.3, 139.7, 144.8, 149.8,	Overlapping AB's	8	c, d, e, f
167.5	M	1	a (trans)
179.3	M		a (cis)
210.0	D of M, J_{FH}=42	1	b (trans)
229.3	D of M, J_{FH}=42		b (cis)

M.Wt. 326·5 No.73

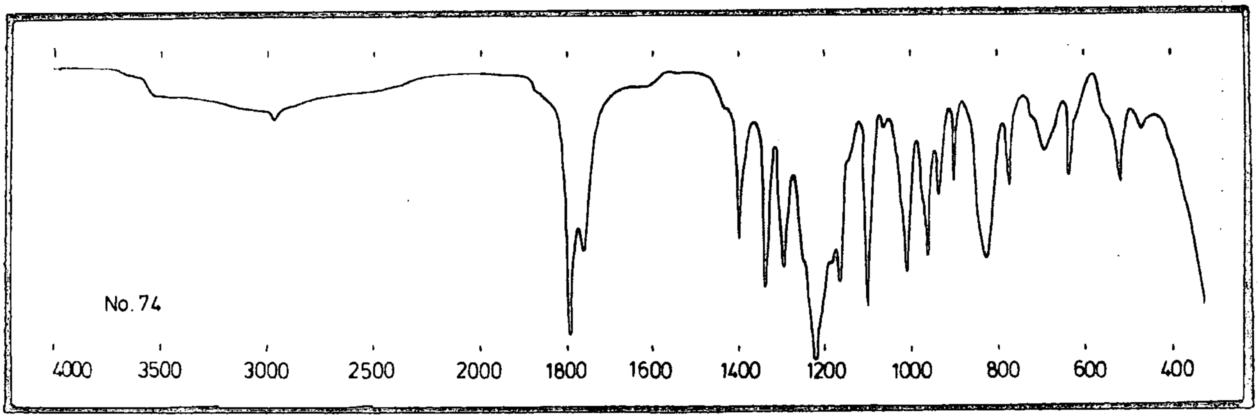


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE			
1	28.13	3.88	28	90.97	1.51	54	163.01	9.13
2	29.00	1.42	29	93.04	1.27	55	164.03	0.51
3	30.92	0.76	30	94.06	1.10	56	171.01	0.42
4	32.02	0.68	31	99.92	4.44	57	175.03	5.79
5	35.17	0.71	32	100.97	0.56	58	176.06	0.59
6	36.17	0.32	33	108.94	1.59	59	178.99	0.37
7	44.15	0.59	34	111.94	0.37	60	181.01	6.52
8	50.96	31.75	35	112.49	0.29	61	190.97	0.71
9	51.07	3.35	36	113.01	31.58	62	193.00	5.52
10	52.06	0.32	37	114.05	1.25	63	193.98	0.90
11	62.60	0.37	38	116.02	0.51	64	197.02	0.71
12	63.05	100.00	39	118.99	6.42	65	209.00	0.61
13	63.23	5.10	40	125.06	1.71	66	213.02	3.66
14	63.45	0.39	41	128.97	1.54	67	214.10	0.46
15	64.03	3.27	42	130.98	13.60	68	225.06	0.61
16	65.02	56.53	43	131.16	4.08	69	237.84	0.34
17	65.27	0.42	44	131.97	0.71	70	243.00	5.23
18	66.04	0.76	45	140.99	0.71	71	244.02	0.42
19	67.01	0.95	46	143.02	0.88	72	258.91	3.74
20	68.94	34.80	47	144.01	9.21	73	260.95	1.83
21	69.13	0.39	48	145.05	0.88	74	262.95	16.19
22	69.90	0.56	49	146.98	1.12	75	263.97	0.85
23	75.10	4.57	50	148.91	0.44	76	291.05	14.58
24	80.96	0.46	51	155.04	0.51	77	291.69	4.22
25	82.04	1.27	52	159.93	0.61			
26	85.04	4.05	53	161.99	1.68			
27	87.03	1.07						



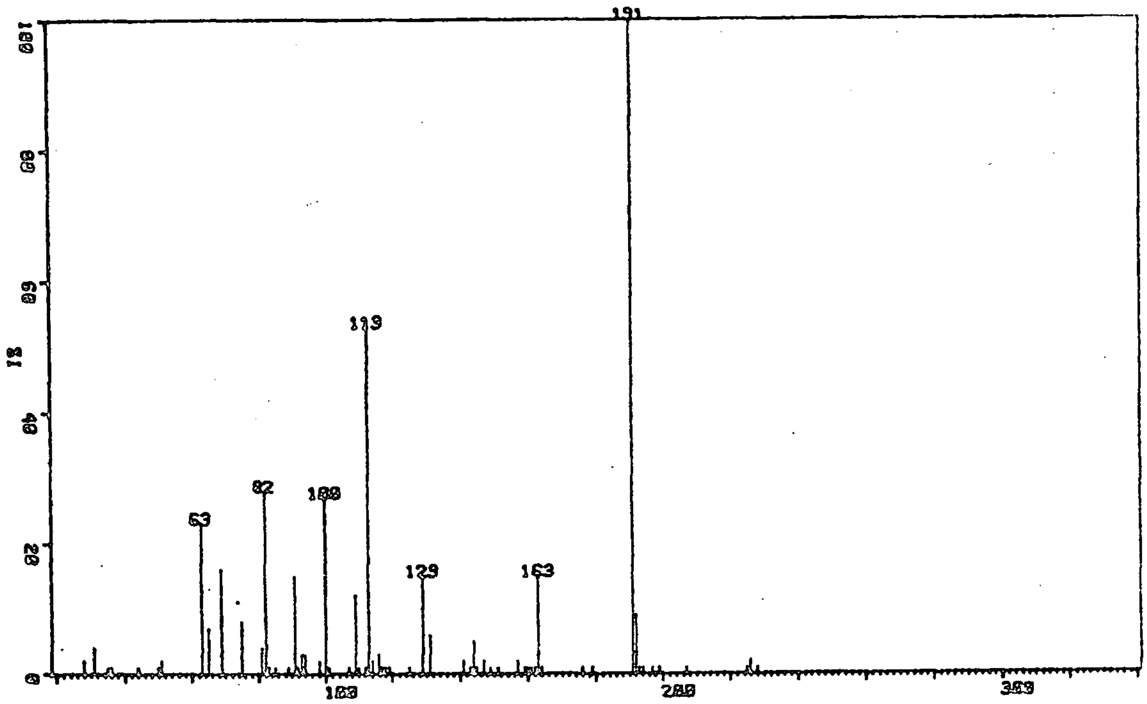
No 74

1,2,3,3,4,4-Hexafluorocyclobutylmethanoyl chloride (<u>140</u>).



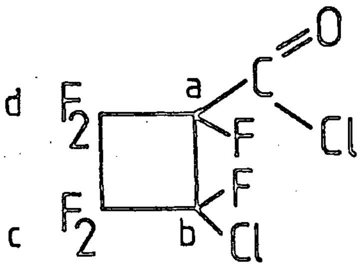
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
5.3	D of M, J_{HF}=46	-	b
^{19}F			
126.9	M	2	c and d
118.6	AB, J=230 (D of D of M, J=10,5,1)	2	
136.9	(M)		
161.8	D of D of D of M, J=16,9,5.	1	a
212.0	D of M, J_{FH}=46	1	b

M.Wt. 226·5 No.74

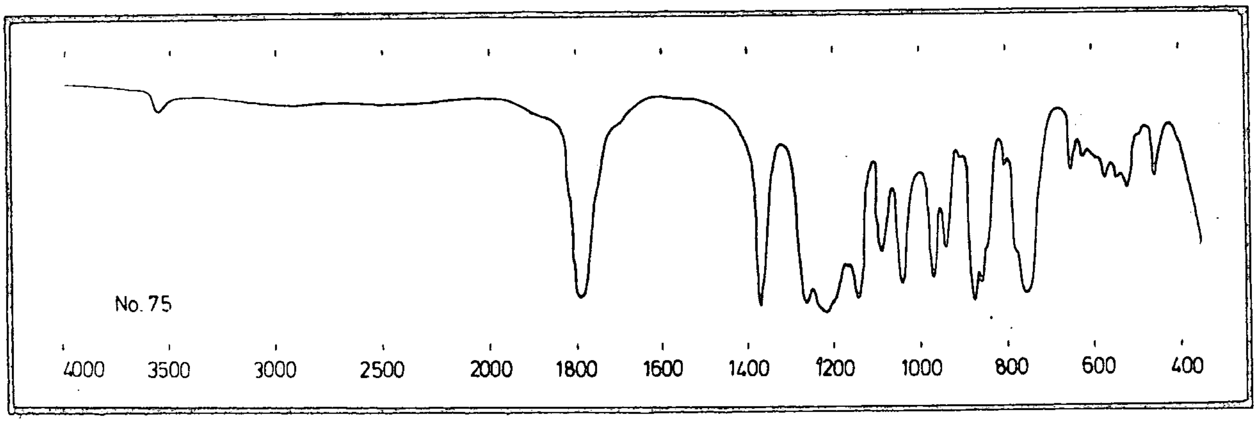


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE			
1	28.13	1.75	28	112.00	1.09	54	190.99	100.00
2	30.92	3.57	29	113.05	52.96	55	191.74	9.25
3	35.17	0.73	30	114.09	1.87	56	193.07	0.54
4	36.16	0.97	31	116.04	2.96	57	193.66	0.54
5	44.14	0.67	32	116.97	0.54	58	197.08	1.03
6	49.89	0.79	33	117.99	1.27	59	199.06	0.79
7	50.96	2.18	34	119.00	0.91	60	207.12	0.79
8	63.06	23.28	35	125.05	1.15	61	225.11	1.45
9	65.07	6.71	36	128.98	15.11	62	226.02	2.18
10	68.98	16.26	37	130.97	5.68	63	228.06	0.85
11	75.06	8.16	38	141.01	1.81			
12	80.90	4.11	39	143.06	1.09			
13	81.99	27.51	40	144.05	5.38			
14	83.01	0.79	41	145.08	0.67			
15	85.03	1.15	42	147.01	1.63			
16	89.91	0.67	43	148.96	0.85			
17	90.96	14.87	44	151.01	0.79			
18	91.19	0.67	45	157.00	1.57			
19	91.97	0.73	46	158.99	1.45			
20	93.01	3.26	47	159.95	1.03			
21	94.02	2.96	48	160.94	0.67			
22	97.99	2.42	49	161.99	1.21			
23	99.93	27.27	50	163.03	14.69			
24	100.97	0.97	51	164.05	0.85			
25	107.03	0.67	52	176.03	0.54			
26	108.98	11.73	53	178.98	0.91			
27	109.92	0.67						

No.75

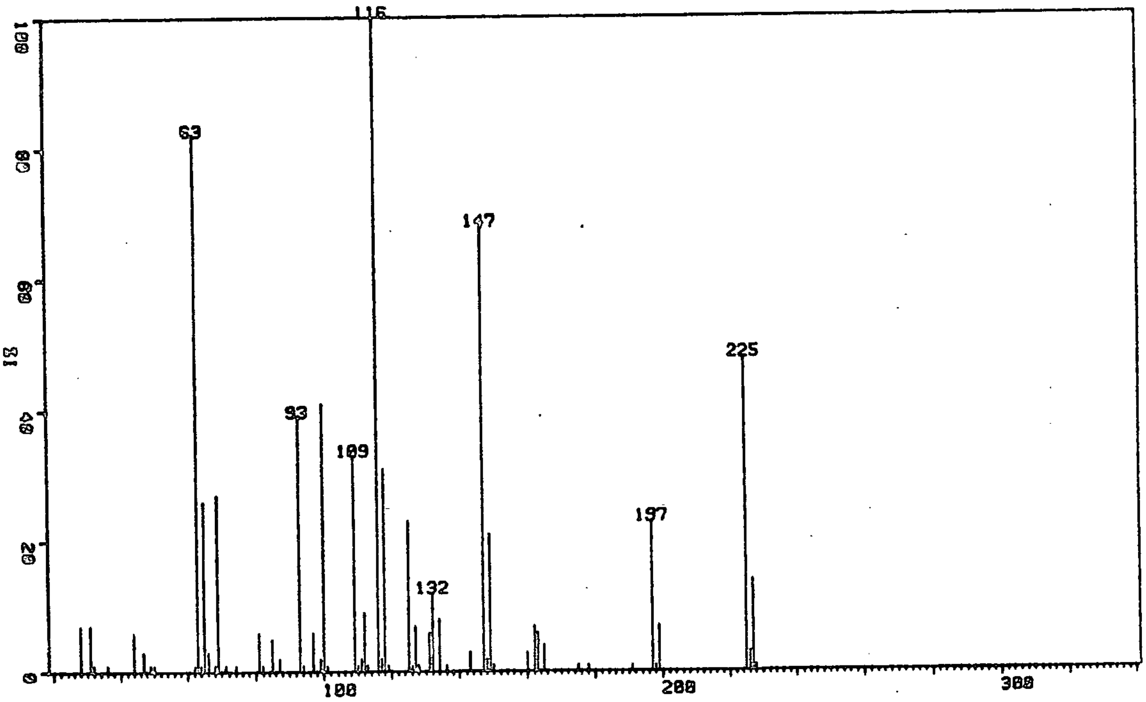


3-Chlorohexafluorocyclobutylmethanoyl chloride (141).

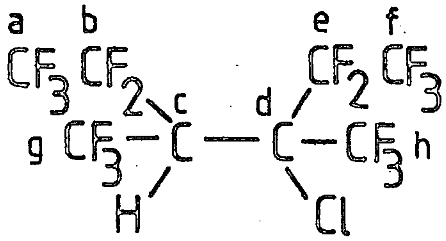


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
126.8	M	2	c or d
122.6, 131.4	AB, J_{FF}=214	2	d or c
136.2	M	1	b
141.4	M		
159.0	M	1	a
168.1	M		

M.Wt. 261 No.75

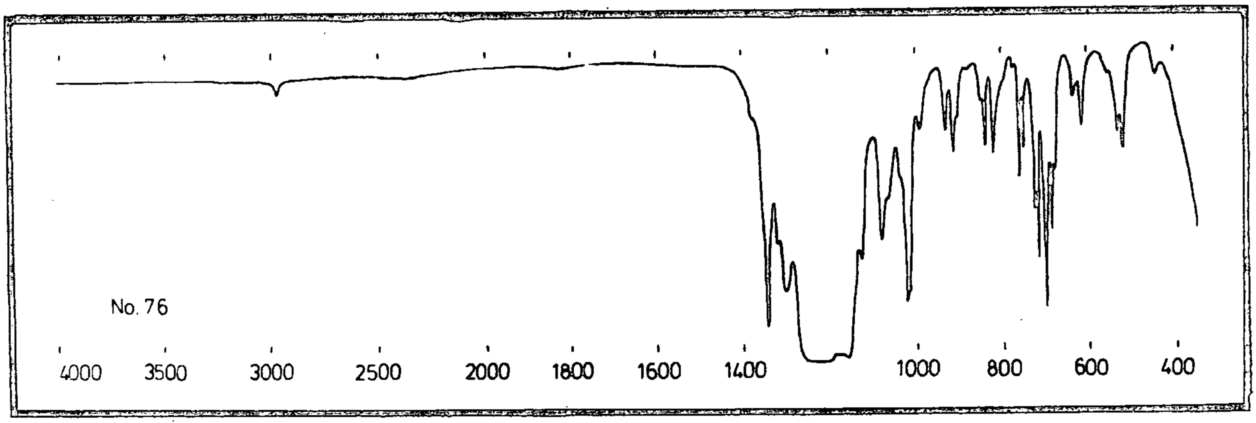


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE			
1	28.13	7.36	28	108.99	32.52	54	175.06	0.65
2	30.92	7.17	29	109.95	1.22	55	178.04	1.11
3	32.02	1.03	30	110.95	1.56	56	191.04	0.65
4	36.16	1.49	31	112.02	9.34	57	197.03	23.03
5	44.12	5.49	32	113.05	1.07	58	198.04	0.84
6	47.08	3.09	33	116.03	100.00	59	198.99	7.13
7	48.94	0.72	34	117.02	2.06	60	225.04	47.77
8	49.88	0.50	35	118.00	30.84	61	226.01	2.59
9	62.04	1.33	36	118.97	0.57	62	227.03	14.49
10	63.05	82.08	37	125.03	23.29	63	228.01	0.69
11	64.07	0.53	38	126.05	0.65			
12	65.08	25.58	39	127.03	7.28			
13	66.08	2.59	40	128.00	0.69			
14	68.02	0.50	41	131.01	5.64			
15	68.99	26.57	42	131.97	11.97			
16	70.98	0.84	43	134.00	7.85			
17	74.09	0.57	44	136.00	0.91			
18	80.96	5.79	45	143.07	3.05			
19	82.00	1.18	46	147.03	67.82			
20	85.03	5.41	47	148.02	2.21			
21	87.01	1.56	48	148.98	21.08			
22	93.03	38.62	49	149.98	0.42			
23	94.06	1.11	50	159.92	3.13			
24	97.01	5.76	51	162.01	7.09			
25	98.96	1.83	52	163.00	6.06			
26	99.94	41.14	53	165.01	3.51			
27	100.95	0.95						



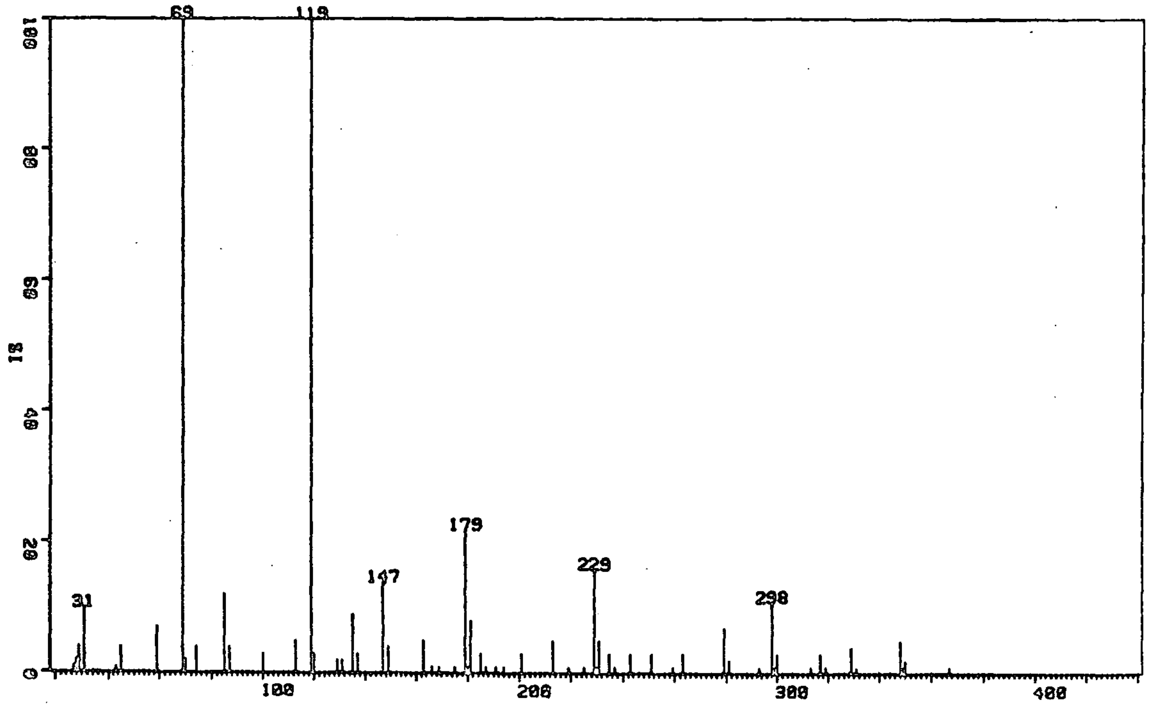
No.76

3-Chloro-3,4-di(trifluoromethyl)-1,1,1,2,2,5,5,6,6,6-decafluorohexane (142).



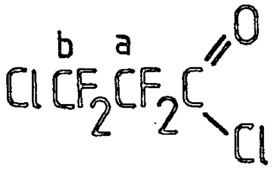
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
4.07	M	-	c
^{19}F			
58.3	M	3	g
59.7	M		
69.0	M	3	h
79.8	M	3	a
81.0	M		
86.8	M	3	f
87.7	M		
107.7	M(broad)	4	b, e

M.Wt. 436·5 No.76

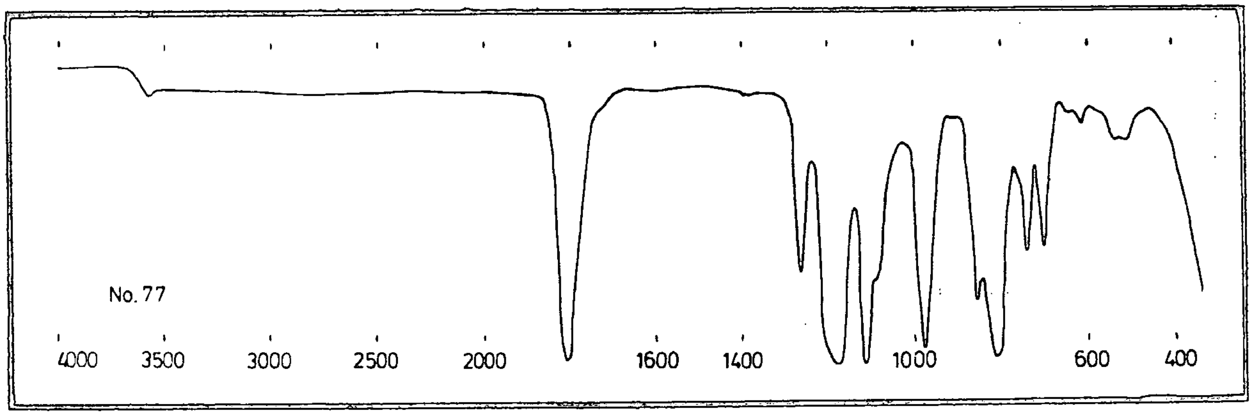


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE			
1	27.25	1.25	32	178.94	21.83	54	246.94	0.49
2	28.13	2.15	33	179.94	0.93	55	250.94	2.64
3	29.02	4.18	34	180.96	7.84	56	258.97	0.61
4	30.93	10.35	35	181.98	0.34	57	263.02	2.78
5	40.98	0.46	36	185.01	2.91	58	278.98	6.91
6	43.11	1.05	37	186.99	0.66	59	280.00	0.37
7	45.17	3.76	38	190.97	0.46	60	280.99	2.15
8	59.02	6.62	39	193.03	0.32	61	292.95	0.59
9	68.97	100.00	40	194.04	0.56	62	296.94	0.29
10	69.91	1.81	41	197.03	0.46	63	297.93	10.96
11	73.11	0.32	42	200.99	2.66	64	298.86	0.78
12	74.14	4.03	43	210.00	0.32	65	299.93	3.25
13	75.06	0.46	44	213.02	4.66	66	309.00	0.42
14	84.97	12.38	45	218.99	1.29	67	313.07	1.10
15	86.94	3.83	46	225.03	0.59	68	317.00	3.42
16	99.87	2.98	47	228.94	16.21	69	318.98	0.95
17	113.01	4.71	48	229.92	0.88	70	328.95	4.18
18	118.95	100.00	49	230.94	5.10	71	330.93	1.37
19	119.92	3.00	50	235.00	3.08	72	347.96	5.10
20	125.03	0.32	51	237.00	0.76	73	348.94	0.34
21	128.94	2.10	52	240.98	0.42	74	349.92	1.64
22	130.94	1.54	53	242.98	2.81	75	367.00	1.05
23	134.99	8.74						
24	136.96	3.15						
25	146.98	14.48						
26	147.97	0.42						
27	148.93	4.32						
28	163.00	4.79						
29	165.97	0.61						
30	168.98	0.61						
31	175.02	1.39						

No. 77

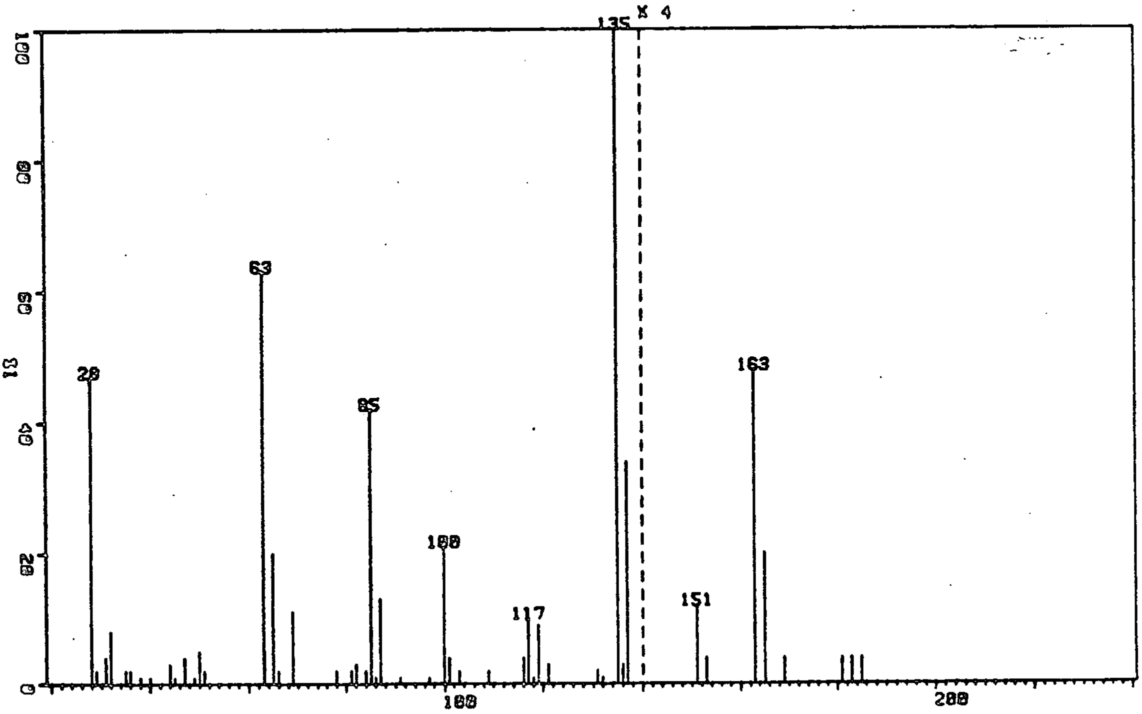


3-Chlorotetrafluoropropanoyl chloride (144).

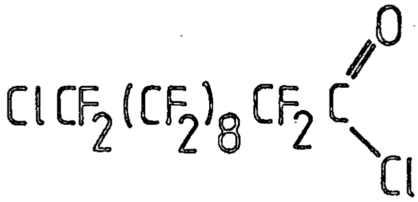


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
71.3	T, J=4	2	b
113.8	T, J=4	2	a

M.Wt.199 No.77

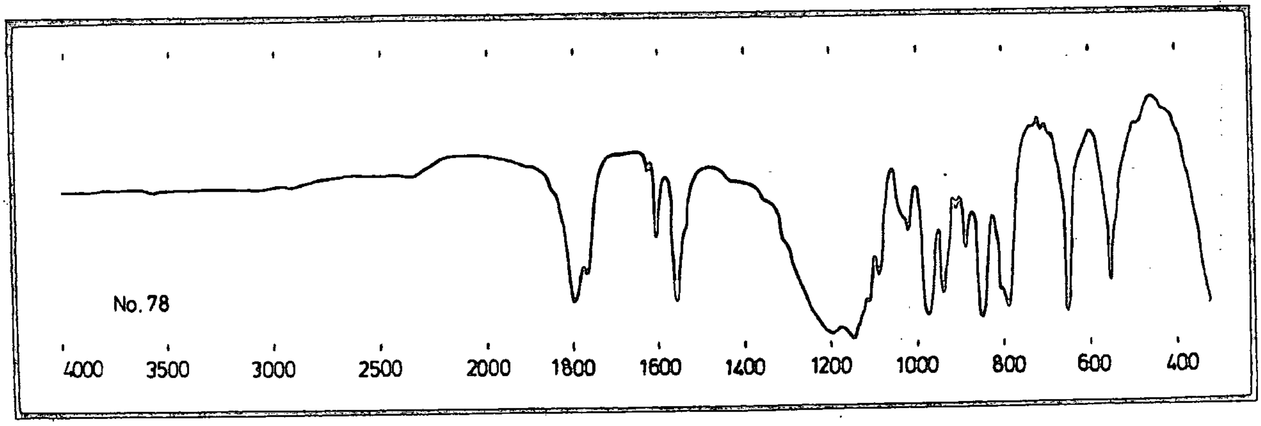


PEAK NO.	MASS	%HT. BASE
1	28.13	46.57
2	29.00	1.76
3	30.91	4.11
4	32.02	8.16
5	35.16	1.57
6	36.16	1.83
7	38.05	1.05
8	39.84	0.98
9	44.12	2.42
10	45.15	1.31
11	47.07	3.53
12	48.94	1.18
13	49.88	5.29
14	50.95	1.83
15	63.02	62.70
16	63.10	4.90
17	65.06	20.38
18	66.06	1.83
19	68.96	10.78
20	78.00	1.76
21	80.94	1.50
22	81.91	2.55
23	83.96	2.09
24	85.00	41.61
25	86.01	1.18
26	86.98	12.67
27	91.01	1.05
28	97.02	1.05
29	99.90	20.57
30	100.91	3.98
31	102.94	2.29
32	108.95	1.63
33	115.96	3.79
34	116.92	9.54
35	117.93	0.98
36	118.89	9.21
37	120.88	2.61
38	130.98	1.89
39	132.03	0.78
40	135.02	100.00
41	136.01	2.68
42	136.98	34.16
43	150.93	3.40
44	153.00	1.24
45	162.98	12.34
46	164.99	4.83
47	168.95	1.05
48	180.99	1.11
49	182.97	1.37
50	185.01	0.78



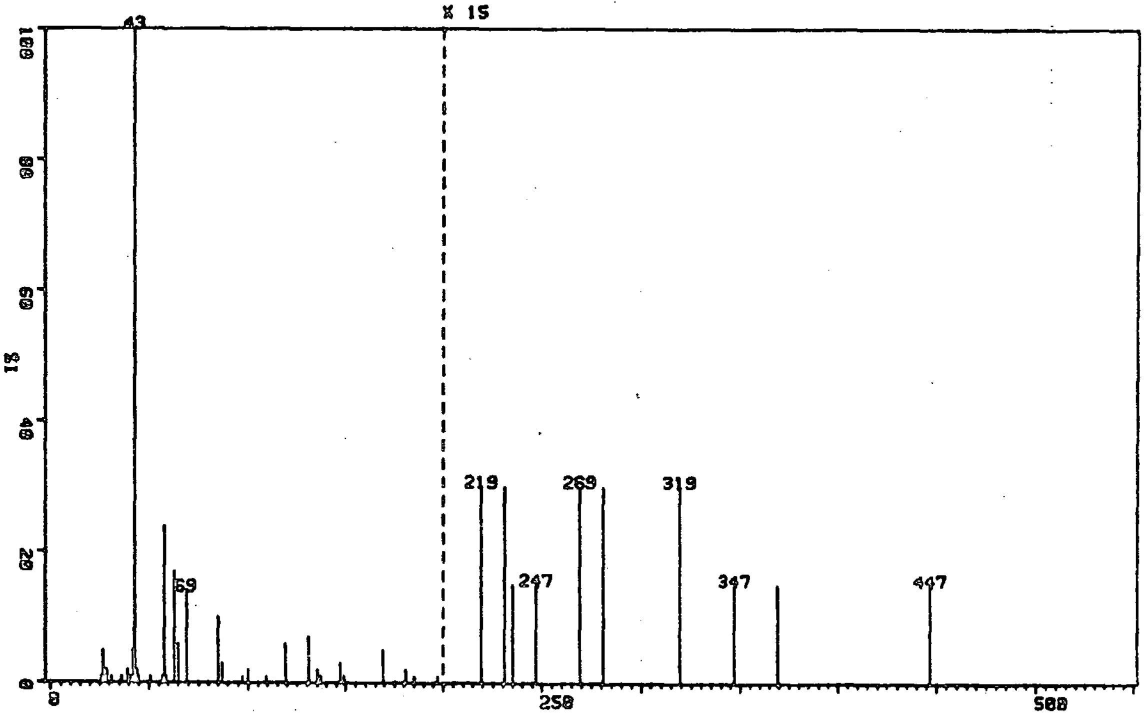
No. 78

11-Chloroeicosafluoroundecanoyl chloride (146).

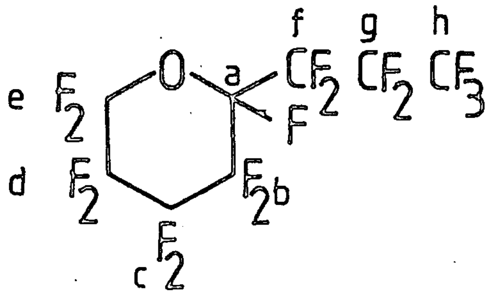


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
<u>^{19}F</u>			
68.3	M	2	a
112.8	M	2	c
120.0	M	16	b
121.3	M		

M.Wt. 599 No.78

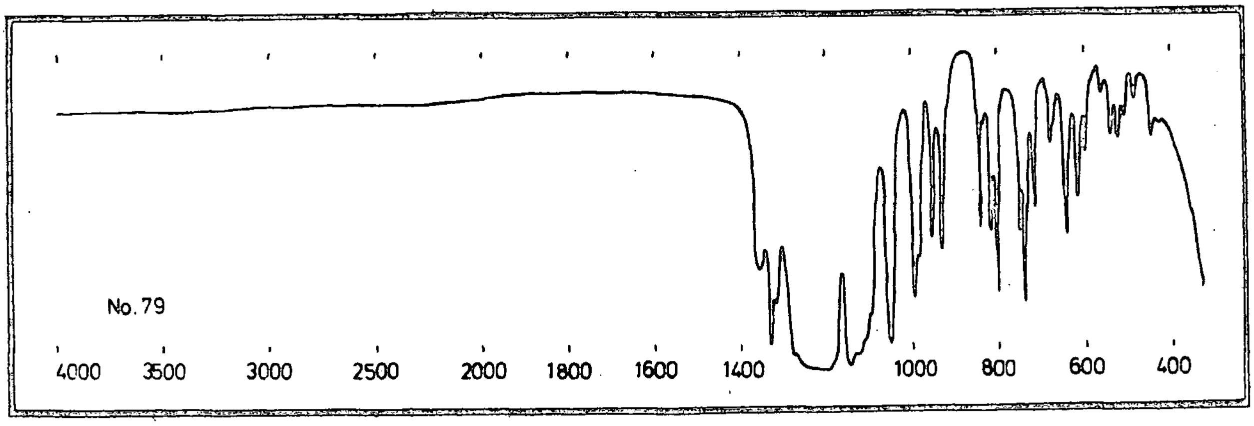


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	26.00	1.00*	36	197.00	1.00*
2	27.00	5.00*	37	219.00	2.00*
3	28.00	2.00*	38	231.00	2.00*
4	29.00	2.00*	39	235.00	1.00*
5	31.00	1.00*	40	247.00	1.00*
6	36.00	1.00*	41	269.00	2.00*
7	39.00	2.00*	42	281.00	2.00*
8	40.00	1.00*	43	319.00	2.00*
9	41.00	1.00*	44	347.00	1.00*
10	42.00	5.00*	45	369.00	1.00*
11	43.00	100.00*	46	447.00	1.00*
12	44.00	2.00*	47	534.00	1.00*
13	45.00	1.00*	48	562.00	1.00*
14	51.00	1.00*	49	564.00	1.00*
15	57.00	1.00*			
16	58.00	24.00*			
17	59.00	1.00*			
18	63.00	17.00*			
19	65.00	6.00*			
20	69.00	14.00*			
21	85.00	10.00*			
22	85.00	10.00*			
23	87.00	3.00*			
24	97.00	1.00*			
25	100.00	2.00*			
26	109.00	1.00*			
27	119.00	6.00*			
28	131.00	7.00*			
29	135.00	2.00*			
30	137.00	1.00*			
31	147.00	3.00*			
32	149.00	1.00*			
33	169.00	5.00*			
34	181.00	2.00*			
35	185.00	1.00			



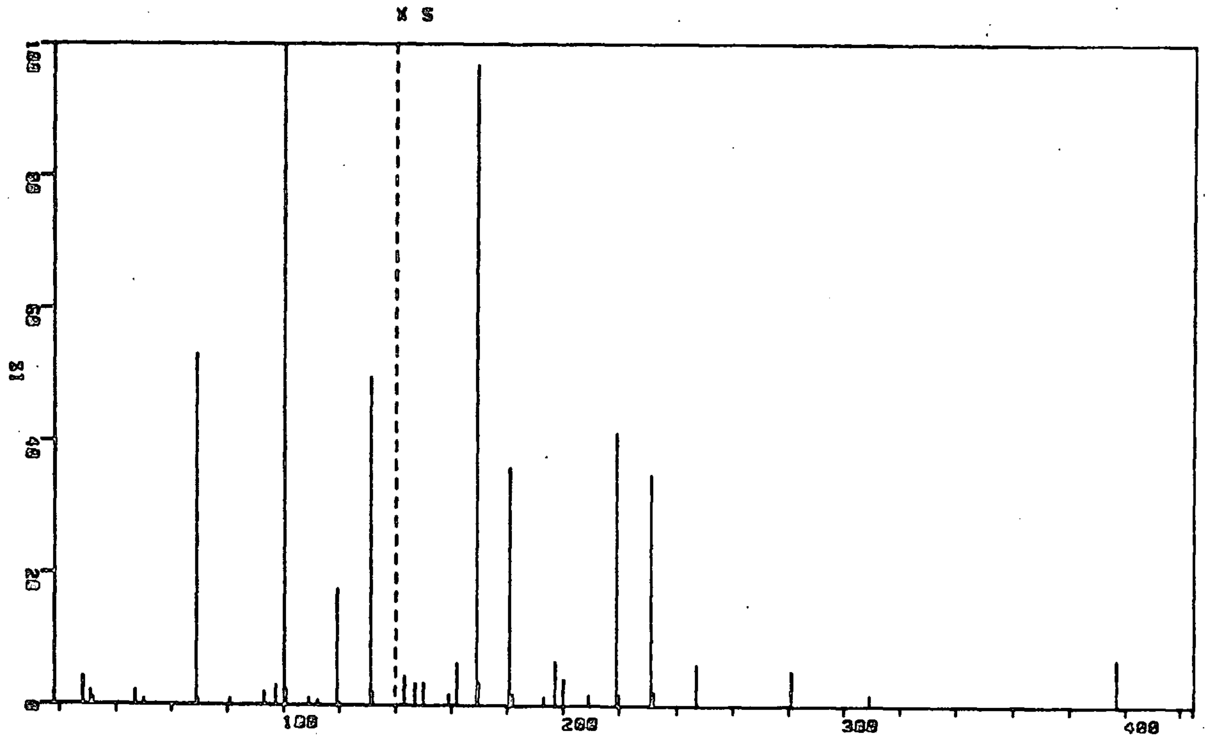
No.79

Perfluoro-2-propyloxane (156).



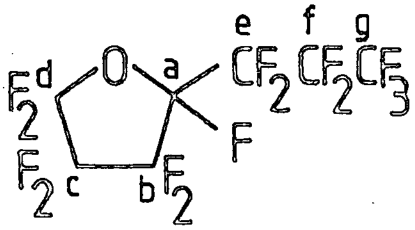
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
81.2, 95.0	AB, J_{FF}=164	2	e
84.5	M	3	h
117.7, 123.0, 124.3, 125.2, 128.0, 129.8, 132.0, 133.2, 139.7, 141.8, 144.7, 146.8,	Overlapping AB's	11	a, b, c, d, f, g

M.Wt. 416 No. 79

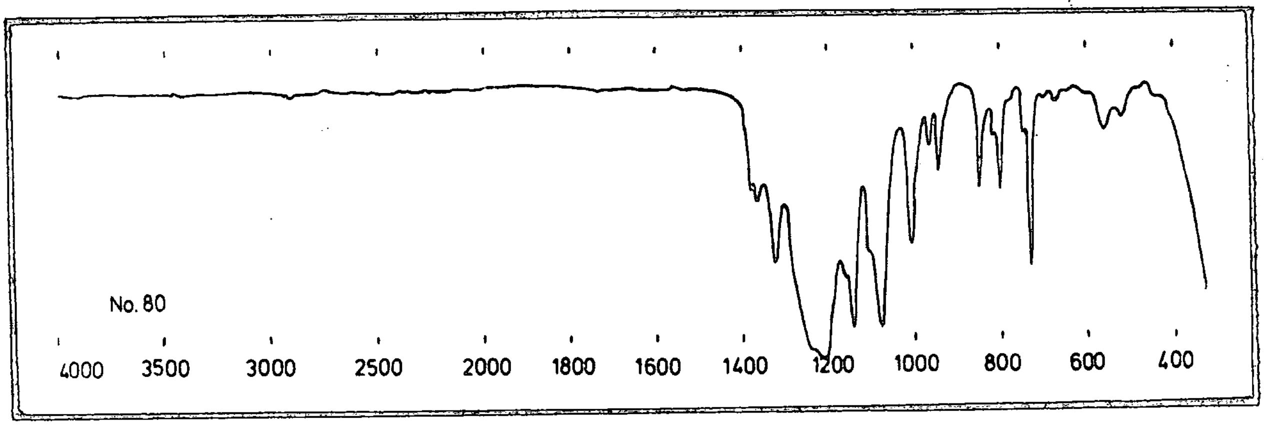


PEAK NO.	MASS	% INT BASE	PEAK NO.	MASS	% INT BASE
1	28.13	4.31	26	180.91	7.23
2	30.90	2.06	27	181.89	0.39
3	32.02	0.93	28	182.15	0.26
4	47.08	2.19	29	192.99	0.28
5	49.87	0.85	30	196.96	1.39
6	68.97	53.01	31	199.90	0.80
7	69.92	0.72	32	208.97	0.39
8	80.94	0.90	33	218.94	8.28
9	93.01	1.99	34	219.95	0.39
10	97.01	3.07	35	230.87	7.05
11	99.90	100.00	36	231.94	0.46
12	100.94	2.30	37	246.92	1.29
13	108.94	1.11	38	280.88	1.11
14	111.98	0.72	39	309.03	0.39
15	118.94	17.63	40	396.89	1.42
16	119.91	0.41			
17	130.94	49.63			
18	131.97	1.88			
19	142.99	0.90			
20	146.97	0.67			
21	149.91	0.67			
22	158.99	0.36			
23	161.94	1.32			
24	168.92	19.35			
25	169.92	0.70			

No.80

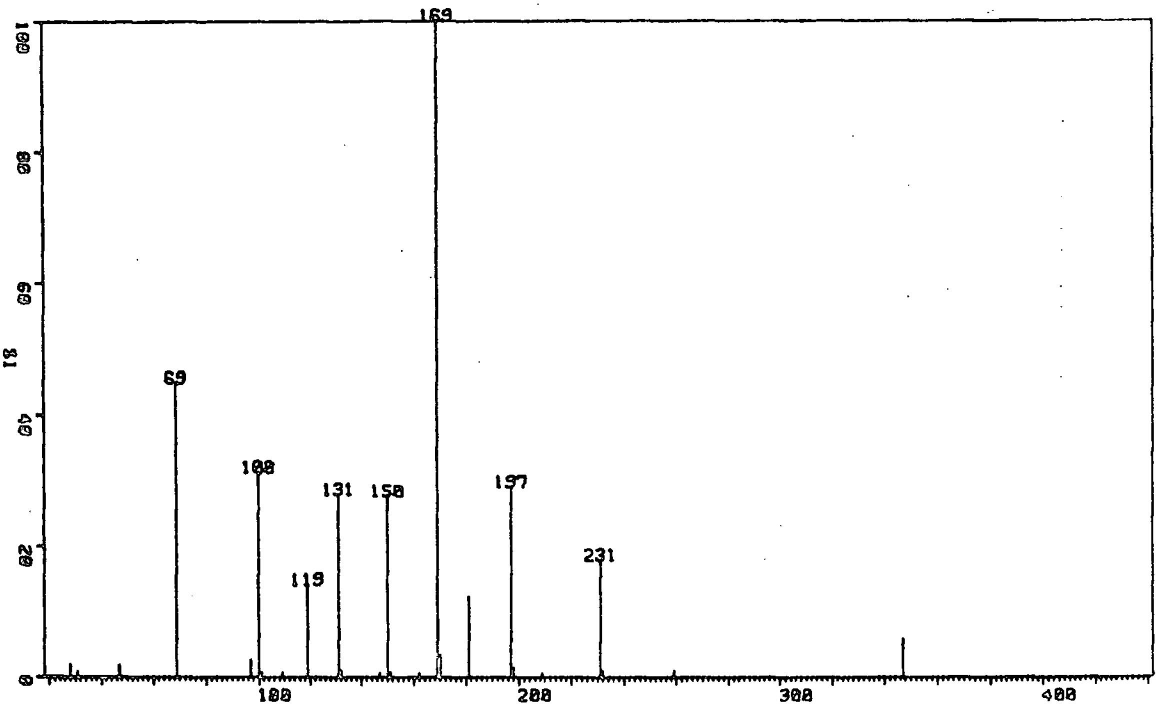


Perfluoro-2-propyloxolane (157).

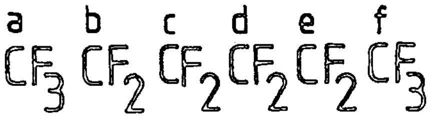


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
81.3	M	3	g
82.3, 84.5	AB, J_{FF}=132	2	d
121.4, 124.3	AB, J_{FF}=339	2	b or c
124.0	M	1	a
125.8	M	2	e or f
128.3	M	2	f or e
127.0, 136.3	AB, J_{FF}=254	2	c or b

M.Wt.366 No.80



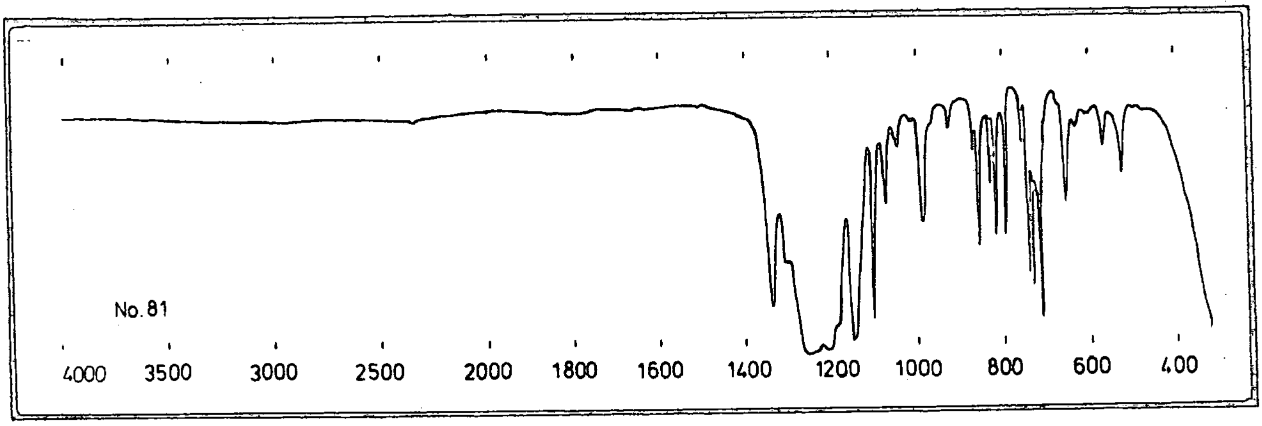
PEAK NO.	MASS	%HT. BASE
1	28.13	1.99
2	30.91	0.92
3	47.11	1.84
4	69.01	44.86
5	97.09	2.67
6	99.98	31.33
7	101.04	0.73
8	109.02	0.78
9	119.06	14.16
10	131.06	27.98
11	132.09	0.97
12	147.10	0.63
13	150.00	27.69
14	151.06	0.82
15	162.08	0.63
16	169.06	100.00
17	170.06	3.35
18	181.05	12.32
19	197.07	29.10
20	198.08	1.36
21	209.04	0.68
22	231.02	17.99
23	232.08	0.87
24	259.10	1.02
25	347.10	5.92



$\overset{a}{CF_3}\overset{b}{CF_2}\overset{c}{CF_2}\overset{d}{CF_2}\overset{e}{CF_2}\overset{f}{CF_3}$

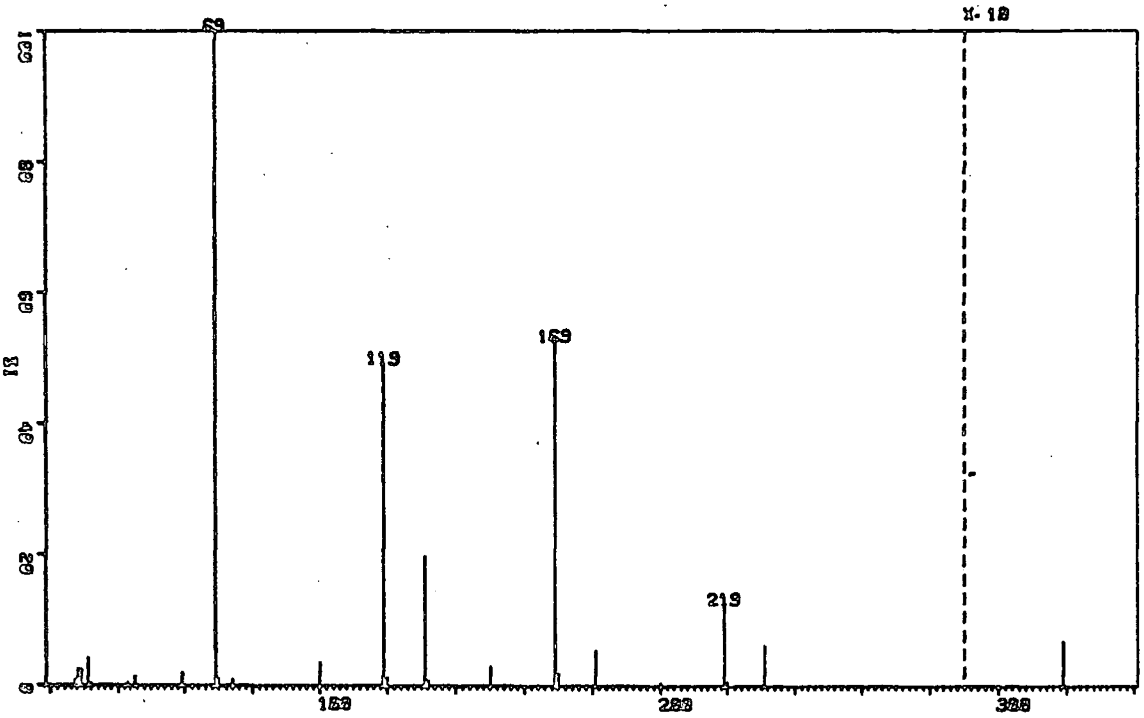
No. 81

Perfluorohexane (158).



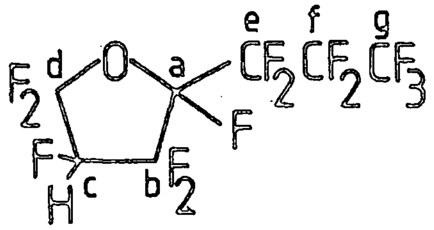
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
84.7	M	6	a , f
125.7	M	4	c , d
129.2	M	4	b , e

M.Wt. 338 No. 81

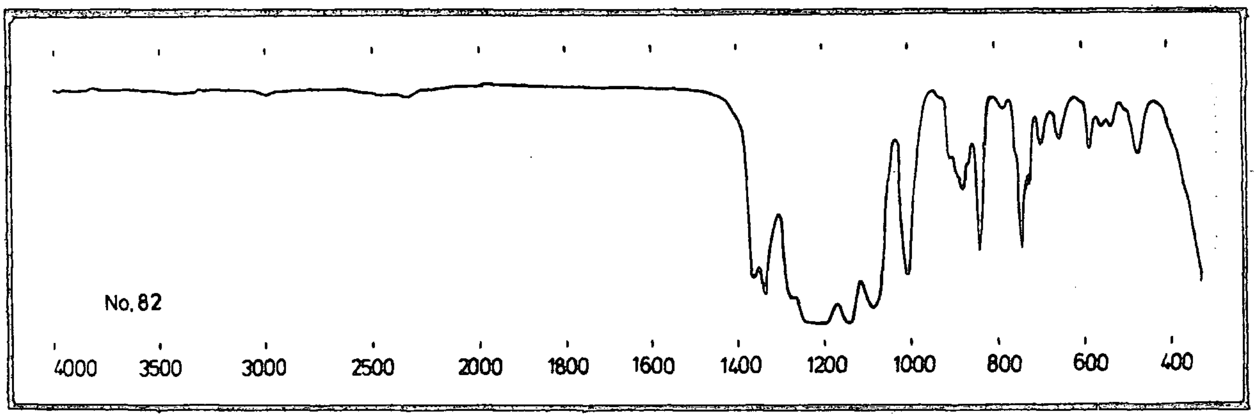


PEAK NO.	MASS	%HT. BASE
1	27.25	0.87
2	28.13	2.48
3	29.02	2.44
4	30.92	4.08
5	32.01	0.40
6	43.11	0.40
7	45.17	1.38
8	59.03	1.86
9	68.97	100.00
10	69.22	0.36
11	69.38	0.51
12	69.91	1.13
13	74.14	0.98
14	99.87	3.57
15	118.49	0.36
16	118.97	49.27
17	119.94	1.24
18	130.96	19.77
19	131.97	0.76
20	149.90	3.02
21	168.94	52.66
22	169.94	1.86
23	180.93	5.43
24	199.87	0.47
25	218.94	12.53
26	219.96	0.62
27	230.90	6.15
28	318.92	0.69

No.82

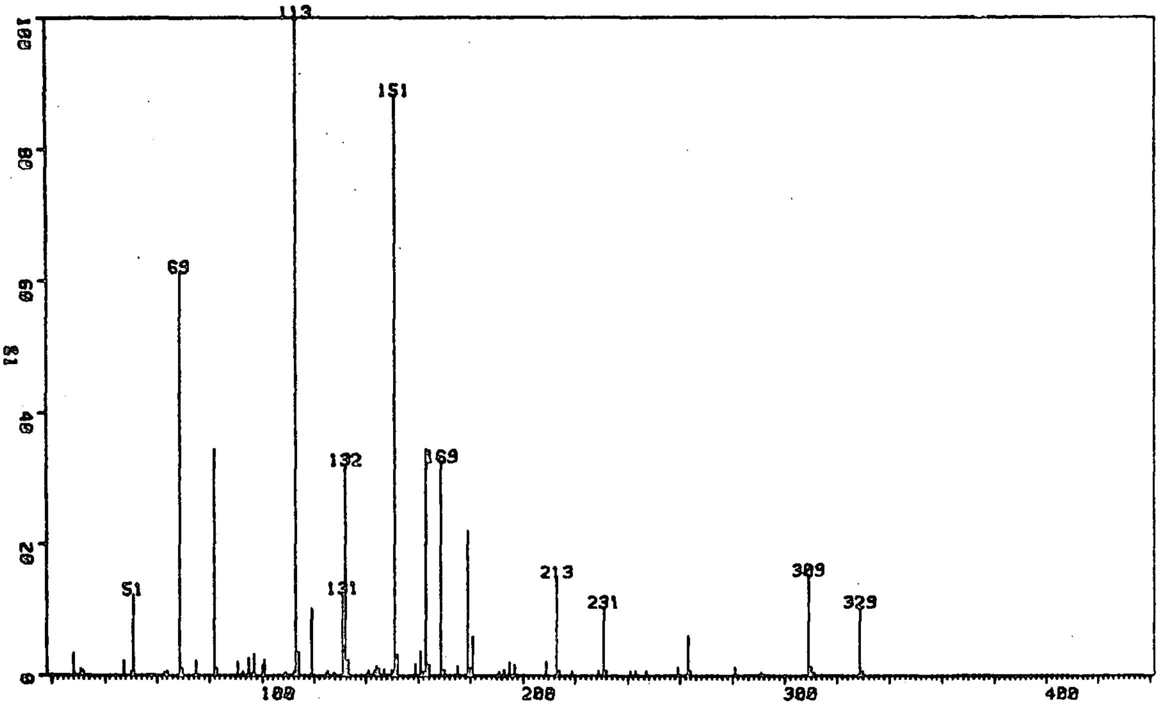


2,3,3,4,5,5-Hexafluoro-2-(heptafluoropropyl)oxolane (161).



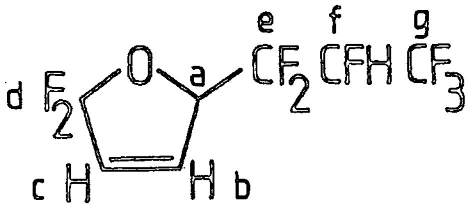
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
5.07	D of M, J_{FH}=48	-	c
^{19}F			
72.4, 80.3	AB, J_{FF}=141	2	d
81.0	M	3	g
116.3	M	7	a, b, e, f
121.7	M		
122.8	M		
125.3	M		
205.3	D of M, J_{FH}=45	1	c

M.Wt. 348 No. 82

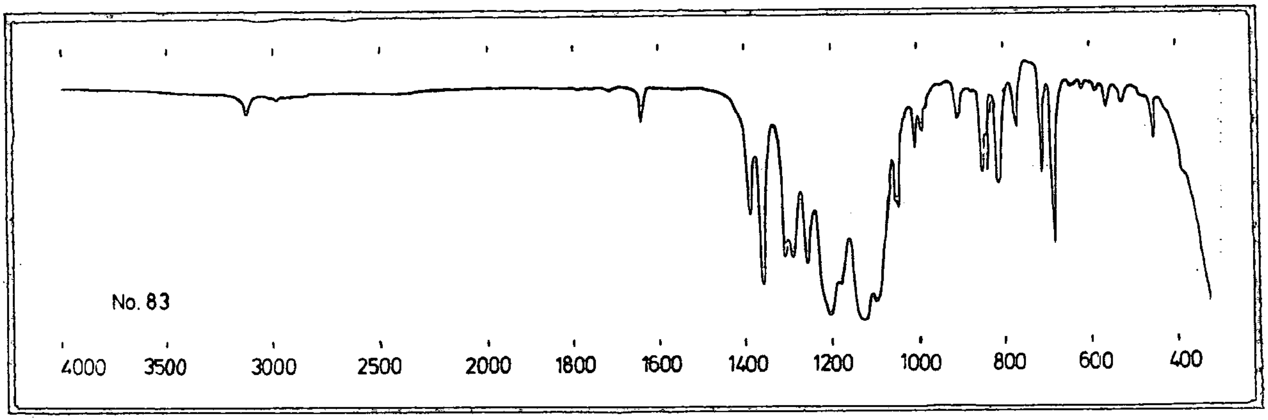


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.14	3.36	36	143.99	1.39	71	290.95	0.44
2	30.92	0.98	37	145.01	1.02	72	309.00	15.36
3	32.03	0.61	38	146.96	0.88	73	309.97	1.25
4	47.13	2.20	39	149.91	0.85	74	311.01	0.47
5	49.91	0.54	40	150.94	88.10	75	328.88	10.47
6	50.98	12.31	41	151.95	3.15	76	329.94	0.68
7	63.13	0.37	42	158.95	1.76			
8	64.16	0.71	43	160.95	3.69			
9	68.71	0.37	44	161.97	0.44			
10	68.97	61.32	45	162.97	34.47			
11	69.91	0.88	46	163.99	1.59			
12	75.05	2.24	47	168.91	32.58			
13	81.95	34.37	48	169.88	0.85			
14	82.98	0.95	49	175.02	1.36			
15	90.94	2.03	50	178.94	22.07			
16	93.00	0.51	51	179.90	1.08			
17	95.07	2.64	52	180.92	6.00			
18	96.41	0.37	53	190.90	0.44			
19	96.98	3.22	54	192.95	0.95			
20	99.93	1.59	55	194.97	1.93			
21	100.97	2.41	56	196.93	1.59			
22	108.93	0.44	57	208.92	2.17			
23	111.95	0.44	58	212.94	15.02			
24	112.17	0.47	59	213.98	0.78			
25	112.47	0.61	60	218.95	0.68			
26	112.99	100.00	61	228.94	0.64			
27	113.99	3.56	62	230.89	10.41			
28	118.94	10.20	63	231.98	0.58			
29	125.04	0.64	64	241.00	0.68			
30	127.58	0.37	65	242.97	0.78			
31	130.95	12.51	66	246.98	0.78			
32	131.99	32.10	67	258.95	1.22			
33	133.02	2.41	68	263.02	6.03			
34	140.97	0.75	69	264.00	0.68			
35	143.03	0.64	70	280.97	1.25			

No.83

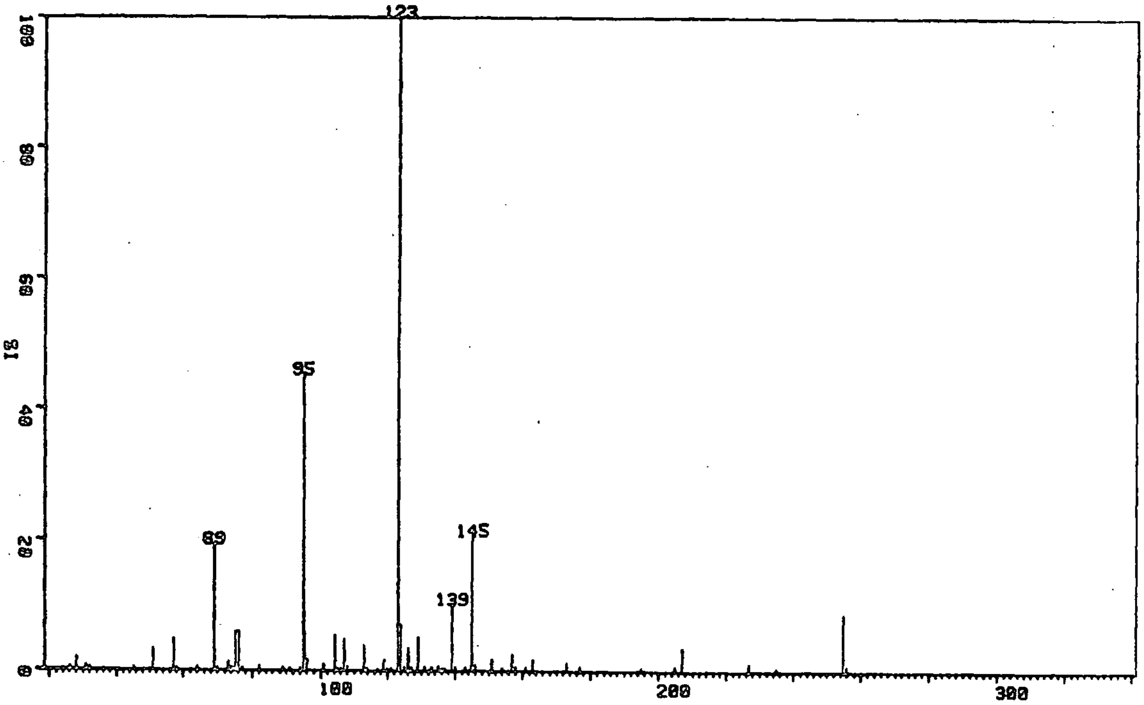


2,5,5-Trifluoro-2-(1,1,2,3,3,3-hexafluoropropyl)oxol-3-en (162).



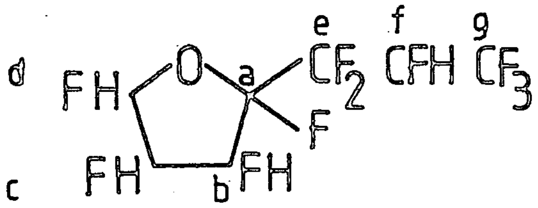
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
4.70	D of M, J_{FH}=42	1	f
6.08	S	2	b, c
^{19}F			
68.2, 75.9	AB, J_{FF}=127	2	d
76.8	M	3	g
121.2	M	1	a
124.8, 129.1	AB, J_{FF}=288	2	e
214.7	D of M, J_{FH}=42	1	f

M.Wt. 274 No.83

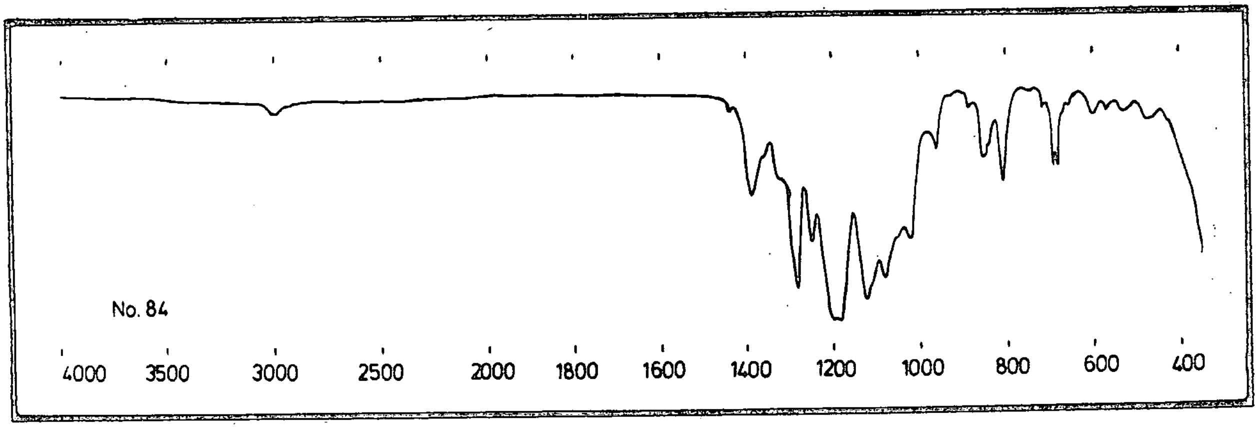


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	26.31	0.43	36	118.92	1.82
2	28.13	1.89	37	119.88	0.39
3	30.91	0.75	38	120.96	0.36
4	32.02	0.39	39	122.90	100.00
5	45.16	0.46	40	123.70	7.07
6	50.95	3.22	41	124.91	0.71
7	57.10	4.89	42	125.97	3.54
8	58.06	0.32	43	126.93	0.57
9	64.10	0.61	44	128.89	5.25
10	68.95	19.40	45	130.91	0.68
11	69.89	0.50	46	132.97	0.57
12	73.04	1.39	47	135.00	0.79
13	73.35	0.36	48	136.01	0.32
14	73.73	0.46	49	136.96	0.32
15	74.08	0.43	50	138.92	10.15
16	74.38	0.39	51	139.92	0.64
17	75.06	5.97	52	142.99	0.57
18	76.04	5.97	53	144.96	20.76
19	77.03	0.50	54	145.98	0.96
20	81.97	0.75	55	150.92	1.89
21	88.96	0.61	56	153.96	0.50
22	90.94	0.46	57	156.95	2.61
23	94.03	0.54	58	157.93	0.71
24	95.02	45.41	59	160.90	0.68
25	95.28	5.82	60	162.97	1.82
26	95.95	1.68	61	172.98	1.32
27	100.89	1.04	62	176.98	0.82
28	104.00	5.47	63	195.00	0.68
29	105.01	0.46	64	204.96	0.82
30	106.02	0.46	65	206.95	3.61
31	106.99	4.79	66	226.92	1.21
32	107.97	0.75	67	234.91	0.57
33	112.97	3.89	68	254.88	8.72
34	113.98	0.50	69	255.85	0.86
35	116.97	0.32			

No. 84

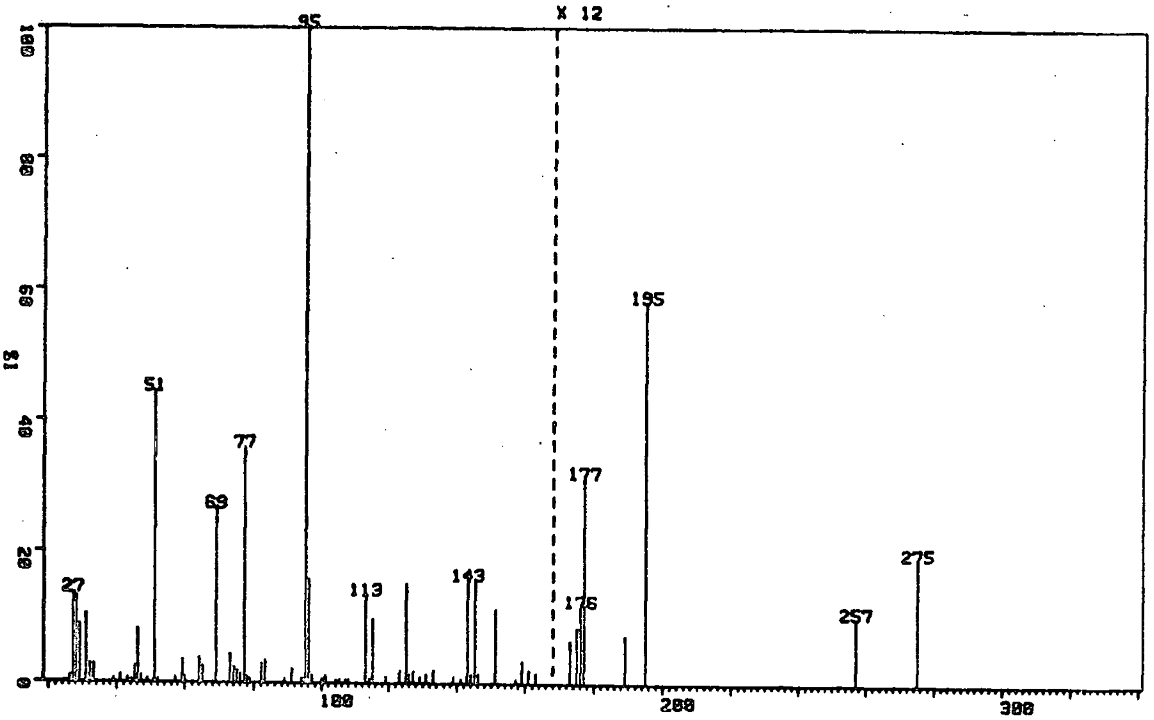


2,3,4,5-Tetrafluoro-2-(1,1,2,3,3,3-hexafluoropropyl)oxolane (163).



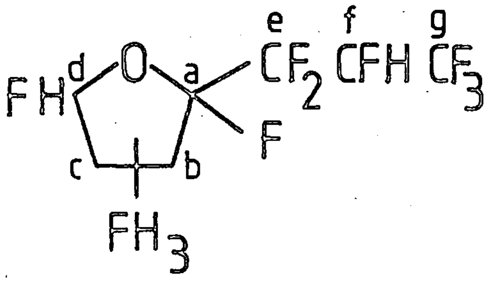
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
5.20	D of M (broad)	3	b, c, f
6.00	D of M (broad)	1	d
^{19}F			
77.3	M	3	g
124.9	M	4	a, d, e
126.8	M		
128.7	M		
130.4	M		
204.4	M	1	b or c
208.8	M	1	c or b
216.0	M	1	f

M.Wt. 294 No. 84

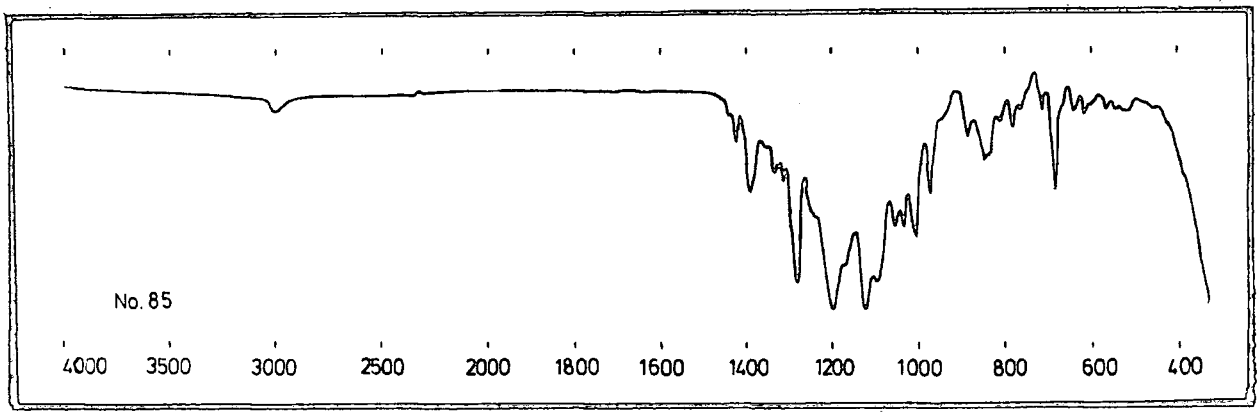


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	26.31	1.05	36	95.07	100.00	71	189.05	0.61
2	27.25	13.68	37	96.09	15.82	72	195.06	4.85
3	28.13	13.20	38	97.07	1.26	73	257.07	0.85
4	29.00	9.00	39	99.98	0.68	74	275.00	1.60
5	30.93	10.45	40	100.99	1.15			
6	32.02	2.95	41	104.09	0.54			
7	33.13	2.85	42	105.10	0.58			
8	39.01	0.51	43	107.02	0.58			
9	41.00	1.19	44	108.01	0.58			
10	43.12	0.78	45	113.00	13.48			
11	44.15	0.54	46	114.06	0.78			
12	45.17	2.51	47	115.04	9.81			
13	46.17	8.21	48	118.99	0.98			
14	47.12	1.12	49	123.06	1.93			
15	48.99	0.61	50	125.08	15.11			
16	50.96	44.43	51	126.06	1.39			
17	52.05	0.54	52	127.08	1.80			
18	57.14	0.92	53	129.02	1.05			
19	59.05	3.53	54	131.02	1.43			
20	59.94	0.98	55	133.08	2.04			
21	64.14	3.80	56	138.99	1.05			
22	65.12	2.58	57	141.03	0.78			
23	68.93	26.61	58	143.04	15.72			
24	73.02	4.38	59	144.06	1.46			
25	74.09	2.44	60	145.06	15.95			
26	75.03	1.93	61	146.05	1.53			
27	76.02	1.49	62	151.00	11.27			
28	76.99	35.88	63	157.11	0.78			
29	77.97	1.05	64	159.00	3.46			
30	78.89	0.71	65	160.99	2.00			
31	81.95	3.02	66	163.03	1.66			
32	83.00	3.46	67	173.11	0.54			
33	88.99	0.64	68	175.04	0.71			
34	90.94	2.17	69	176.10	0.98			
35	94.08	0.92	70	177.04	2.61			

No.85

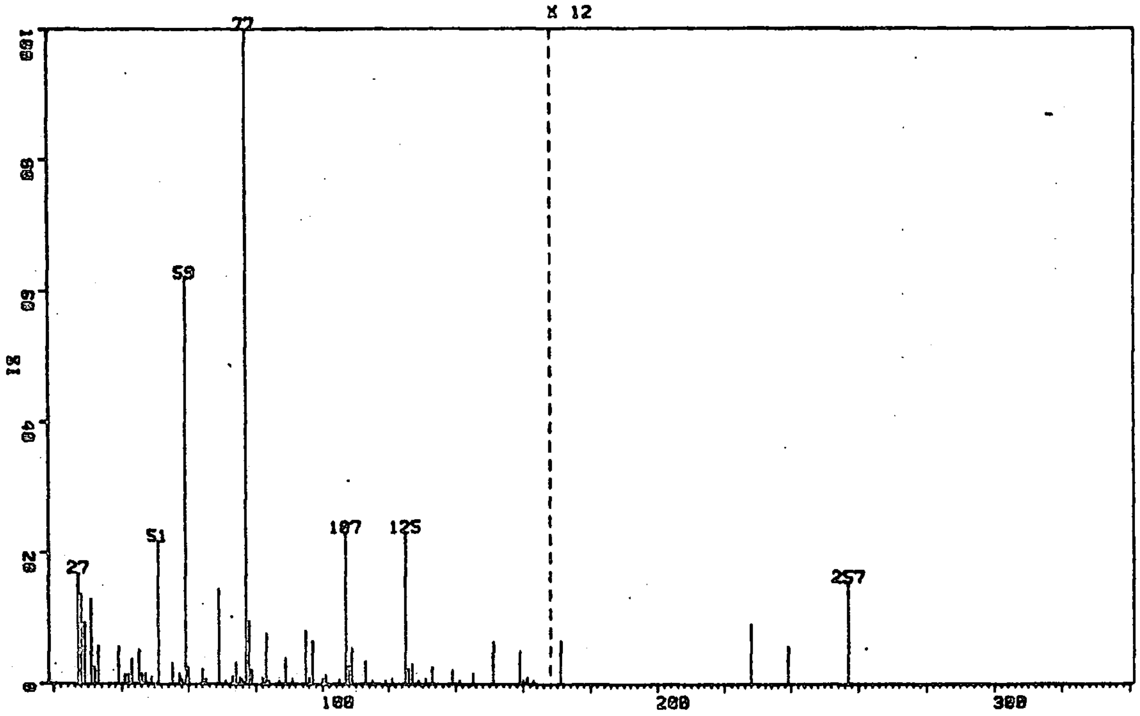


Trifluoro-2-(1,1,2,3,3,3-hexafluoropropyl)oxolane, isomer mixture (<u>164</u>).



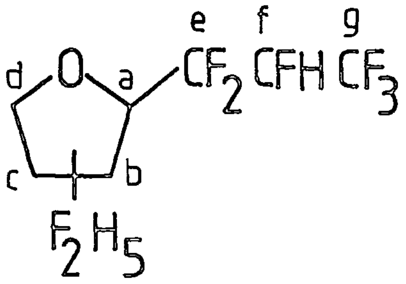
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
<u>^{1}H</u>			
2.30	M(broad)	2	CH_2, b or c
5.13	M(broad)	2	f and CFH, c or b
5.95	M(broad)	1	d
<u>^{19}F</u>			
76.7	M	3	g
106.7, 111.1, 123.1, 124.3, 125.0, 127.1, 128.9, 130.1, 131.7.	Overlapping M's	4	a, d, e
190.4	M	1	CFH, b or c
193.2	M		
214.2	M	1	f
217.7	M		

M.Wt. 276 No.85

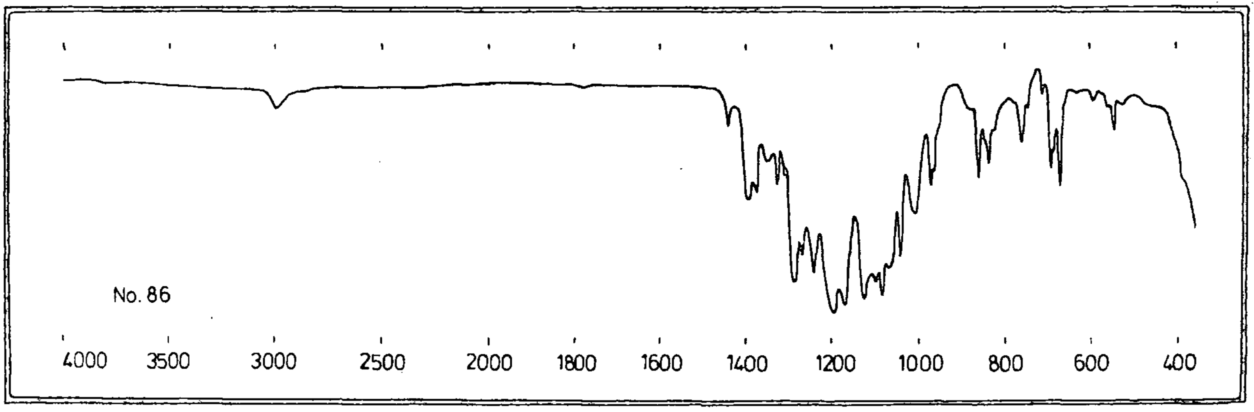


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.25	16.98	36	88.95	4.01
2	28.13	13.61	37	90.96	0.86
3	29.01	9.40	38	95.05	8.20
4	30.93	12.93	39	96.06	0.96
5	32.02	2.67	40	97.04	6.62
6	33.13	5.76	41	99.92	0.89
7	39.01	5.73	42	100.98	1.47
8	41.01	1.47	43	105.04	0.75
9	42.06	1.51	44	107.02	23.18
10	43.12	3.81	45	107.99	2.78
11	45.19	5.14	46	108.95	5.45
12	46.17	1.51	47	113.00	3.53
13	47.14	1.61	48	115.06	0.55
14	49.00	1.13	49	119.01	0.62
15	50.96	21.81	50	121.06	0.93
16	55.16	3.16	51	125.08	23.29
17	57.12	1.68	52	126.06	2.30
18	58.09	0.65	53	127.06	3.12
19	59.03	62.00	54	129.00	0.51
20	59.95	2.57	55	130.99	0.89
21	64.13	2.30	56	133.04	2.64
22	65.12	0.93	57	138.99	2.16
23	68.93	14.54	58	141.05	0.62
24	70.96	0.51	59	145.08	1.78
25	73.05	1.30	60	151.00	6.55
26	74.08	3.33	61	159.03	5.04
27	75.04	1.10	62	159.99	0.58
28	76.01	0.72	63	161.04	1.13
29	77.00	100.00	64	163.08	0.58
30	77.97	9.64	65	171.11	0.55
31	78.91	2.19	66	228.06	0.75
32	81.93	1.06	67	239.16	0.48
33	82.97	7.65	68	257.10	1.30
34	84.03	0.55			
35	87.01	0.48			

No.86

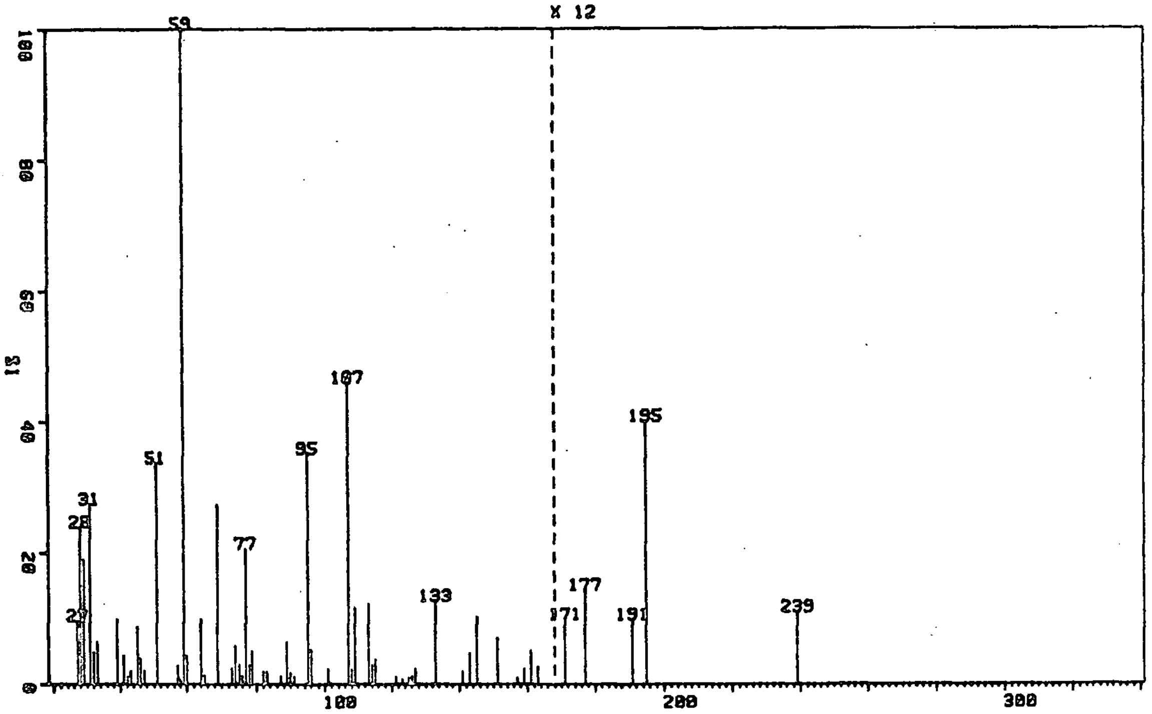


Difluoro-2-(1,1,2,3,3,3-hexafluoropropyl)oxolane, isomer mixture (165).



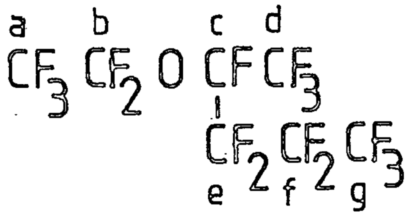
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
2.20	M	1	CH_2, b or c
4.80	M	2	f and CHO, a or d and CHF, c or b.
5.40	M		
^{19}F			
76.7	M	3	g
116.7, 124.6, 125.3, 126.8, 129.3,	Series of M's	3	e and CFO, d or a
193.0, 206.6, 209.6, 214.8, 218.2, 220.9.	Series of M's	2	f and CFH, c or b

M.Wt. 258 No. 86



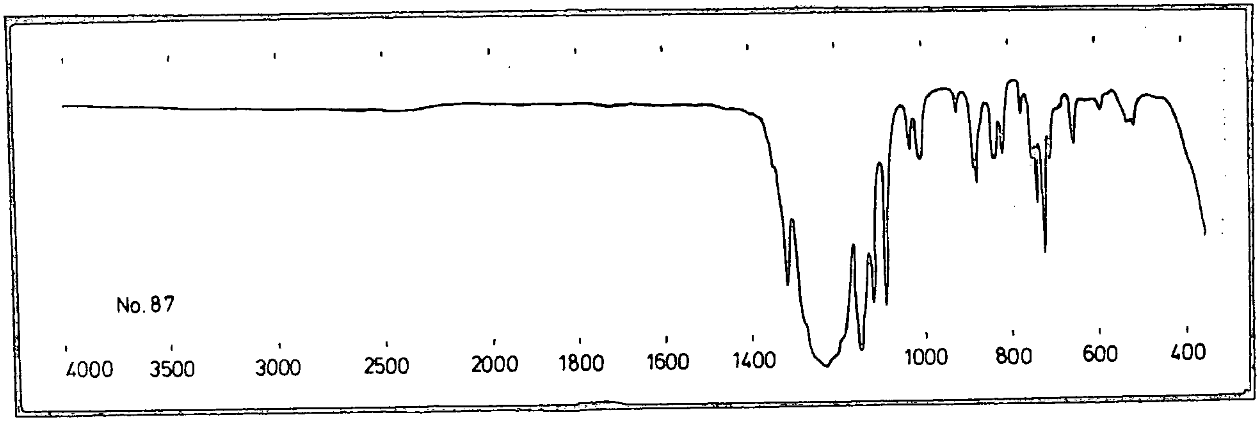
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.25	9.67	36	96.09	5.27
2	28.13	23.93	37	101.00	2.29
3	29.00	18.94	38	107.05	46.03
4	30.93	27.46	39	108.05	2.15
5	32.02	4.86	40	108.99	11.69
6	33.13	6.46	41	113.03	12.24
7	39.01	9.86	42	114.05	3.03
8	41.00	4.45	43	115.09	3.85
9	42.07	1.15	44	121.09	1.19
10	43.13	2.02	45	123.11	0.73
11	45.18	8.85	46	125.10	1.01
12	46.16	3.90	47	126.03	1.24
13	47.10	2.11	48	127.06	2.29
14	50.96	33.75	49	133.03	12.70
15	57.12	2.84	50	140.95	1.97
16	58.09	0.69	51	143.02	4.77
17	59.03	100.00	52	145.03	10.27
18	59.97	4.31	53	151.00	7.11
19	64.14	10.00	54	157.04	1.01
20	65.11	1.38	55	159.03	2.29
21	68.93	27.33	56	160.99	5.14
22	73.02	2.48	57	163.06	2.75
23	74.09	5.96	58	171.08	0.83
24	75.03	3.03	59	177.06	1.19
25	76.01	1.33	60	191.05	0.83
26	77.00	20.68	61	195.09	3.35
27	77.96	2.98	62	239.16	0.92
28	78.92	5.09			
29	81.93	1.97			
30	83.00	1.88			
31	87.03	1.24			
32	88.95	6.51			
33	89.89	1.83			
34	90.98	1.15			
35	95.07	35.17			

No.87



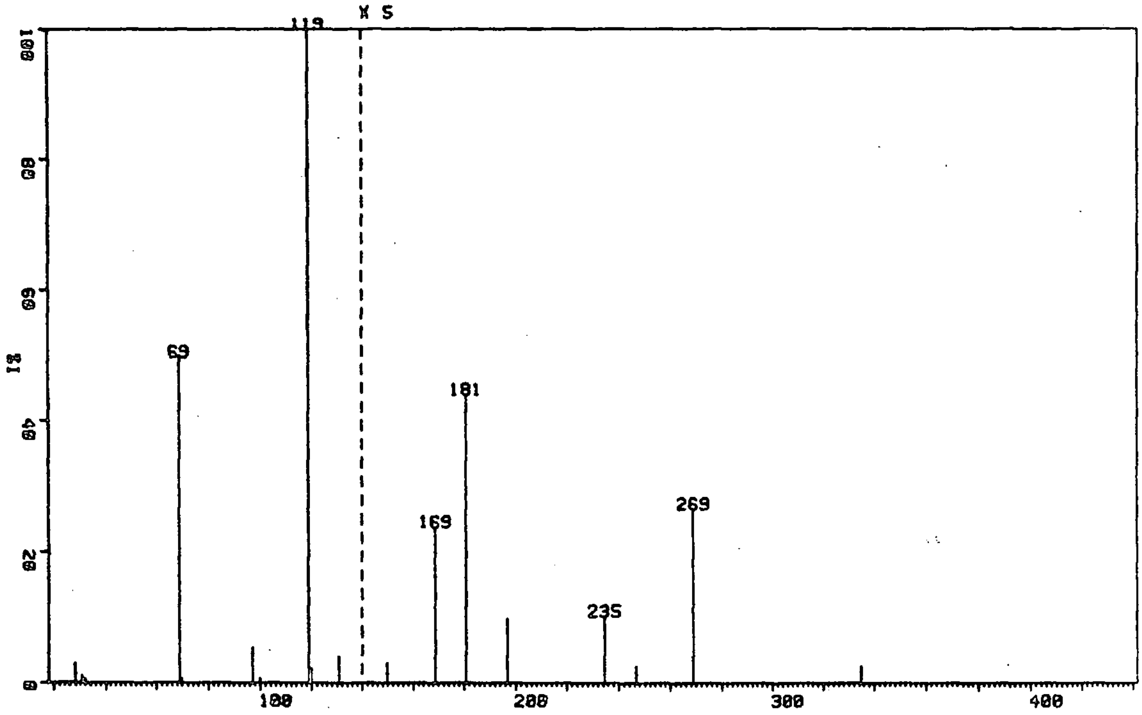
$CF_3CF_2OCF(CF_3)CF_2CF_2CF_3$

Perfluoro-1-methylbutyl ethyl ether (168).



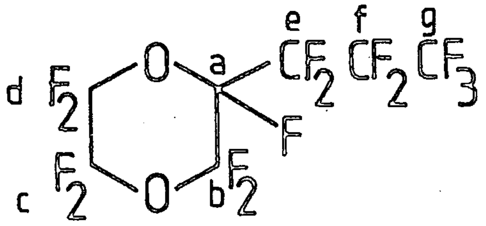
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
82.0	M	3	a or g
84.8	T, J=11	3	g or a
89.3	M	2	b
90.7	M	3	d
124.8	M	2	f
127.4, 130.3	AB, J_{FF}=288	2	e
142.8	M	1	c

M.Wt. 404 No. 87

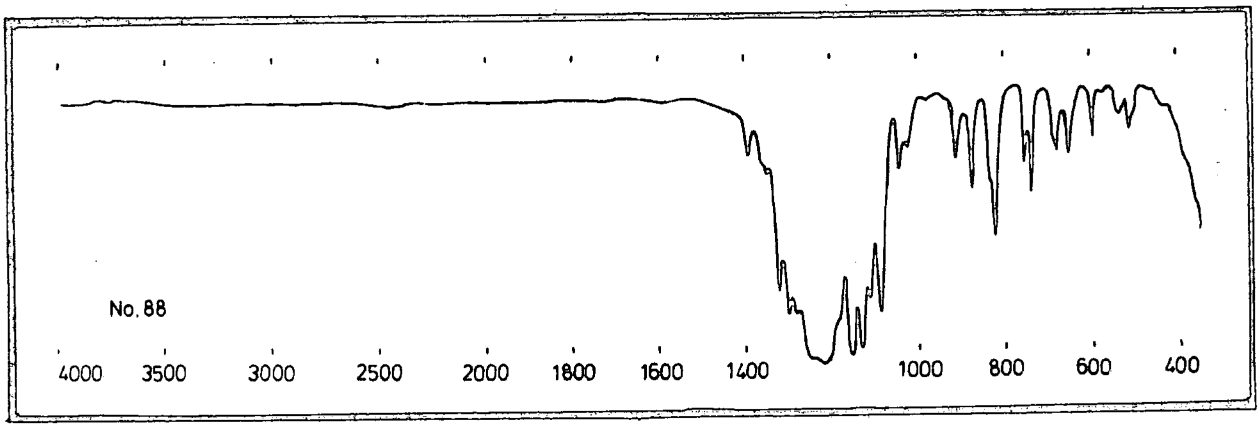


PEAK NO.	MASS	%HT. BASE
1	28.13	2.98
2	30.91	1.02
3	32.02	0.59
4	68.93	49.67
5	69.87	0.59
6	96.99	5.38
7	99.89	0.75
8	118.95	100.00
9	119.91	2.24
10	130.92	4.04
11	149.87	0.63
12	168.88	4.75
13	180.90	8.79
14	196.91	1.96
15	234.83	2.04
16	246.86	0.51
17	268.80	5.30
18	334.74	0.51

No.88

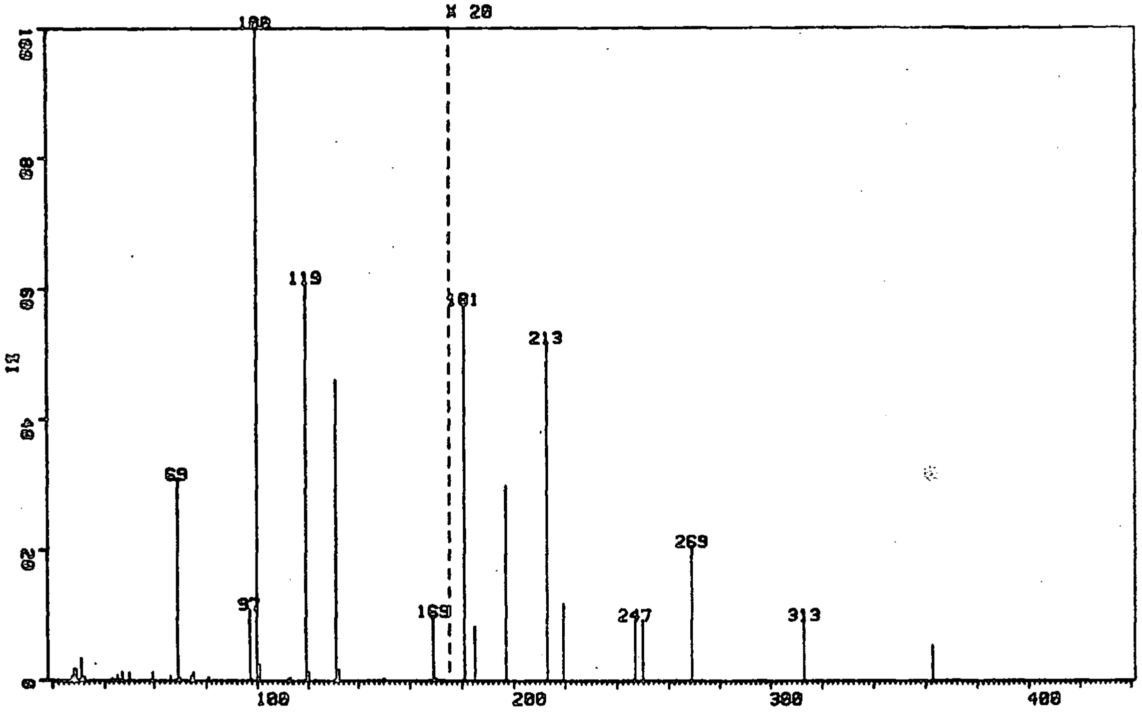


Perfluoro-2-propyl-1,4-dioxan (170).

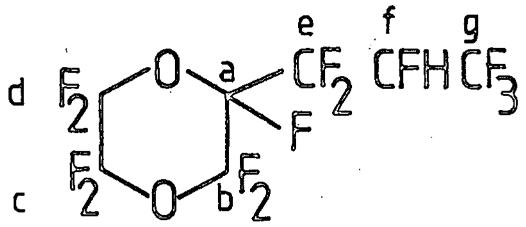


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
79.3, 82.7, 85.2, 88.0, 92.0, 95.0, 98.0.	Overlapping M's	9	b, c, d
84.0	T		g
124.3	M	2	e, f
127.5	M	2	
131.7	M	1	a

M.Wt. 382 No. 88

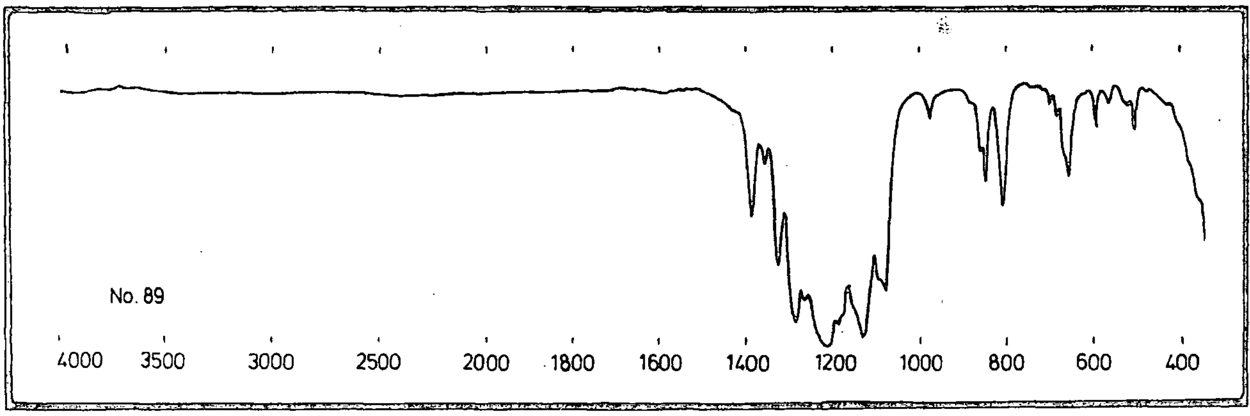


PEAK NO.	MASS	%HT. BASE
1	27.26	0.61
2	28.13	1.83
3	29.02	1.59
4	30.92	3.42
5	32.01	0.49
6	43.10	0.32
7	45.17	0.81
8	47.08	1.34
9	49.85	1.27
10	59.02	1.25
11	66.25	0.78
12	68.90	30.77
13	69.86	0.42
14	74.08	0.71
15	75.00	1.42
16	80.85	0.51
17	96.98	10.87
18	97.97	0.27
19	99.87	100.00
20	100.94	2.44
21	111.96	0.27
22	113.00	0.39
23	118.97	60.93
24	119.93	1.32
25	130.93	46.01
26	131.94	1.68
27	149.86	0.37
28	168.89	9.79
29	169.92	0.32
30	180.89	2.88
31	184.98	0.42
32	196.89	1.49
33	212.89	2.59
34	218.97	0.59
35	246.89	0.46
36	249.81	0.46
37	268.85	1.03
38	312.86	0.46
39	362.84	0.27



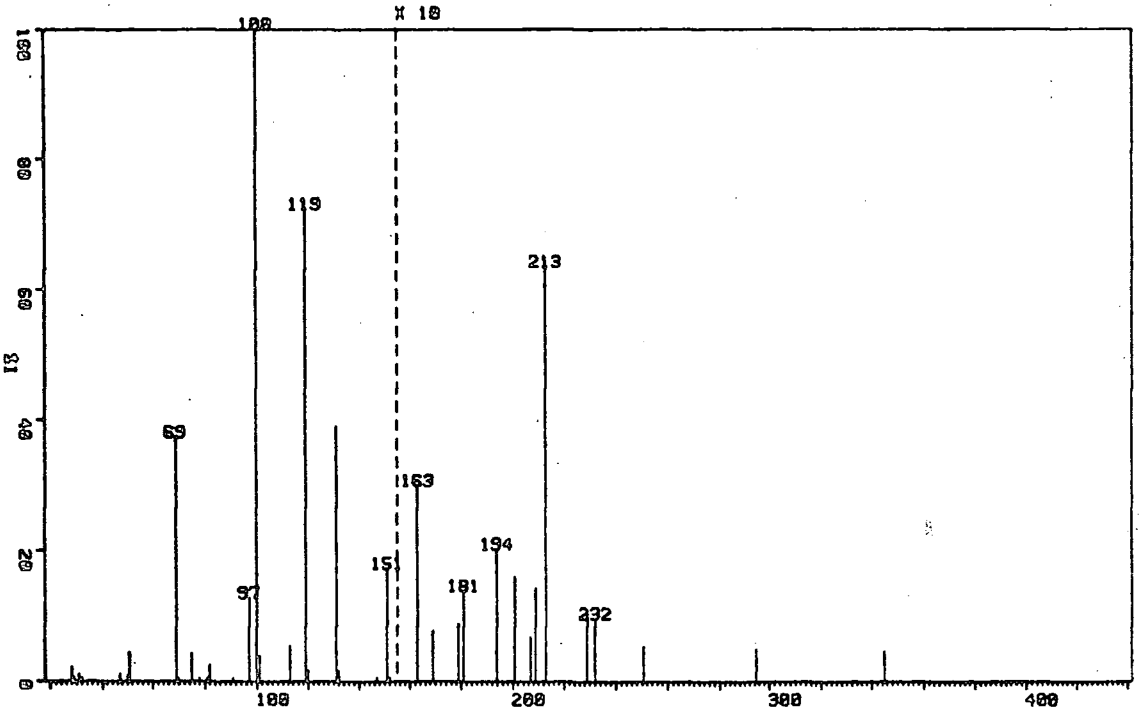
No.89

Heptafluoro-2-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dioxan (171).

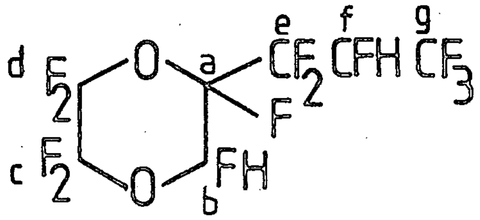


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
4.73	D of M, J_{HF}=40	-	f
^{19}F			
77.5	M	3	g
78.3, 82.7, 84.0, 88.2, 92.3, 95.5, 98.3,	Overlapping M's	6	b, c, d
126.7, 129.3, 131.0, 132.7.	Overlapping M's	3	a, e
214.7	M	1	f

M.Wt. 364 No. 89

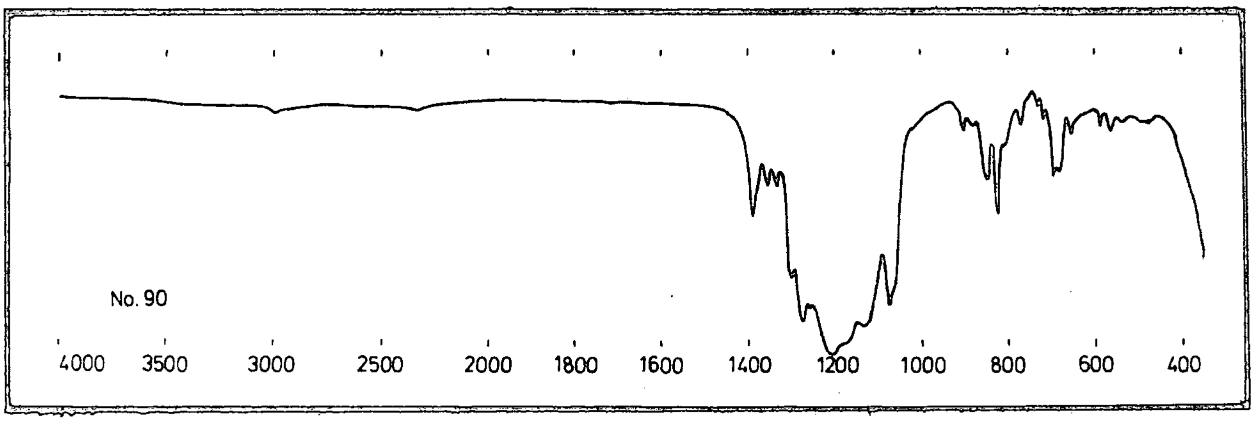


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	2.11	36	231.98	0.96
2	28.99	0.64	37	250.91	0.54
3	30.91	1.03	38	294.87	0.50
4	32.02	0.54	39	344.91	0.46
5	47.08	1.18			
6	49.86	0.96			
7	50.93	4.46			
8	68.97	37.40			
9	69.90	0.39			
10	75.04	4.25			
11	77.98	0.54			
12	80.90	0.54			
13	81.95	2.53			
14	90.92	0.50			
15	96.98	12.81			
16	99.87	100.00			
17	100.95	3.89			
18	113.00	5.42			
19	118.97	72.31			
20	119.95	1.68			
21	130.95	39.01			
22	131.98	1.61			
23	146.94	0.64			
24	150.91	17.34			
25	151.95	0.64			
26	162.94	3.00			
27	168.92	0.79			
28	178.92	0.89			
29	180.90	1.39			
30	193.90	2.03			
31	200.81	1.61			
32	206.91	0.68			
33	208.87	1.43			
34	212.91	6.35			
35	228.97	1.03			



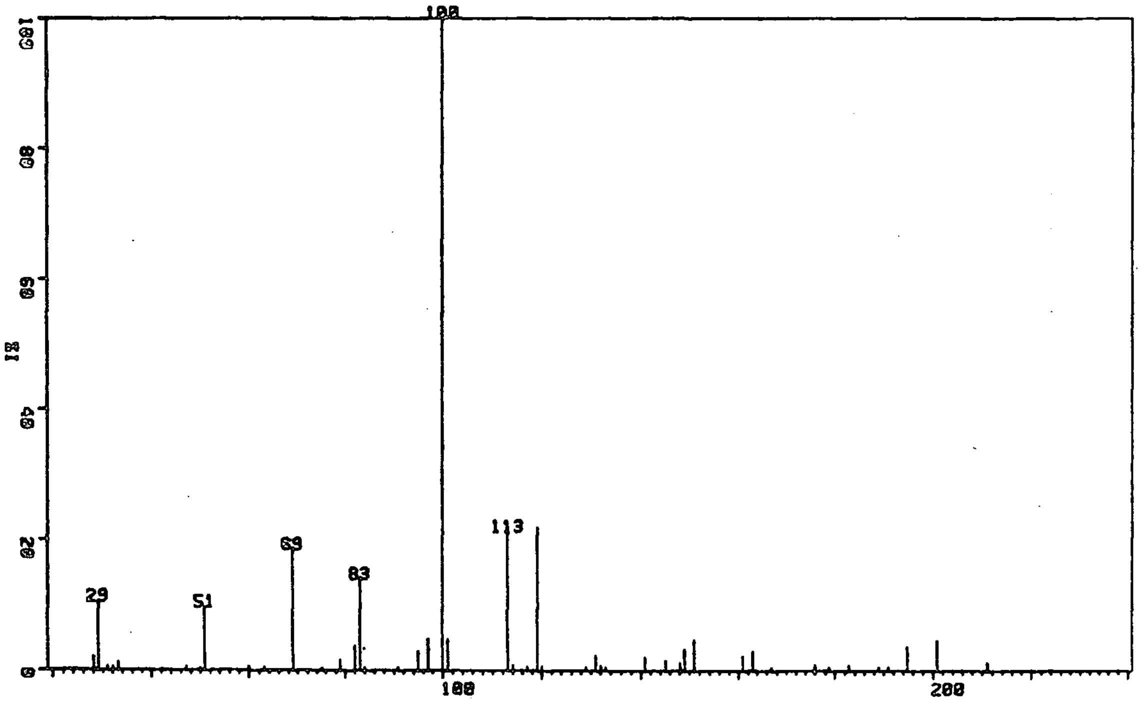
No. 90

2,3,5,5,6,6-Hexafluoro-2-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dioxan, isomer A (172).

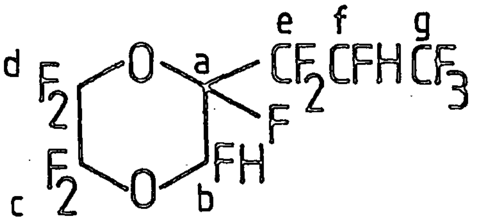


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
4.76	D of M, J_{HF}=40	1	f
5.65	D of M, J_{HF}=50	1	b
5.77	D of M, J_{HF}=50		
^{19}F			
77.5	M	3	g
84.4, 94.8	AB, J_{FF}=147	2	c, d
90.7	M	2	
127.3, 128.0, 128.8, 130.3, 132.2, 135.3, 136.3, 136.8, 137.8, 138.8.	Overlapping M's	3	a, e
147.6	M	1	b
215.7	M	1	f

M.Wt. 346 No. 90

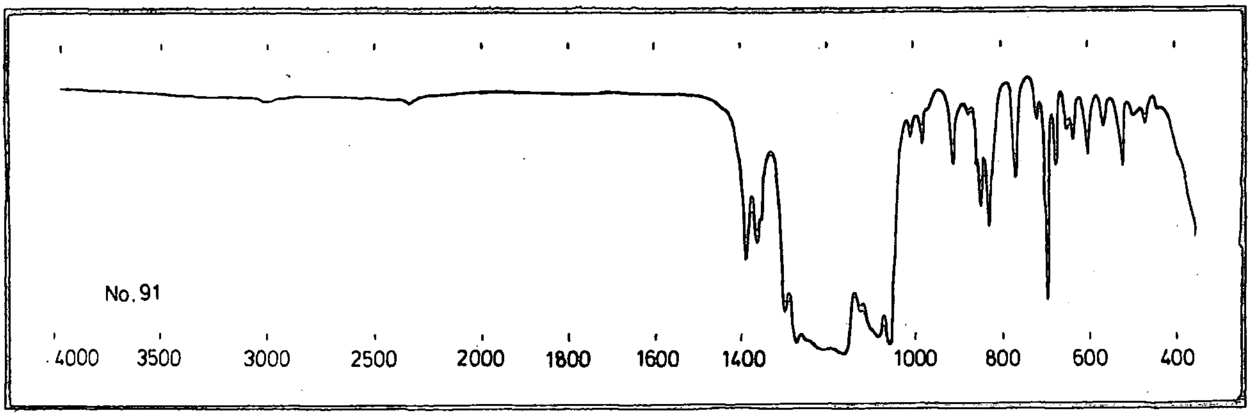


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	2.03	36	160.92	2.34
2	29.00	10.57	37	162.97	2.94
3	30.91	0.64	38	166.96	0.52
4	32.02	0.56	39	175.95	0.99
5	33.13	1.23	40	178.92	0.52
6	47.08	0.60	41	182.94	0.95
7	49.87	0.40	42	188.88	0.64
8	50.94	9.65	43	190.90	0.60
9	59.91	0.60	44	194.88	3.77
10	63.08	0.52	45	200.84	4.69
11	68.97	18.51	46	210.89	1.23
12	75.05	0.44			
13	78.93	1.55			
14	81.96	3.73			
15	82.99	14.06			
16	84.02	0.44			
17	90.92	0.48			
18	95.01	2.98			
19	96.98	4.85			
20	99.87	100.00			
21	100.95	4.77			
22	112.98	21.41			
23	114.03	0.87			
24	117.04	0.60			
25	118.97	22.05			
26	119.95	0.68			
27	128.95	0.52			
28	130.93	2.30			
29	131.98	0.75			
30	133.00	0.60			
31	140.88	2.03			
32	144.98	1.63			
33	147.97	1.23			
34	148.94	3.30			
35	150.92	4.73			



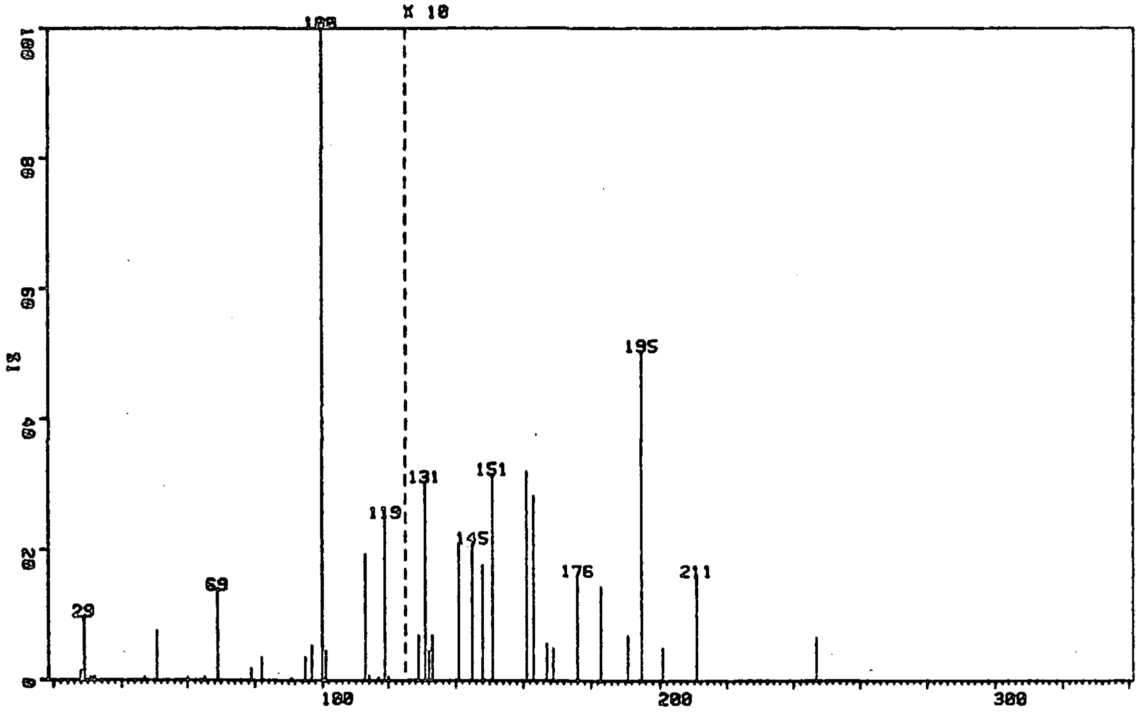
No.91

2,3,5,5,6,6-Hexafluoro-2-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dioxan, isomer B (173).



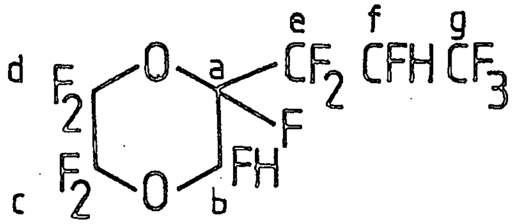
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
4.76	D of M, J_{HF}=44	1	f
5.50	D, J=48	1	b
^{19}F			
77.2	M	3	g
82.5, 85.0, 93.3, 96.0.	Overlapping AB's	4	c , d
124.6, 131.4	AB, J_{FF}=300	2	e
128.8	M	1	a
140.0	M	1	b
214.0	M	1	f

M.Wt. 346 No. 91

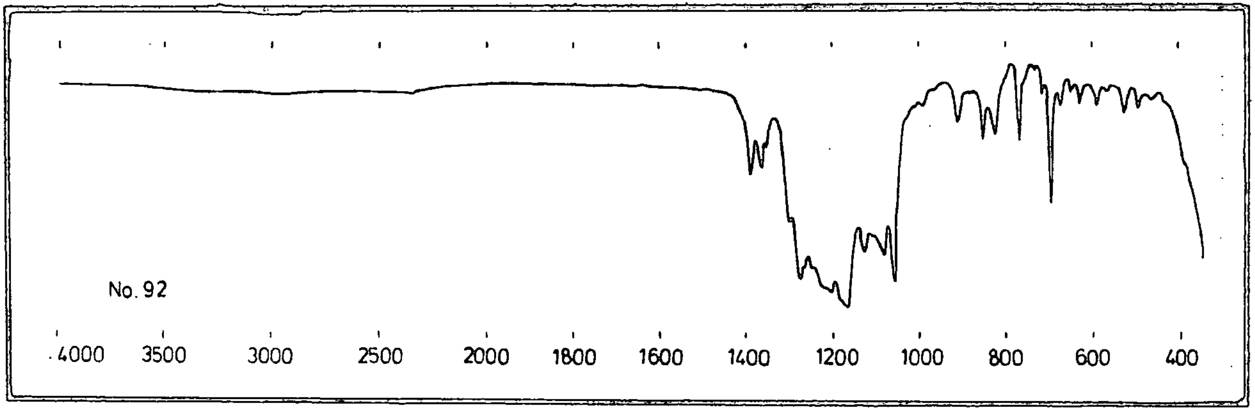


PEAK NO.	MASS	%HT. BASE
1	28.13	1.44
2	29.00	9.74
3	30.91	0.53
4	32.03	0.53
5	47.09	0.53
6	50.94	7.52
7	59.93	0.45
8	65.12	0.58
9	68.94	13.85
10	78.90	1.89
11	81.96	3.49
12	90.90	0.49
13	95.01	3.62
14	96.97	5.38
15	99.87	100.00
16	100.95	4.64
17	113.00	19.31
18	114.02	0.82
19	117.04	0.53
20	118.97	24.94
21	119.95	0.62
22	128.96	0.70
23	130.95	3.04
24	131.96	0.45
25	133.02	0.70
26	140.88	2.10
27	145.00	2.10
28	147.96	1.77
29	150.94	3.16
30	160.95	3.20
31	162.97	2.83
32	166.98	0.58
33	168.92	0.49
34	175.98	1.60
35	182.94	1.44
36	190.87	0.70
37	194.91	5.05
38	200.85	0.49
39	210.82	1.60
40	246.88	0.66

No.92

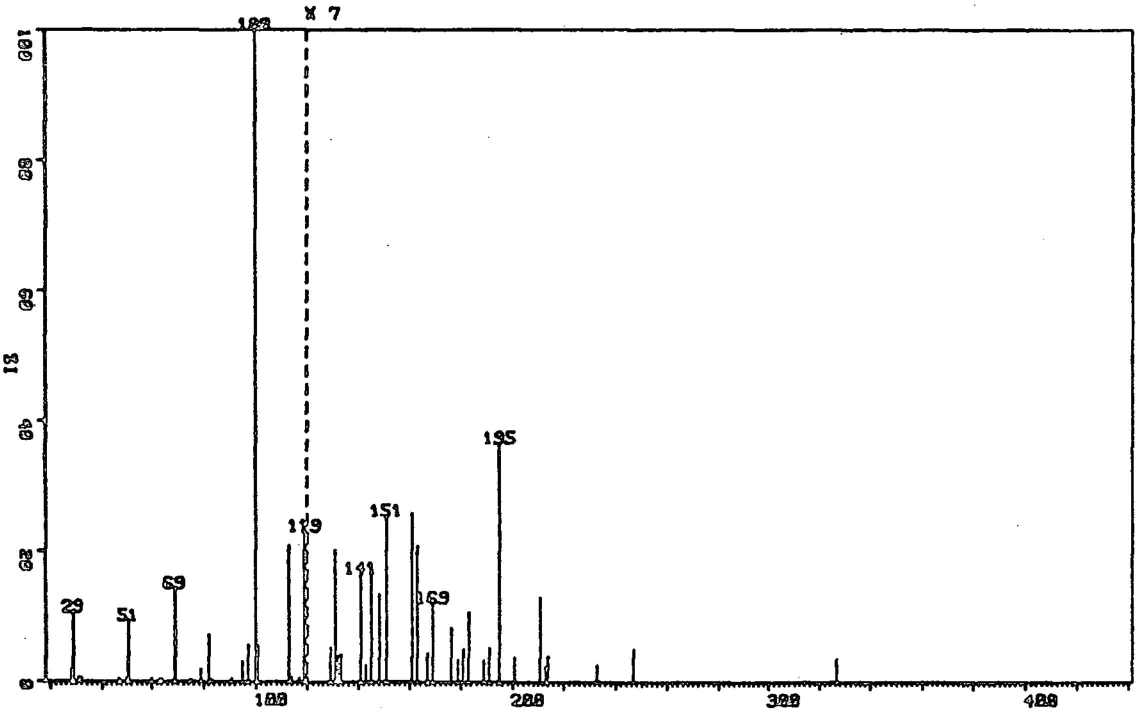


2,3,5,5,6,6-Hexafluoro-2-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dioxan, isomer C (<u>174</u>).



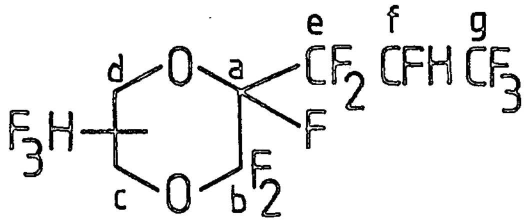
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
<u>^1H</u>			
4.76	D of M, J_{HF}=44	1	f
5.47	D, J=50	1	b
<u>^{19}F</u>			
77.3	M	3	g
82.3, 85.0, 93.3, 96.0.	Overlapping AB's	4	c , d
126.7	M	3	a , e
140.7	M	1	b
215.3	M	1	f

M.Wt. 346 No.92

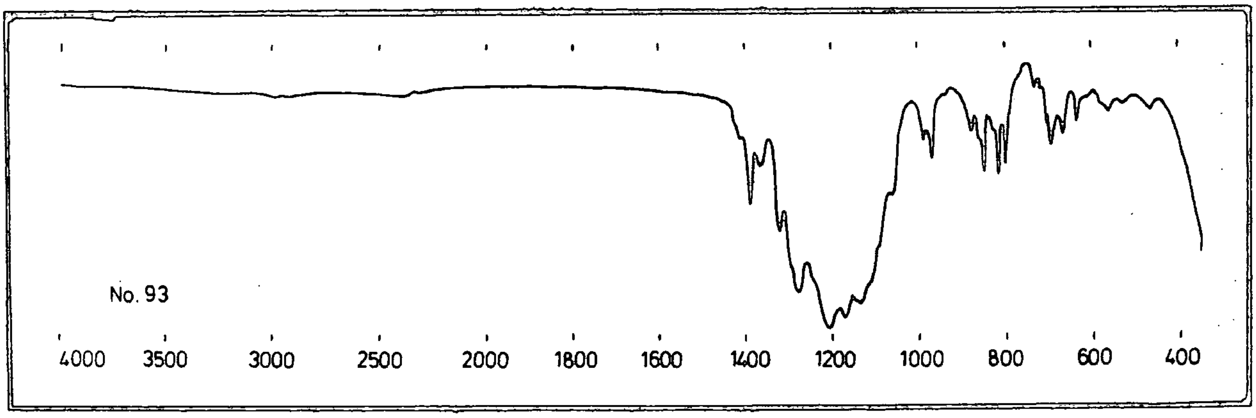


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	1.79	36	162.97	2.98
2	28.99	10.70	37	166.98	0.63
3	30.91	0.69	38	168.92	1.73
4	32.02	0.47	39	175.95	1.19
5	47.08	0.44	40	178.91	0.47
6	49.86	0.44	41	180.89	0.72
7	50.92	9.38	42	182.96	1.54
8	59.91	0.38	43	188.93	0.47
9	63.07	0.35	44	190.89	0.75
10	64.09	0.35	45	194.92	5.24
11	68.96	14.28	46	200.86	0.53
12	75.04	0.35	47	210.86	1.85
13	78.91	1.98	48	212.94	0.35
14	81.93	7.19	49	214.00	0.56
15	82.97	0.35	50	232.98	0.38
16	90.88	0.56	51	246.91	0.72
17	95.01	3.20	52	326.72	0.50
18	96.99	5.59			
19	99.88	100.00			
20	100.95	5.49			
21	112.99	20.94			
22	114.02	0.78			
23	117.01	0.63			
24	118.98	23.16			
25	119.94	0.66			
26	128.95	0.75			
27	130.93	2.89			
28	131.97	0.56			
29	132.98	0.60			
30	140.88	2.39			
31	142.96	0.38			
32	144.98	2.48			
33	147.94	1.91			
34	150.92	3.64			
35	160. 89	3.70			

No. 93

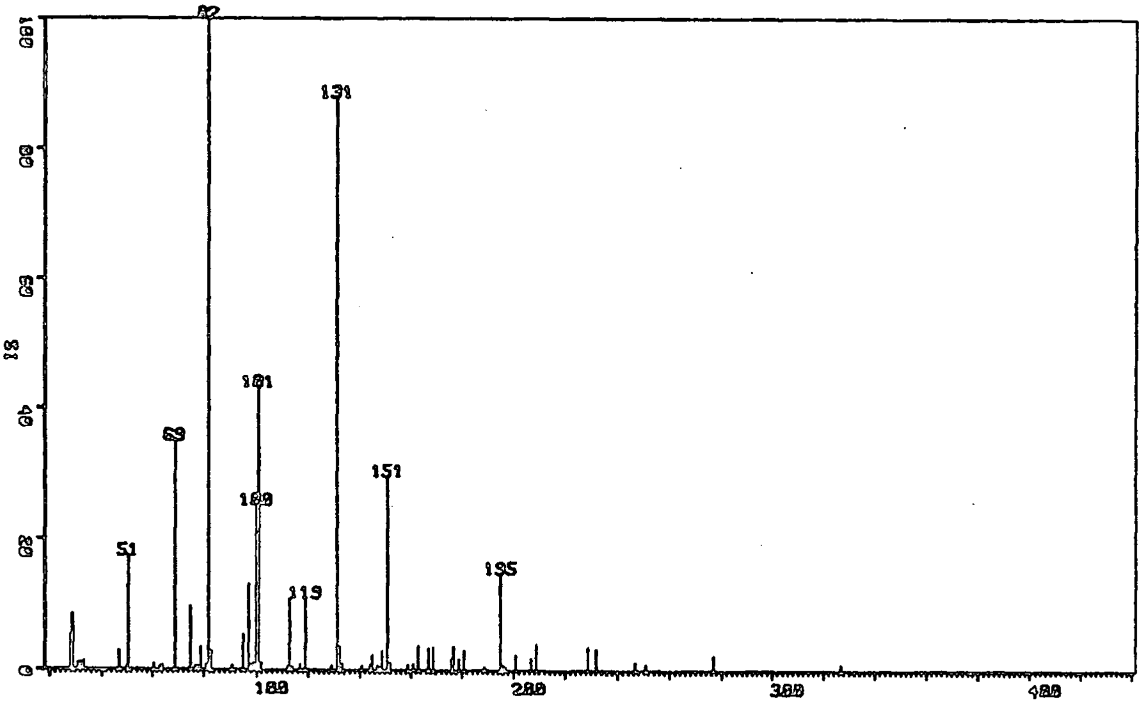


2,3,3-Trifluoro-2-(1,1,2,3,3,3-hexafluoropropyl)trifluoro-1,4-dioxan, isomer A (175).

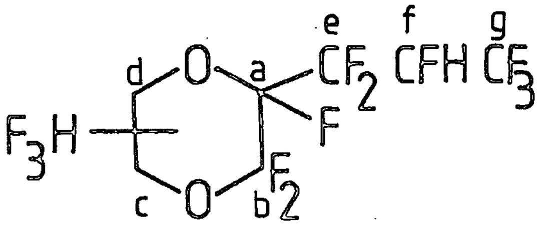


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
4.93	D of M, $J_{HF}=46$	1	f
5.56	D of M, $J_{HF}=50$	1	c or d
^{19}F			
77.3	M	3	g
82.7, 84.0, 84.5, 85.0, 85.8.	Overlapping M's	4	b and (c or d)
126.7	M	2	e
129.8	M	1	a
145.7	M	1	d or c
214.2	M	1	f

M.Wt. 346 No.93

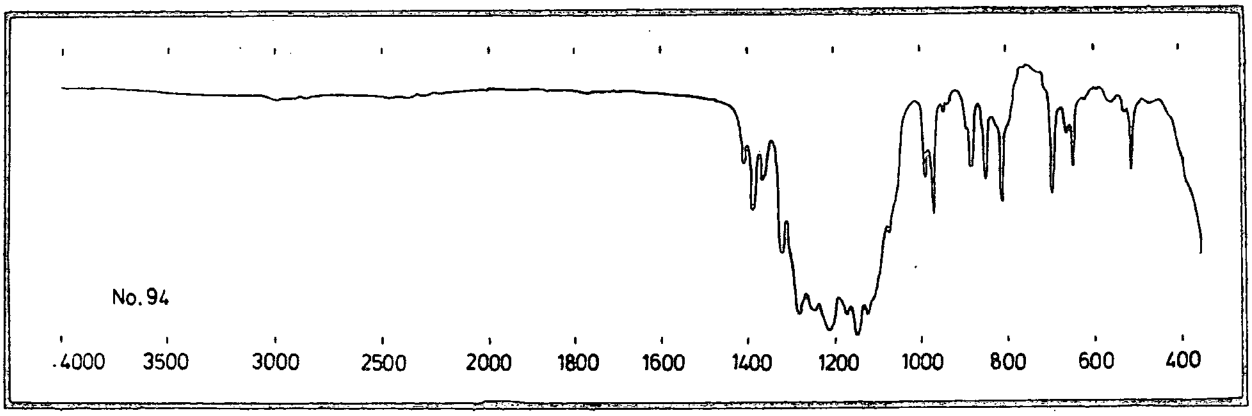


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	5.32	36	133.01	1.06
2	29.00	8.45	37	140.92	0.63
3	30.91	1.06	38	143.99	0.84
4	32.02	1.01	39	144.96	2.32
5	33.13	1.22	40	146.96	0.80
6	47.08	2.83	41	147.98	0.55
7	49.87	0.55	42	148.93	3.04
8	50.94	17.48	43	150.91	29.73
9	60.97	0.97	44	151.97	1.14
10	63.08	0.46	45	158.93	0.80
11	64.11	0.72	46	160.94	0.93
12	68.95	35.14	47	162.93	3.67
13	75.00	9.67	48	166.95	3.34
14	77.01	0.51	49	168.91	3.51
15	77.95	0.51	50	175.94	1.82
16	78.90	3.46	51	176.94	3.63
17	80.90	0.89	52	178.90	1.73
18	81.97	100.00	53	180.88	2.96
19	83.01	2.79	54	188.96	0.46
20	90.92	0.76	55	194.90	14.86
21	95.04	5.41	56	195.93	0.97
22	97.00	13.13	57	196.91	0.46
23	98.00	0.84	58	200.86	2.41
24	98.96	1.14	59	206.87	1.90
25	99.90	25.25	60	208.90	3.97
26	100.97	43.41	61	228.99	3.55
27	102.02	1.18	62	231.96	3.25
28	111.98	0.55	63	246.90	1.22
29	113.00	10.90	64	250.92	0.97
30	114.06	0.42	65	276.88	2.32
31	117.04	0.89	66	326.88	0.97
32	118.99	11.11			
33	128.99	0.72			
34	130.95	87.96			
35	131.98	3.59			



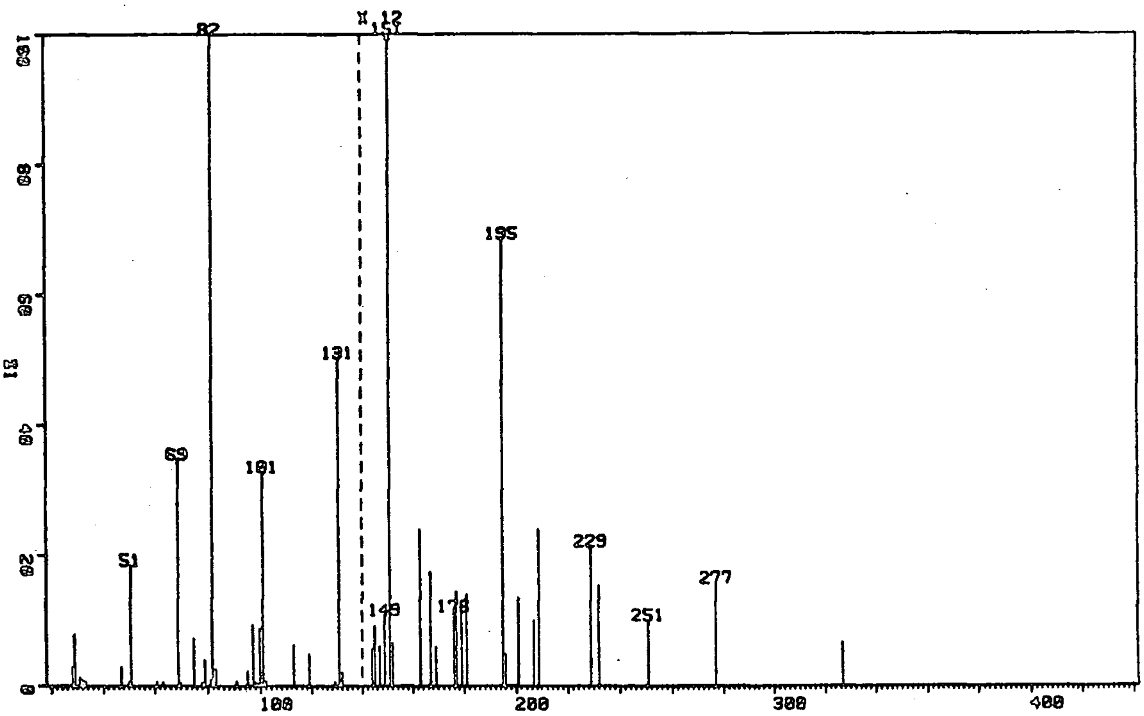
No. 94

2,3,3-Trifluoro-2-(1,1,2,3,3,3-hexafluoropropyl)trifluoro-1,4-dioxan, isomer B, (176).

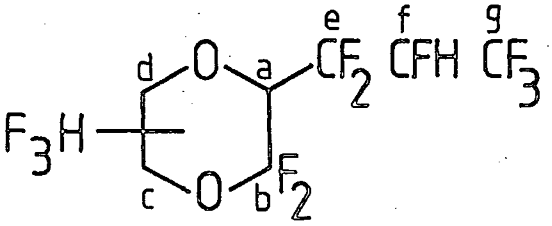


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
5.03	D of M, J=48	1	f
5.37	D of M, J=48 and 17	1	CFH, c or d
^{19}F			
77.0	M	5	g and CF_2O, c or d or b
91.7	T of M, J=179	2	b or CF_2O, d or c
120.3, 125.0, 126.3, 129.7, 132.0, 143.7.	Overlapping M's	4	a and e and CFH, c ord
213.8	M	1	f

M.Wt. 346 No. 94

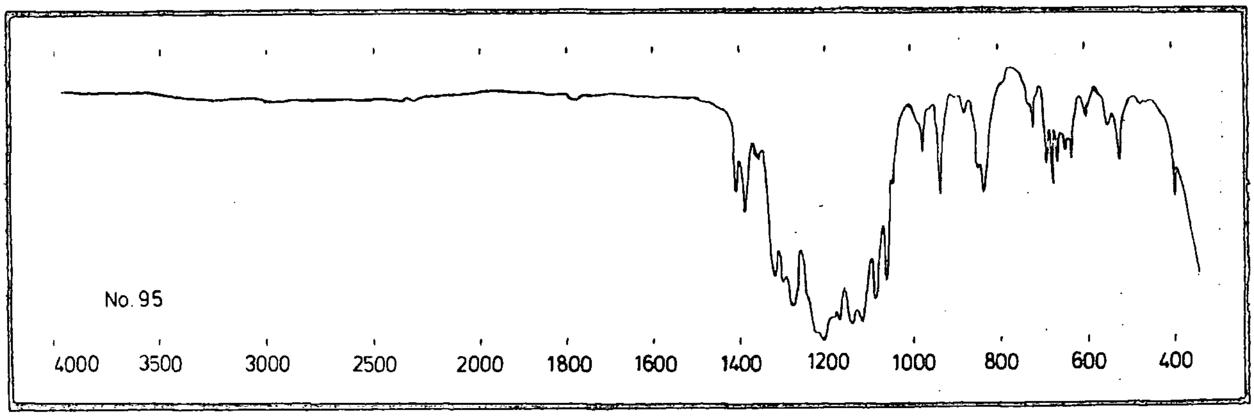


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	2.84	36	150.89	15.99
2	28.99	7.83	37	151.96	0.55
3	30.92	1.27	38	162.97	2.00
4	32.03	0.87	39	166.95	1.46
5	33.13	0.69	40	168.92	0.51
6	47.08	2.91	41	175.95	0.95
7	49.87	0.62	42	176.95	1.20
8	50.93	18.50	43	178.91	0.95
9	60.98	0.58	44	180.89	1.17
10	63.08	0.62	45	194.90	5.72
11	68.97	34.71	46	195.88	0.40
12	69.91	0.47	47	200.80	1.13
13	75.03	7.25	48	206.90	0.84
14	77.96	0.55	49	208.88	2.00
15	78.93	3.97	50	228.94	1.78
16	80.90	0.87	51	231.94	1.27
17	81.95	100.00	52	250.86	0.84
18	82.97	2.59	53	276.89	1.31
19	90.90	0.76	54	326.88	0.55
20	95.01	2.29			
21	96.98	9.32			
22	97.96	0.55			
23	98.94	0.47			
24	99.87	8.70			
25	100.94	32.74			
26	101.98	0.84			
27	112.96	6.23			
28	118.95	4.88			
29	128.95	0.66			
30	130.91	50.33			
31	131.94	2.04			
32	143.92	0.47			
33	144.95	0.76			
34	146.89	0.51			
35	148.91	0.91			



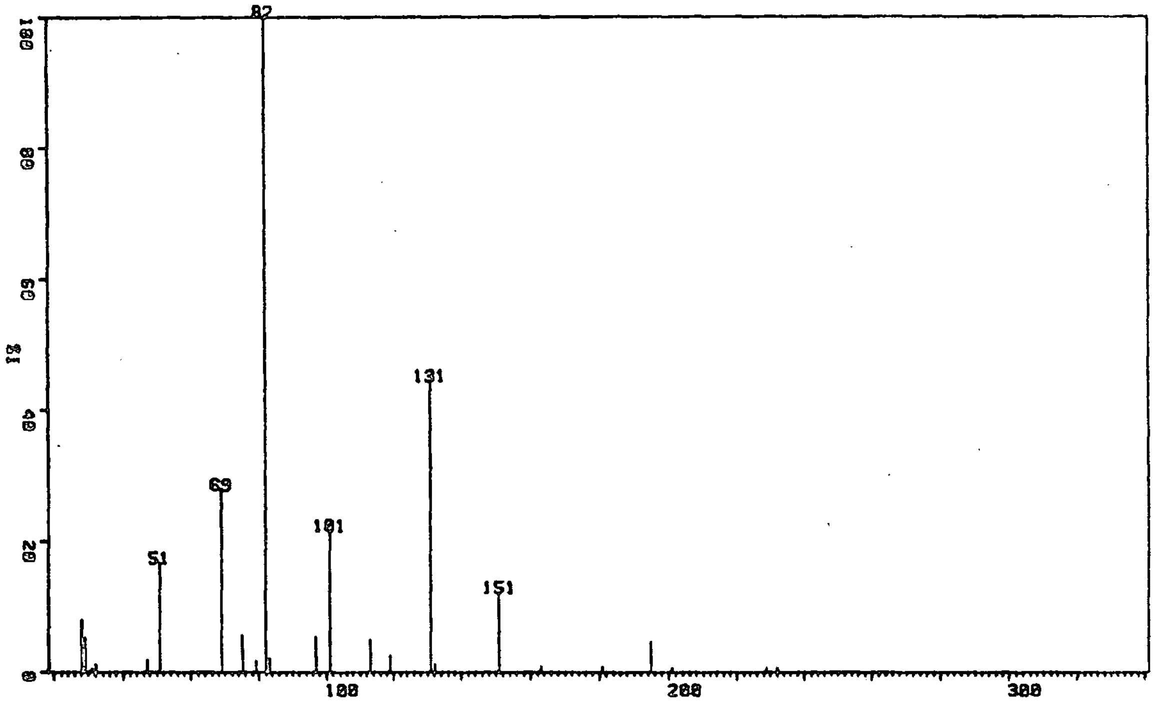
No. 95

2,3,3-Trifluoro-2-(1,1,2,3,3,3-hexafluoropropyl)trifluoro-1,4-dioxan, isomer C (177).



SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
4.80	D of M, J=44	1	f
5.30	D of M, J=50	1	CFH, c or d
^{19}F			
77.0	M	3	g
80.7, 81.7, 83.7, 87.7, 90.7.	Overlapping AB's	4	b and CF_2O, d or c
119.8, 125.2, 129.0, 131.2, 134.0, 141.7.	Series of M's	4	a, e, and CFH, c or d
213.8	M	1	f

M.Wt. 346 No.95



PEAK NO.	MASS	%HT. BASE
1	28.13	7.95
2	28.99	5.27
3	30.92	0.56
4	32.02	1.27
5	47.07	1.98
6	50.91	16.69
7	68.94	27.82
8	75.03	5.68
9	78.93	1.79
10	81.95	100.00
11	83.00	2.20
12	96.96	5.49
13	100.91	21.62
14	112.97	4.93
15	118.91	2.61
16	130.86	44.44
17	131.95	1.23
18	150.89	12.17
19	162.96	0.93
20	180.87	0.86
21	194.95	4.71
22	200.92	0.75
23	228.88	0.67
24	231.93	0.78

No. 96

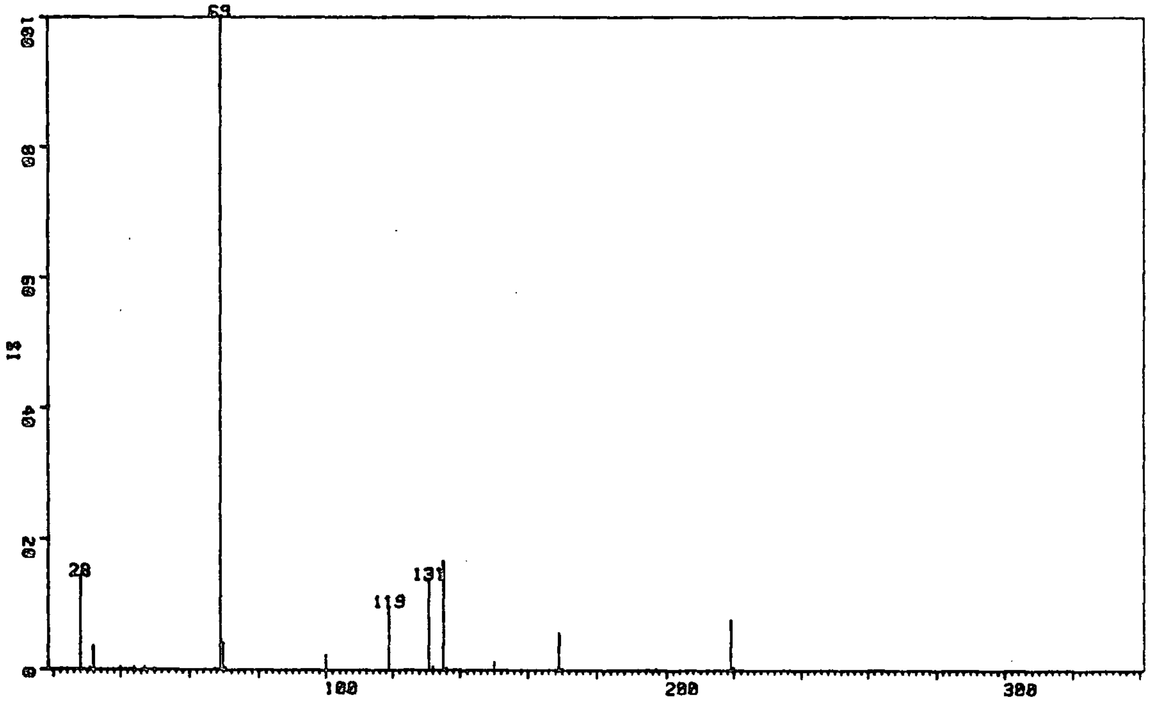
$CF_3CF_2CF_2CF_2OCF_3$

Perfluoro butyl methyl ether. (178).

No Spectrum.

SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
	No Spectrum.		

M.Wt. 304 No.96



PEAK NO.	MASS	%HT. BASE
1	28.13	14.33
2	30.90	0.42
3	32.02	3.59
4	39.84	0.46
5	44.12	0.51
6	47.09	0.51
7	49.88	0.27
8	67.37	0.27
9	68.94	100.00
10	69.48	4.13
11	70.22	0.34
12	70.54	0.24
13	99.94	2.37
14	118.96	9.67
15	130.95	13.94
16	131.98	0.61
17	135.03	16.68
18	136.03	0.46
19	149.93	1.27
20	168.95	5.74
21	169.94	0.32
22	197.01	0.29
23	218.92	7.69
24	219.96	0.42

No.97

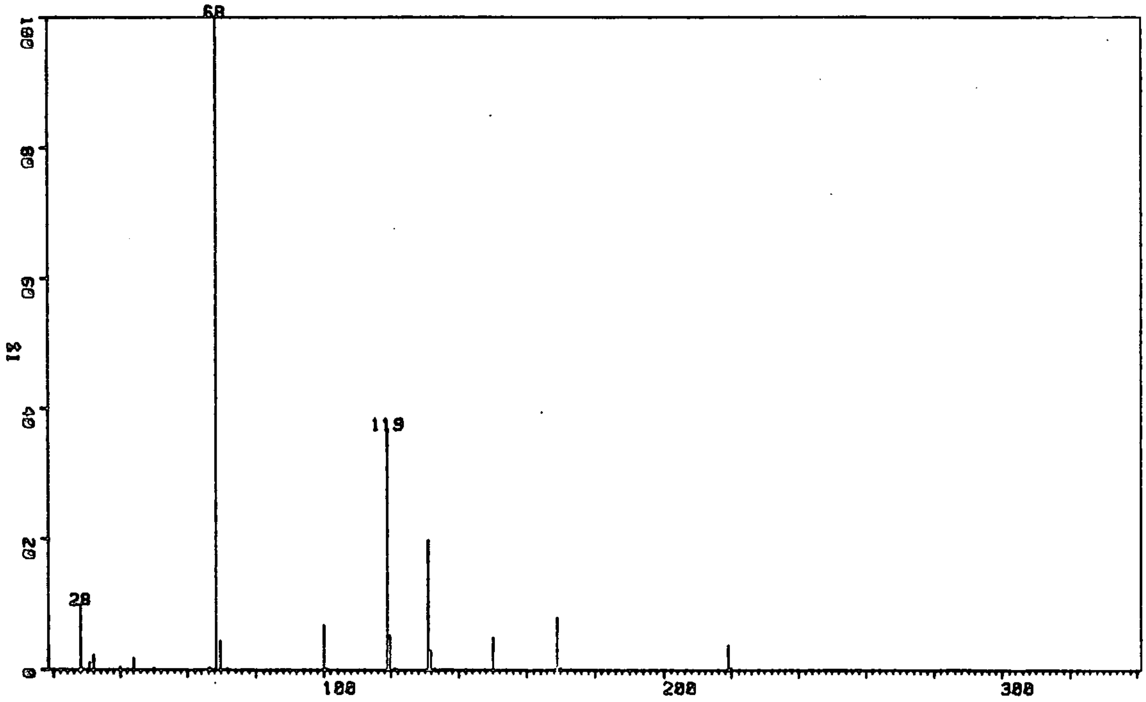
$CF_3CF_2CF_2CF_3$

Perfluorobutane. (179).

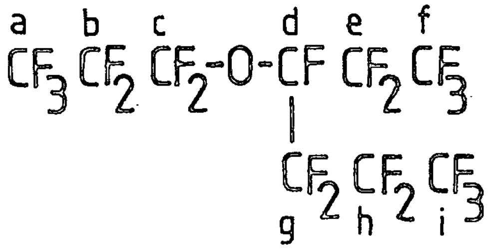
No spectrum.

SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
	No Spectrum.		

M.Wt. 238 No. 97

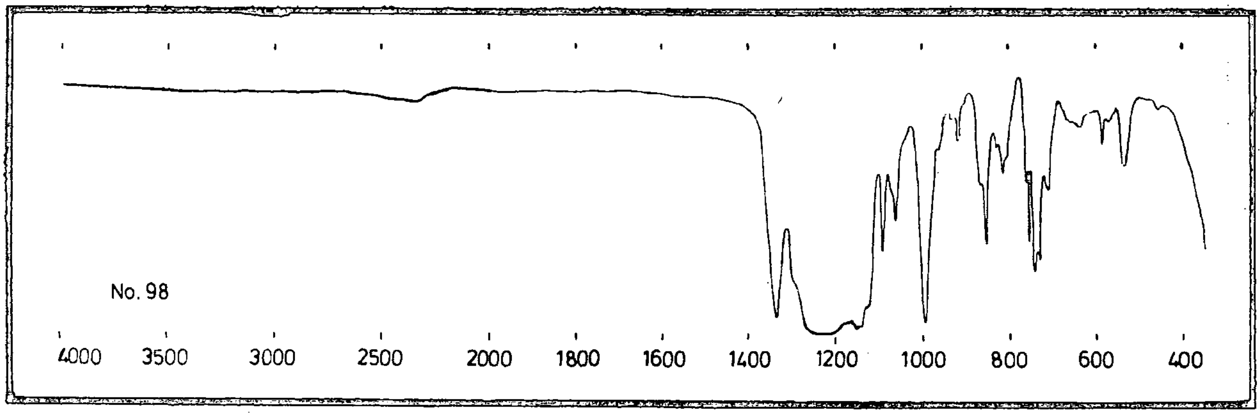


PEAK NO.	MASS	%HT. BASE
1	28.13	9.94
2	28.27	0.27
3	30.91	1.10
4	32.02	2.27
5	39.85	0.49
6	44.13	1.83
7	49.88	0.34
8	66.08	0.24
9	66.26	0.27
10	66.39	0.27
11	66.52	0.24
12	66.74	0.34
13	66.93	0.32
14	67.07	0.27
15	68.48	100.00
16	69.69	4.42
17	71.60	0.27
18	99.95	6.81
19	101.00	0.24
20	118.89	36.78
21	119.68	5.25
22	120.97	0.24
23	121.26	0.27
24	130.91	19.83
25	131.70	2.88
26	132.87	0.24
27	150.00	4.91
28	169.03	7.99
29	170.00	0.34
30	219.02	3.83
31	219.95	0.34



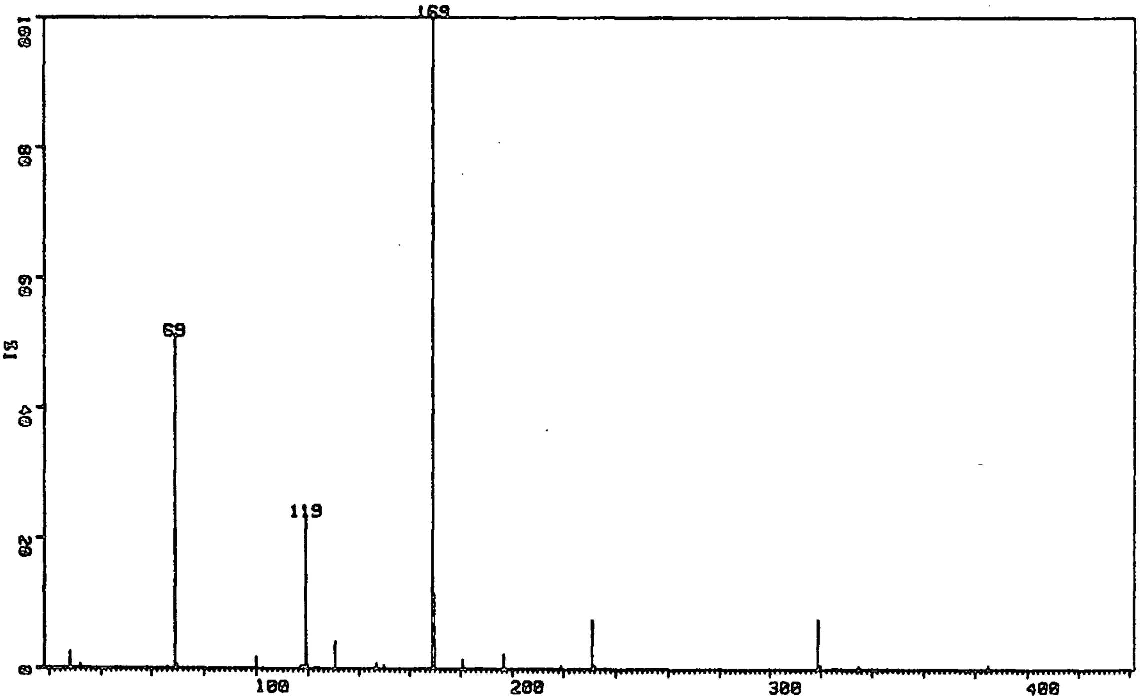
No.98

Perfluoro 1-ethylbutyl propyl ether (180).



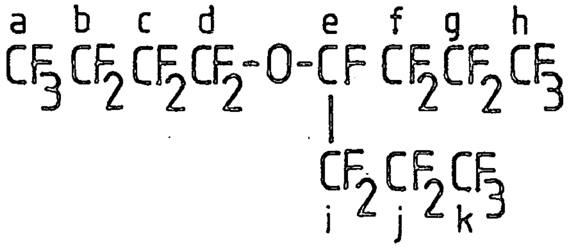
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
83.5	M	2	c
84.0	M	3	a, f, i
85.0	M	6	
85.4	M		
122.3	M	2	b, e, g, h.
125.7	M	2	
128.2	M	2	
132.5	M	2	
141.7	M	1	d

M.Wt. 504 No.98



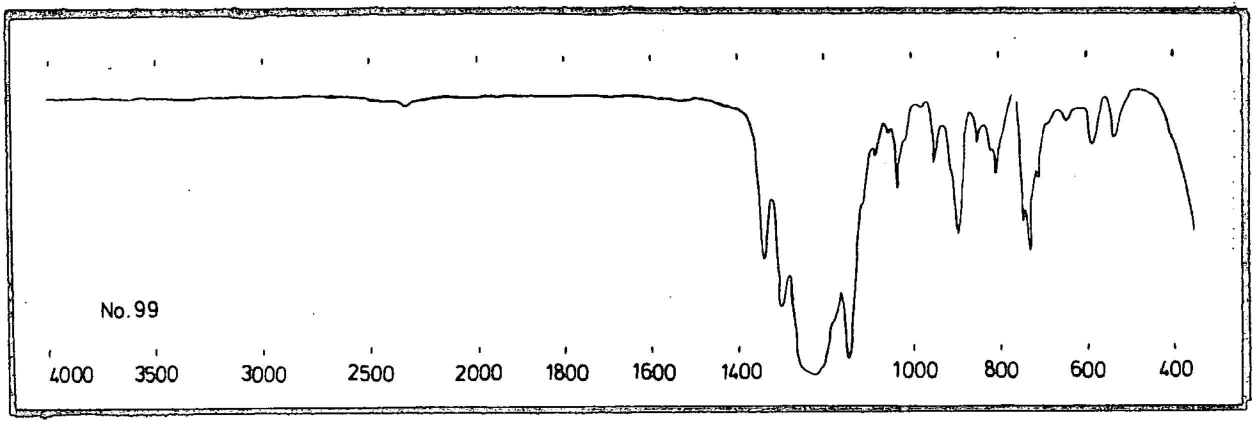
PEAK NO.	MASS	%HT. BASE
1	28.13	2.44
2	32.02	0.55
3	66.12	0.29
4	68.96	51.10
5	69.06	21.31
6	69.91	0.63
7	99.87	1.89
8	117.06	0.47
9	118.08	0.29
10	118.97	23.39
11	119.41	3.33
12	119.93	0.52
13	130.93	4.20
14	146.87	0.89
15	149.92	0.63
16	168.93	100.00
17	169.62	11.55
18	169.87	3.36
19	180.93	1.39
20	196.87	2.20
21	218.96	0.58
22	230.87	7.53
23	231.96	0.47
24	318.79	7.69
25	319.90	0.55
26	334.90	0.47
27	384.72	0.68

No. 99



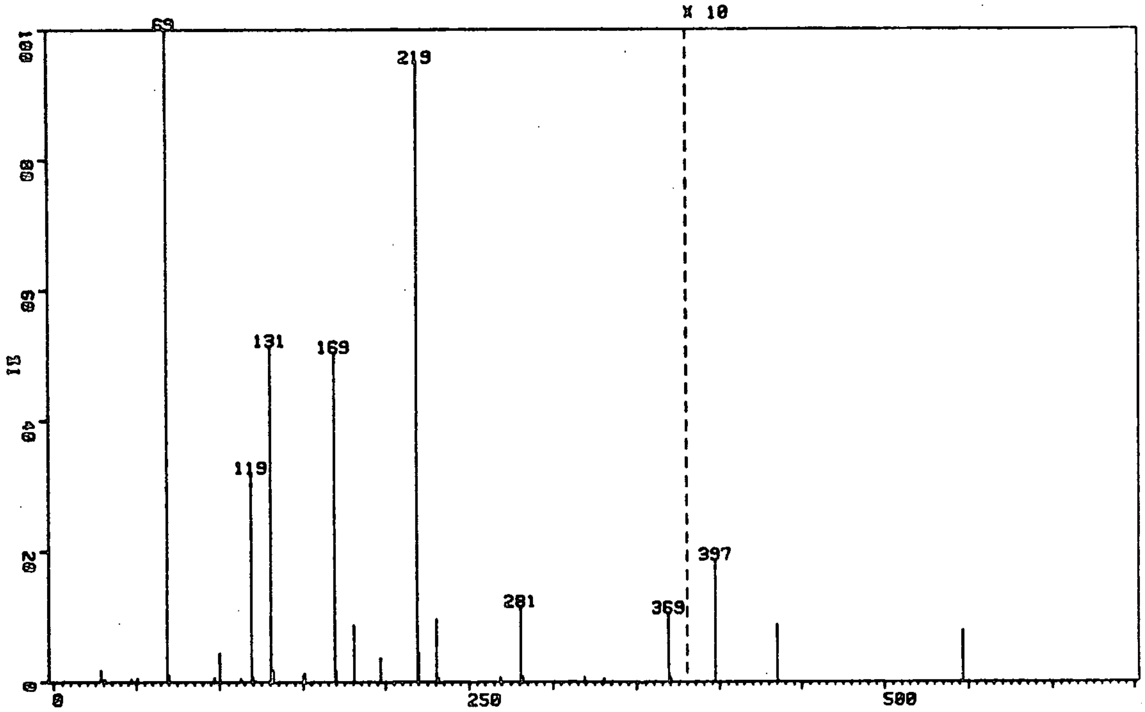
$\overset{a}{CF_3}\overset{b}{CF_2}\overset{c}{CF_2}\overset{d}{CF_2}-O-\overset{e}{CF}(\underset{i}{CF_2}\underset{j}{CF_2}\underset{k}{CF_3})\overset{f}{CF_2}\overset{g}{CF_2}\overset{h}{CF_3}$

Perfluoro 1-propylbutyl butyl ether (182).



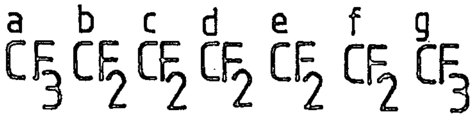
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
82.0	M	2	d
84.5	M	9	a, h, k
121.5	M	4	f , i
128.0	M	6	b, g, j
129.0	M	2	c
140.3	M	1	e

M.Wt. 604 No. 99



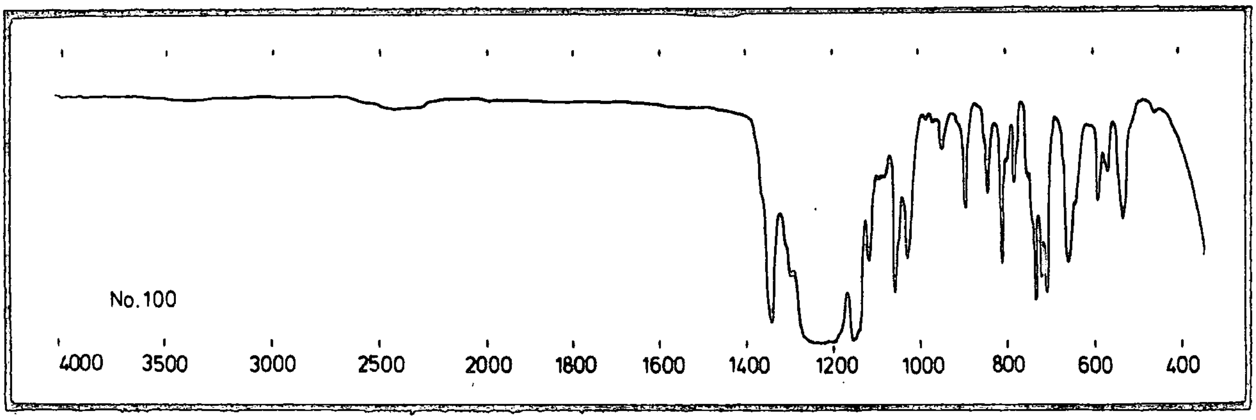
PEAK NO.	MASS	%HT. BASE
1	28.13	1.74
2	30.91	0.39
3	47.09	0.48
4	50.95	0.61
5	68.97	100.00
6	69.90	1.09
7	97.01	0.74
8	99.92	4.36
9	113.06	0.52
10	118.96	32.04
11	119.94	0.83
12	130.97	51.57
13	131.98	1.79
14	149.95	0.92
15	150.99	1.35
16	168.95	50.57
17	169.92	1.70
18	180.96	8.67
19	196.98	3.66
20	218.92	94.94
21	219.89	4.49
22	230.97	9.55
23	232.03	0.61
24	269.00	0.74
25	280.98	11.60
26	282.03	0.83
27	318.97	0.83
28	330.92	0.61
29	368.88	10.59
30	369.93	0.74
31	396.94	1.87
32	434.95	0.87
33	546.80	0.78

No.100



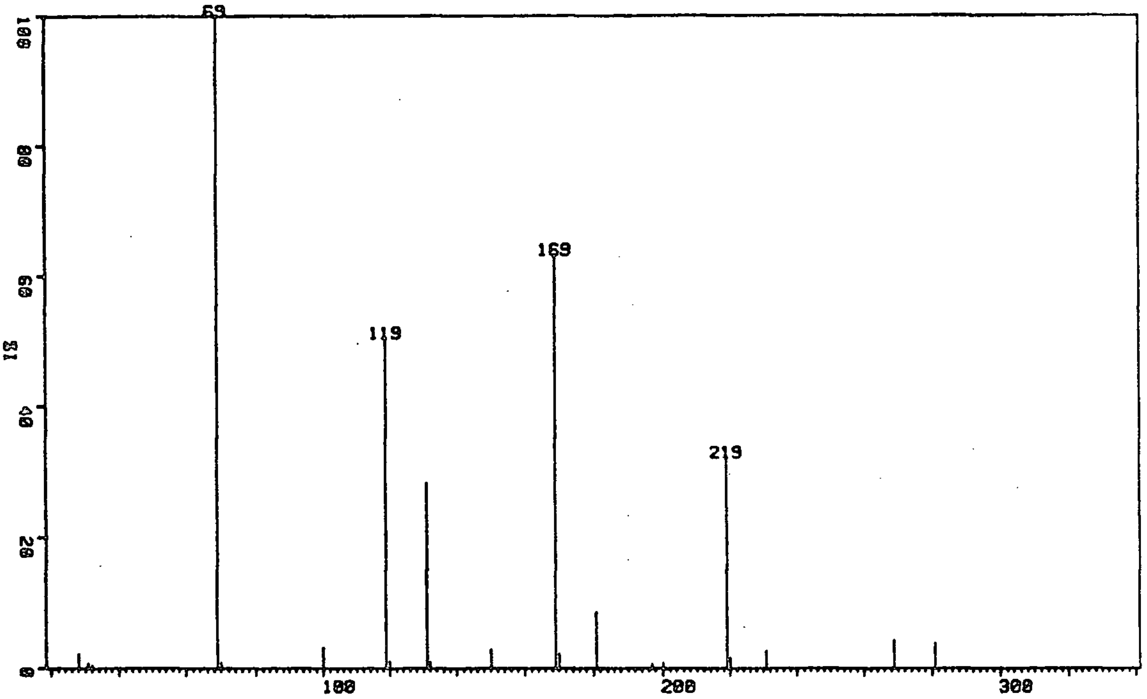
$\overset{a}{CF_3}\overset{b}{CF_2}\overset{c}{CF_2}\overset{d}{CF_2}\overset{e}{CF_2}\overset{f}{CF_2}\overset{g}{CF_3}$

Perfluoroheptane (181).



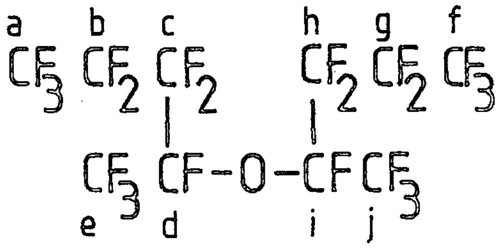
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
84.3	M	6	a , g
124.7	M	2	d
125.2	M	4	c , e
128.8	M	4	b , f

M.Wt. 388 No.100

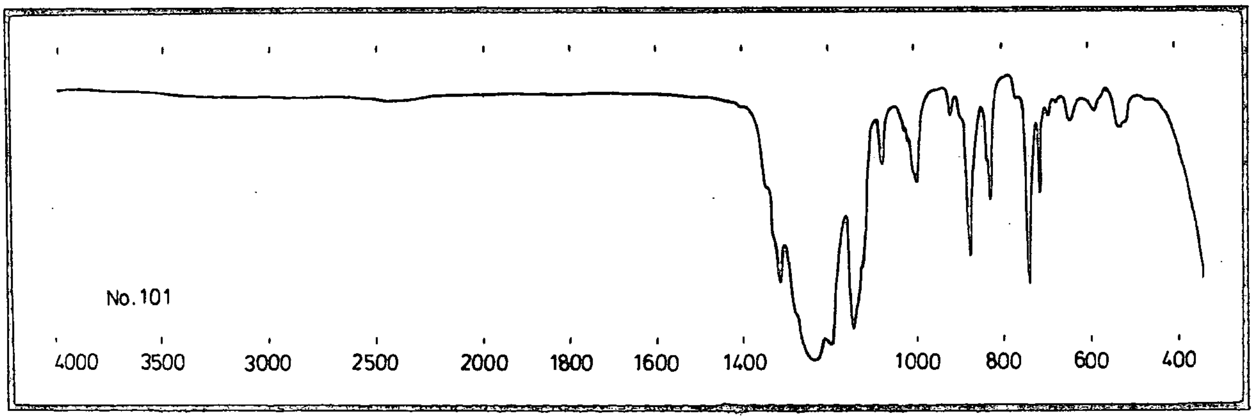


PEAK NO.	MASS	%HT. BASE
1	28.13	2.20
2	30.92	0.83
3	32.03	0.47
4	68.98	100.00
5	69.91	0.94
6	99.94	3.22
7	118.98	50.56
8	119.96	1.05
9	130.99	28.30
10	132.03	0.98
11	149.95	2.89
12	168.98	63.32
13	169.97	2.28
14	180.96	8.53
15	197.01	0.69
16	200.00	0.80
17	218.95	32.27
18	219.93	1.63
19	230.98	2.71
20	268.97	4.34
21	281.00	3.83

No.101

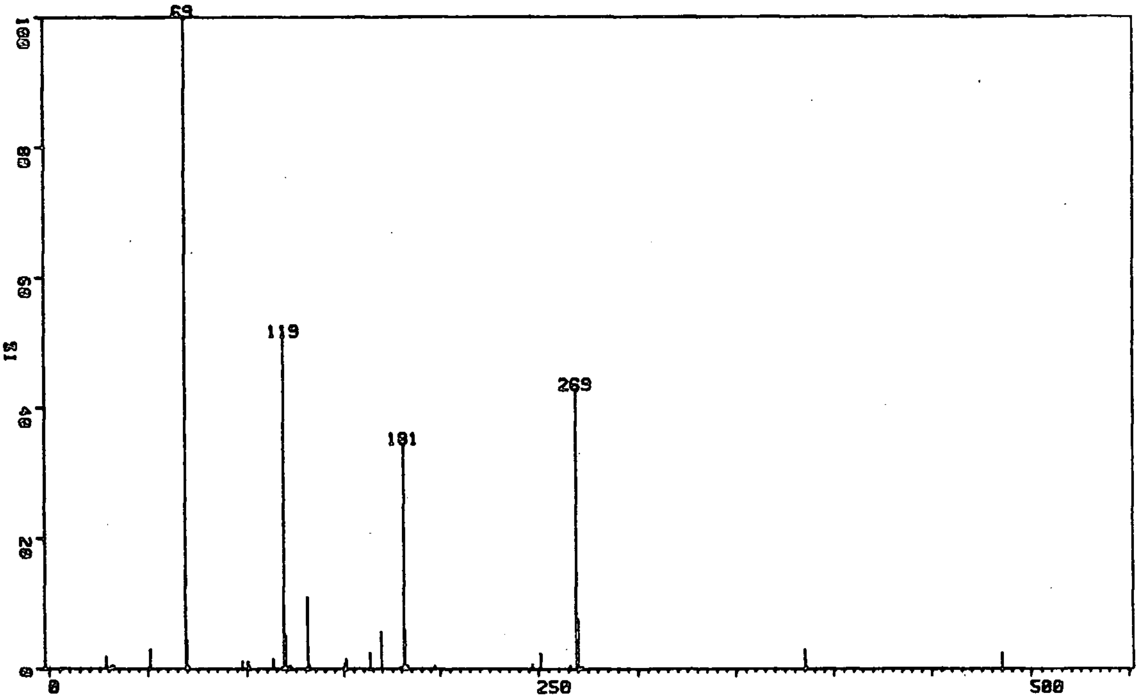


Perfluoro di(1-methylbutyl) ether (183).



SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
80.0	M	3	e , j
81.3	M		
84.2	T, J=11	3	a , f
122.8	M	2	c , h
127.5, 128,2.	M	2	b , g
136.8	M	1	d , i

M.Wt. 554 No. 101

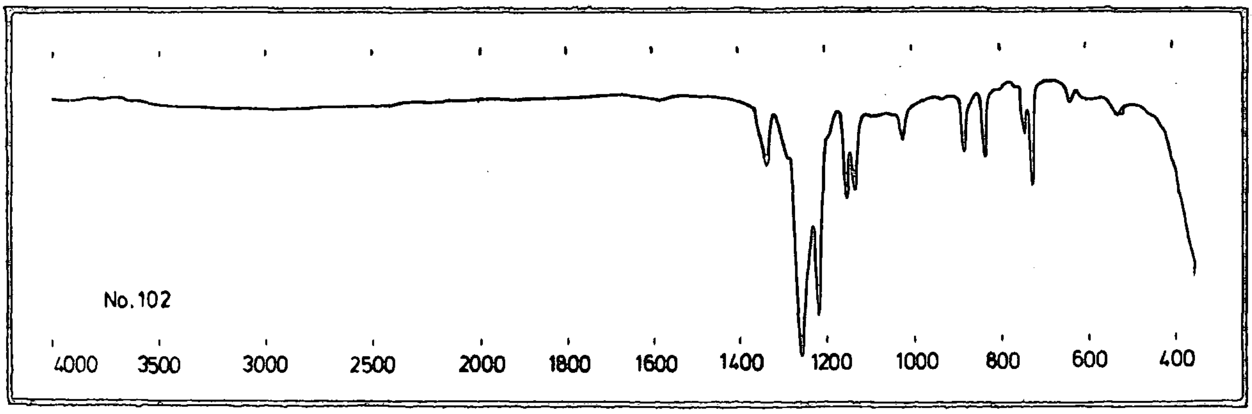


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	1.82	36	269.70	7.46
2	30.91	0.44	37	271.19	0.34
3	32.02	0.44	38	272.25	0.30
4	50.94	3.07	39	384.94	3.14
5	68.92	100.00	40	385.97	0.30
6	69.45	4.39	41	485.07	2.46
7	70.26	0.44			
8	96.99	1.18			
9	99.87	1.11			
10	100.95	0.44			
11	113.00	1.52			
12	117.73	0.30			
13	118.95	51.00			
14	119.55	5.16			
15	120.30	0.37			
16	121.59	0.37			
17	121.84	0.51			
18	122.05	0.37			
19	122.34	0.44			
20	130.99	10.93			
21	131.33	0.37			
22	132.05	0.57			
23	149.95	0.84			
24	150.98	1.55			
25	163.01	2.43			
26	168.99	5.77			
27	179.42	0.40			
28	180.91	34.46			
29	181.59	6.11			
30	183.01	0.44			
31	196.94	0.51			
32	246.90	0.84			
33	250.88	2.50			
34	265.83	0.51	35	268.81	42.73

$\overset{a}{CF_3}\overset{b}{CF_2}\overset{c}{CF_2}\overset{d}{CF_2}\overset{e}{CF_3}$

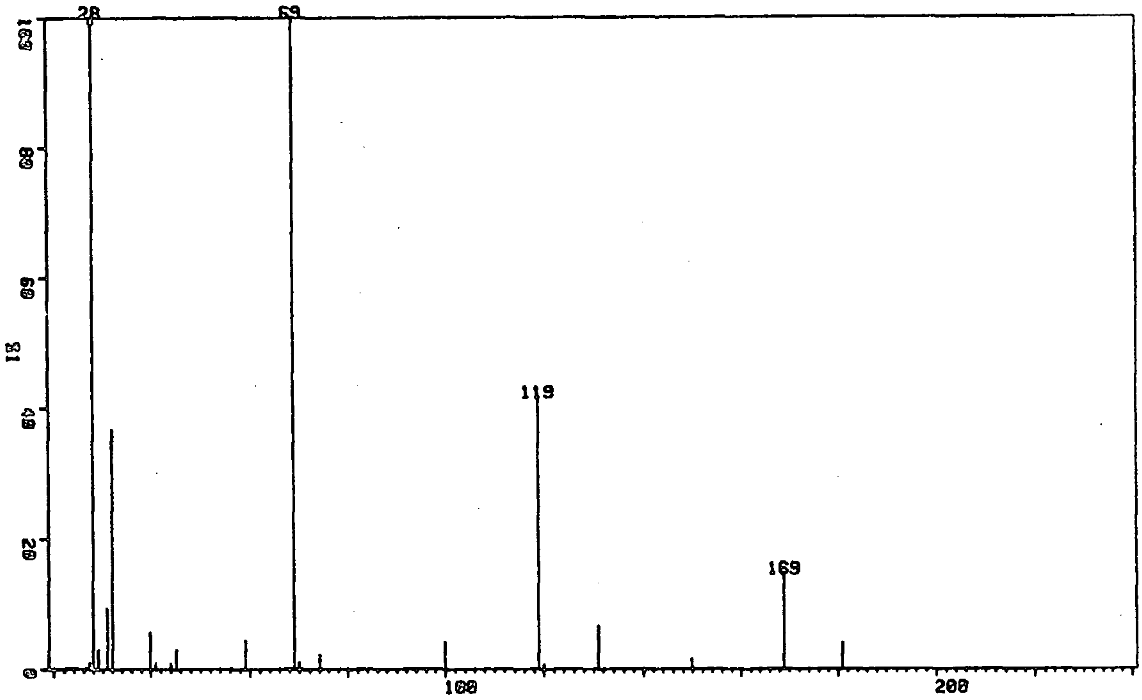
No. 102

Perfluoropentane (169).



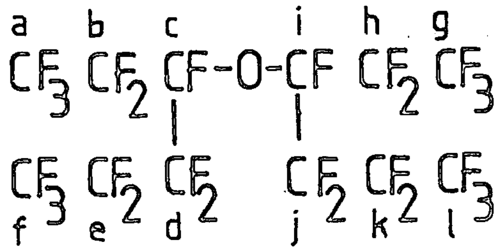
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
81.3	M	3	a , e
124.1	M	1	c
126.9	M	2	b , d

M.Wt. 288 No.102

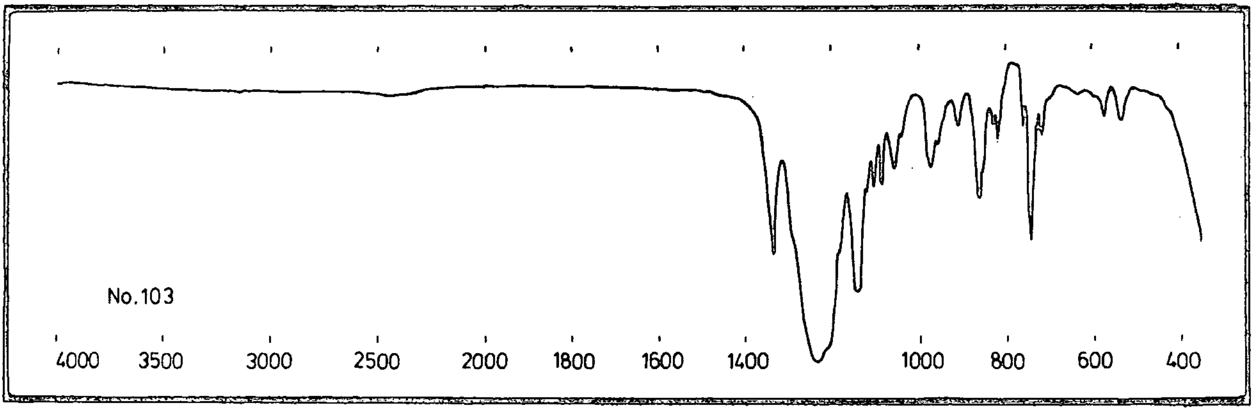


PEAK NO.	MASS	%HT. BASE
1	27.25	0.63
2	28.13	100.00
3	29.02	1.93
4	30.92	5.93
5	32.01	23.29
6	39.82	3.57
7	40.98	0.63
8	44.11	0.63
9	45.16	1.88
10	59.02	2.80
11	68.96	63.65
12	69.90	0.72
13	74.12	1.49
14	99.83	2.65
15	118.93	26.47
16	119.92	0.48
17	130.91	4.19
18	149.84	1.01
19	168.92	9.35
20	180.89	2.56

No.103

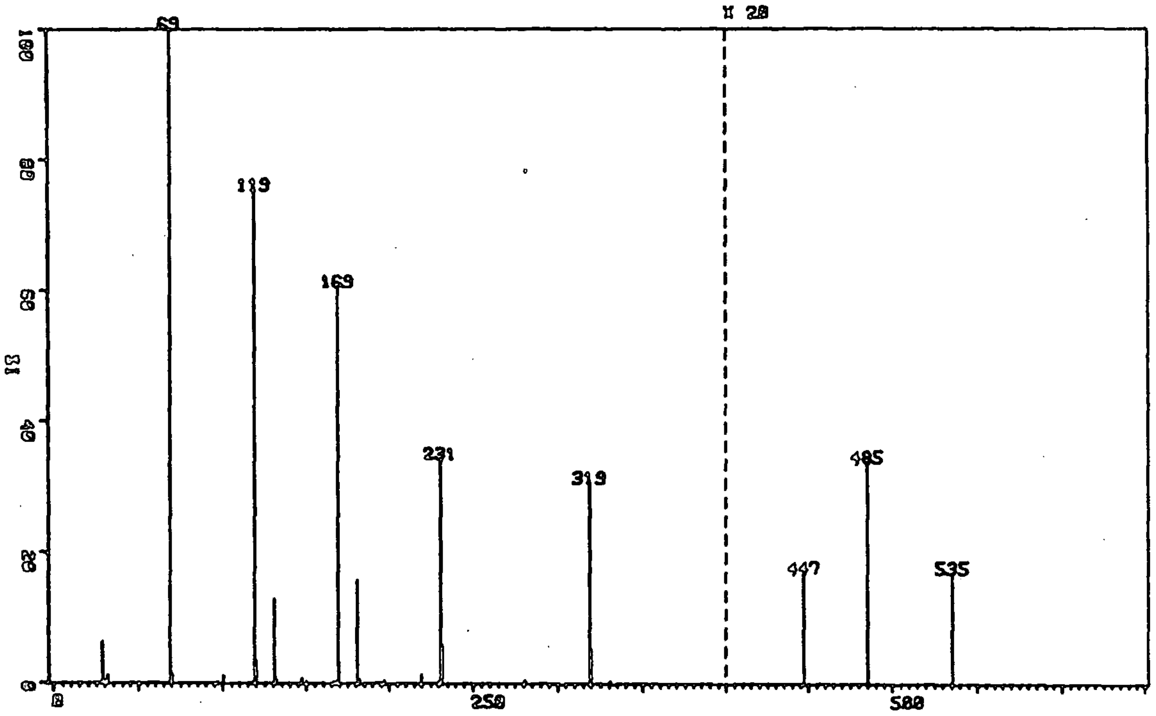


Perfluoro di(1-ethylbutyl) ether (184).



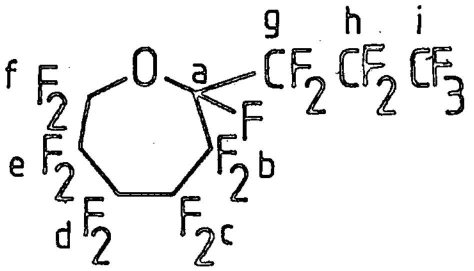
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
83.5	M	3	(a , g) and (f , l)
84.8	M	3	
120.7	M	2	(b , h) and (d , j)
123.7	M	2	
128.0	M	2	e , k
130.8	M	1	c , i

M.Wt. 654 No.103

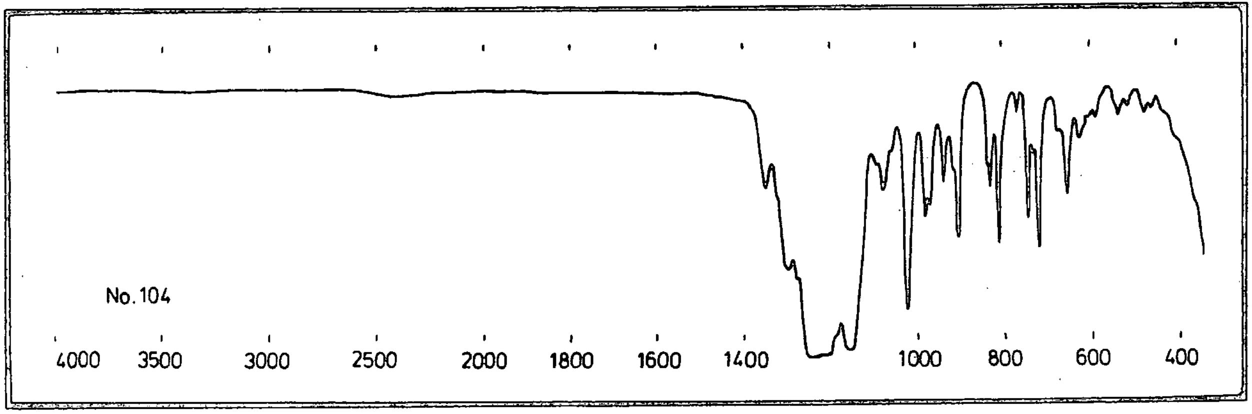


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	6.35	36	535.24	0.85
2	30.91	0.50			
3	32.02	1.26			
4	68.41	0.38			
5	68.98	100.00			
6	69.38	0.32			
7	69.92	1.35			
8	97.01	0.26			
9	99.90	1.20			
10	117.91	0.26			
11	118.97	75.44			
12	119.30	3.48			
13	119.96	1.87			
14	130.96	12.92			
15	132.02	0.50			
16	146.98	0.73			
17	149.90	0.32			
18	166.76	0.35			
19	167.09	0.32			
20	167.67	0.26			
21	168.95	60.64			
22	169.64	3.42			
23	180.96	15.76			
24	181.98	0.56			
25	196.97	0.50			
26	218.98	1.32			
27	229.51	0.32			
28	230.90	34.42			
29	231.61	5.82			
30	280.90	0.56			
31	318.84	30.70			
32	319.62	5.29			
33	330.94	0.38			
34	447.02	0.85			
35	485.08	1.70			

No.104

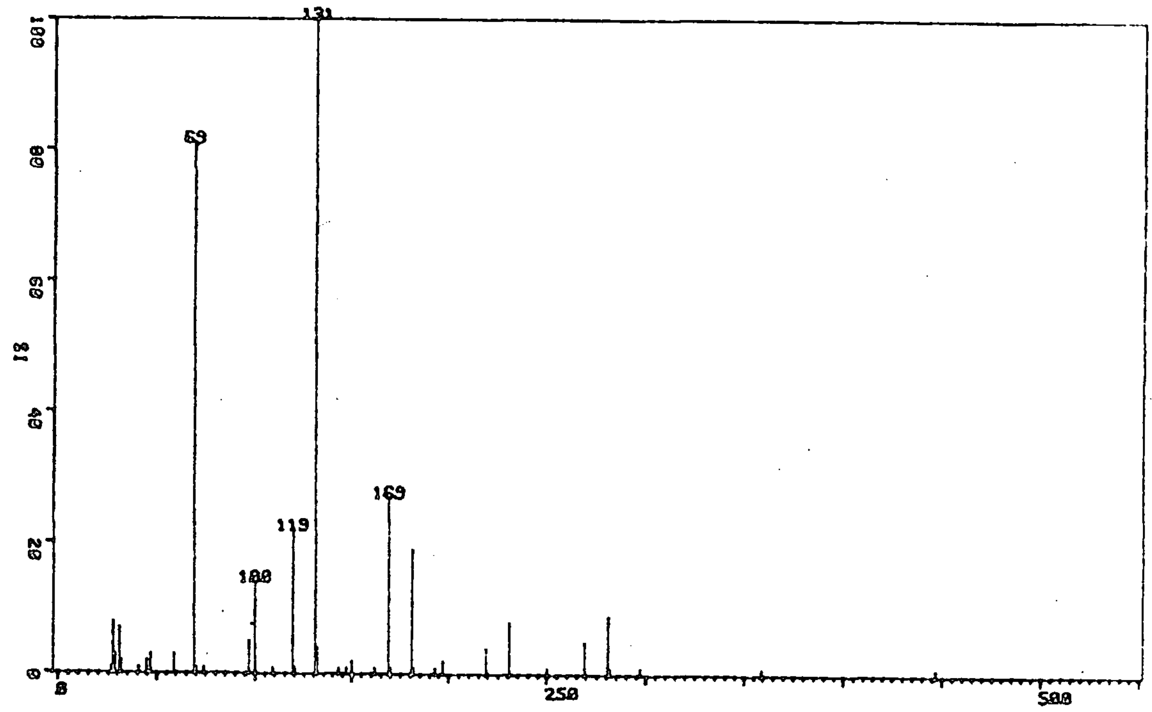


Perfluoro 2-propyloxepane (186).



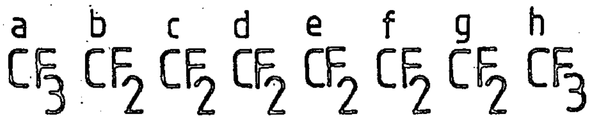
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
82.0	M	2	f
84.3	T, J=11	3	i
123.3, 124.5, 127.0, 128.0, 131.0, 131.8, 134.2, 136.3.	Overlapping AB's	13	b, c, d, e, g, h.

M. Wt. 466 No. 104



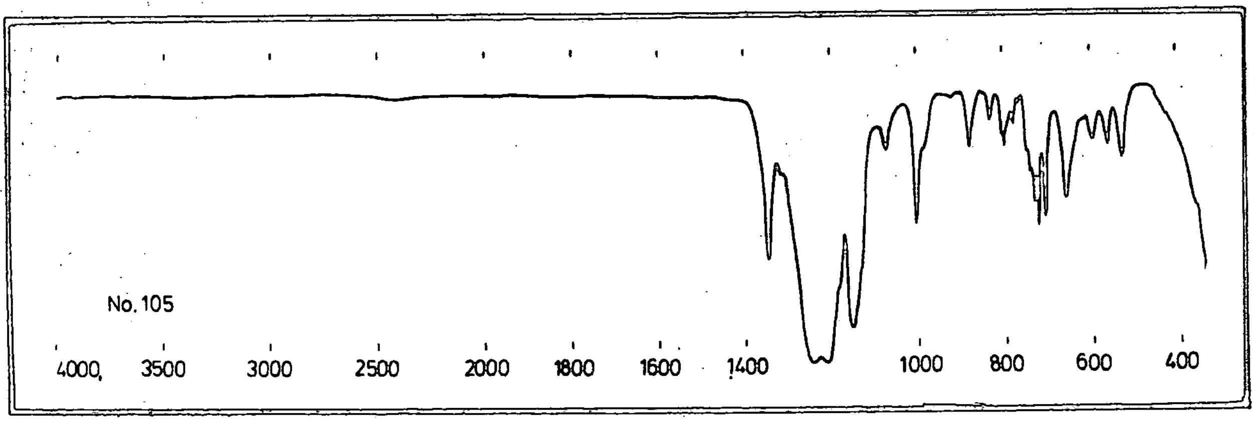
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.25	0.86	36	281.07	8.69
2	28.13	7.89	37	282.13	0.73
3	29.02	2.94	38	297.14	1.16
4	30.93	6.54	39	359.15	0.59
5	32.02	1.55	40	447.07	0.50
6	40.99	0.59			
7	45.19	1.59			
8	47.09	2.97			
9	59.05	2.41			
10	69.00	80.85			
11	69.93	1.06			
12	74.18	1.12			
13	93.04	0.36			
14	97.04	4.76			
15	99.94	14.27			
16	109.02	0.50			
17	118.98	22.46			
18	119.95	0.53			
19	130.16	0.33			
20	131.01	100.00			
21	132.02	3.53			
22	143.06	0.53			
23	147.06	0.76			
24	149.98	1.65			
25	162.06	0.86			
26	169.07	27.18			
27	170.07	0.92			
28	181.07	18.53			
29	182.10	0.83			
30	193.11	1.22			
31	197.06	2.05			
32	219.02	4.36			
33	231.07	7.73			
34	250.09	0.56			
35	269.08	4.46			

No.105



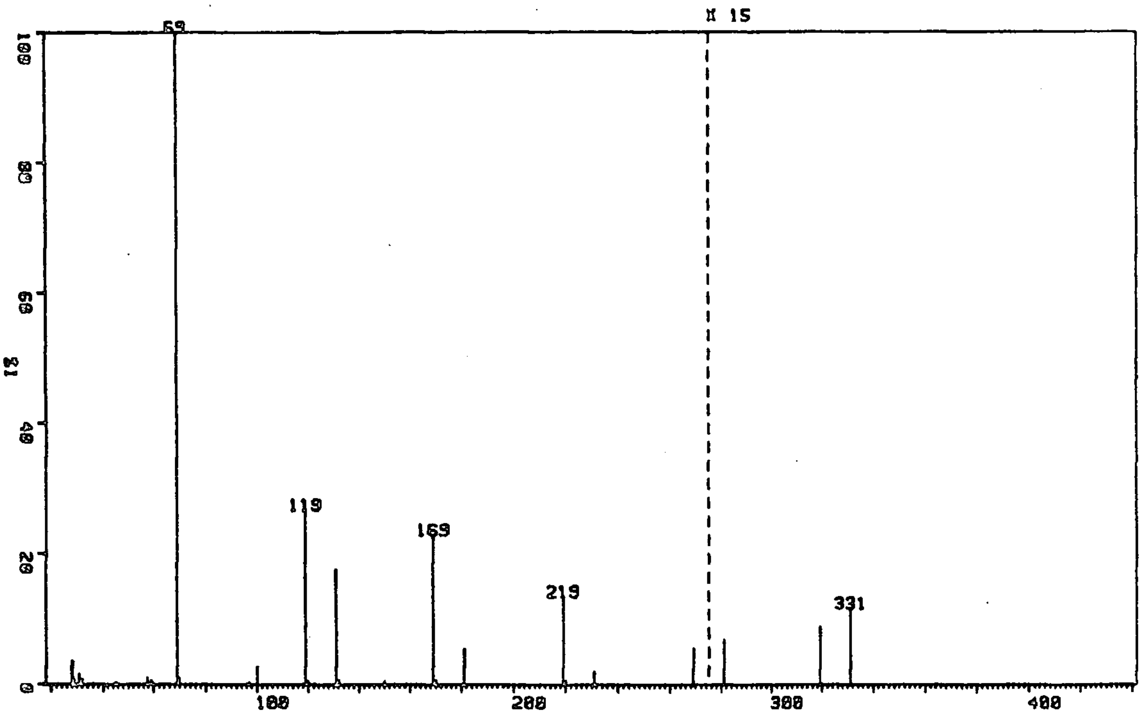
$\overset{a}{CF_3}\,\overset{b}{CF_2}\,\overset{c}{CF_2}\,\overset{d}{CF_2}\,\overset{e}{CF_2}\,\overset{f}{CF_2}\,\overset{g}{CF_2}\,\overset{h}{CF_3}$

Perfluoro-octane (187).

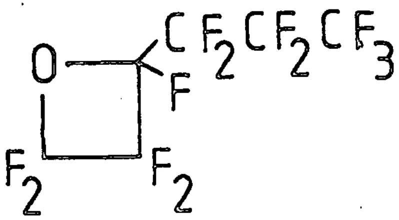


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
84.5	M (T)	3	a , h
124.3	M	2	d , e
124.8	M	2	c , f
128.8	M	2	b , g

M.Wt. 438 No.105



PEAK NO.	MASS	%HT. BASE
1	28.13	3.62
2	29.02	0.83
3	30.92	1.50
4	32.02	0.78
5	45.19	0.35
6	57.41	1.02
7	59.04	0.62
8	68.99	100.00
9	69.93	1.05
10	97.09	0.35
11	99.98	2.71
12	119.03	26.65
13	120.00	0.51
14	131.04	17.67
15	132.07	0.67
16	150.02	0.54
17	169.08	22.92
18	170.06	0.72
19	181.09	5.50
20	219.06	13.49
21	220.08	0.59
22	231.14	1.93
23	269.07	5.55
24	281.11	0.46
25	319.13	0.59
26	331.11	0.78



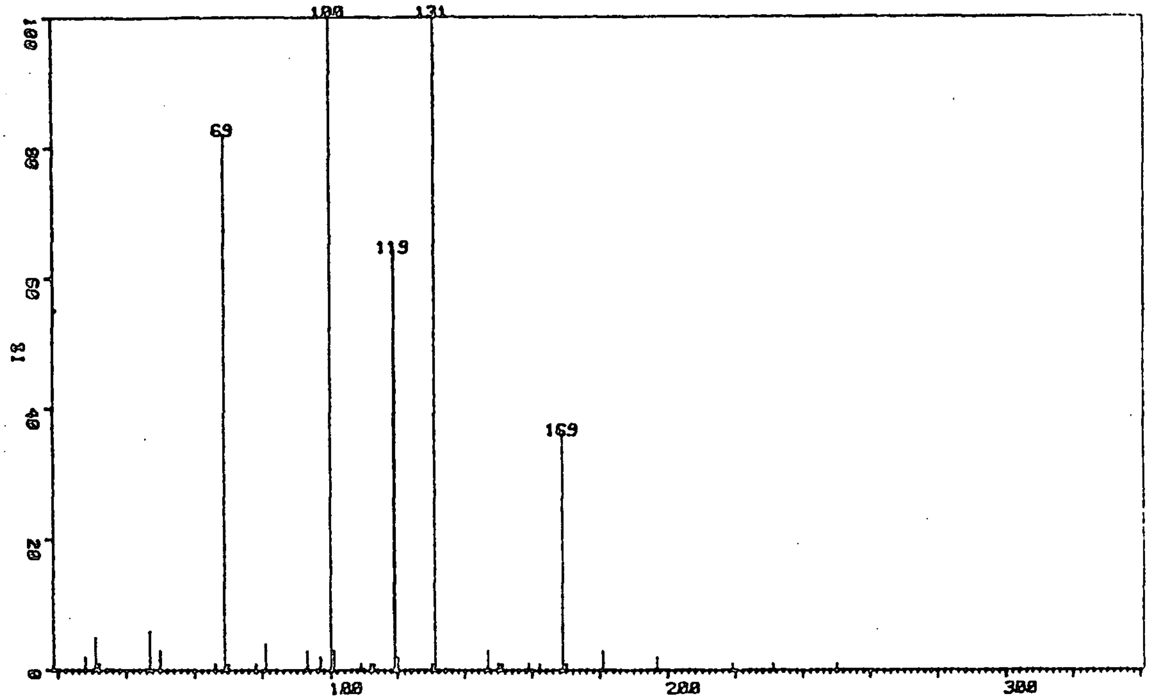
No.106

Perfluoro-2-propyloxetane. (188)

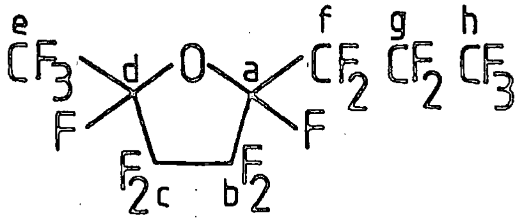
No Spectrum.

SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
	No Spectrum.		

M.Wt 316 No.106

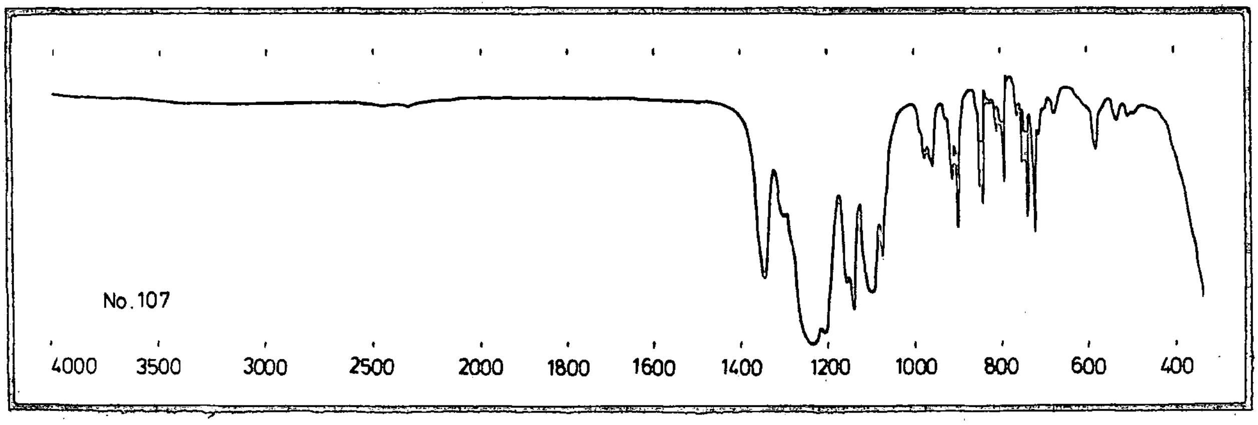


PEAK NO.	MASS	% INT BASE
1	28.13	1.59
2	30.90	4.91
3	32.02	0.66
4	47.08	5.98
5	49.86	2.93
6	50.94	0.37
7	62.01	0.27
8	66.07	0.49
9	68.96	81.83
10	69.90	1.00
11	77.99	0.49
12	80.92	3.74
13	92.99	3.39
14	97.01	2.32
15	99.89	100.00
16	100.96	2.76
17	108.96	1.37
18	111.99	1.44
19	113.02	0.51
20	118.95	64.35
21	119.93	1.59
22	130.12	0.32
23	130.97	100.00
24	146.98	2.59
25	149.90	0.73
26	150.93	0.85
27	158.97	0.37
28	161.94	0.51
29	168.91	36.09
30	169.89	1.03
31	180.94	3.44
32	196.98	2.32
33	218.94	0.32
34	230.87	0.56
35	249.92	0.36



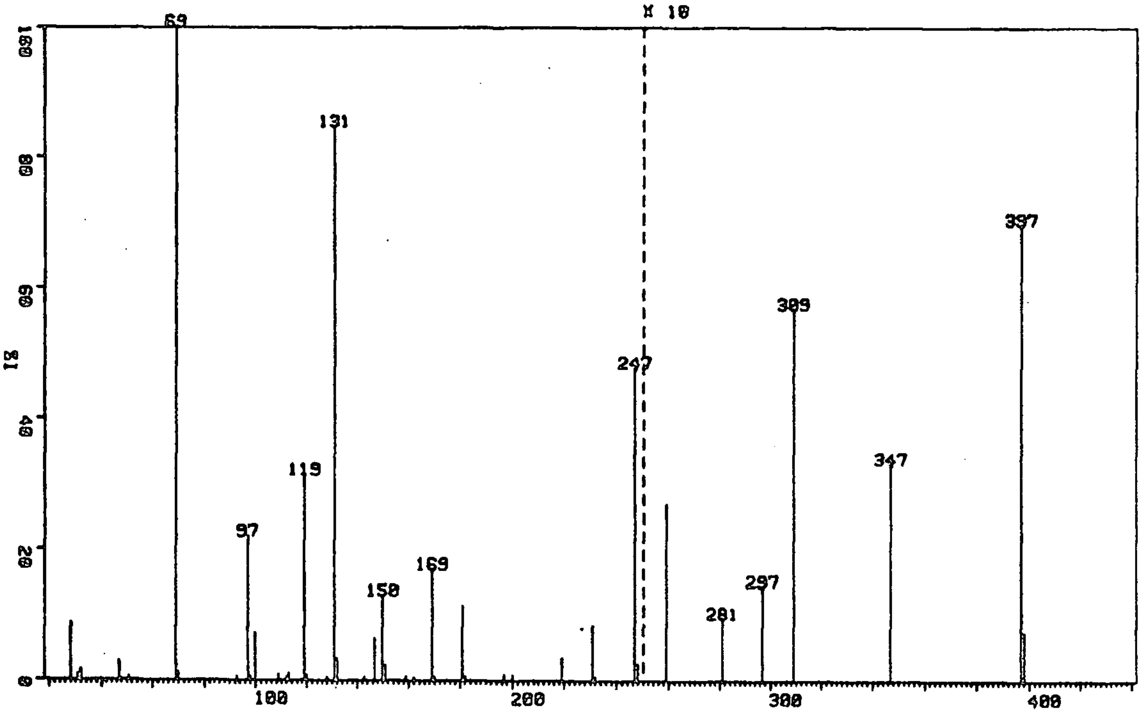
No. 107

Perfluoro 2-methyl-5-propyloxolane (190).



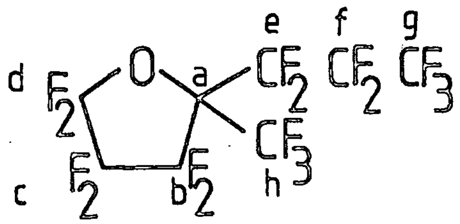
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
83.7	M (D of D, J=11 and30	3	e
84.3	M (T J=11)	3	h
119.2, 121.8, 122.3, 124.3, 125.3, 126.3, 126.8, 127.7, 128.0, 129.5, 131.5, 132.2, 133.7, 135.5, 138.2, 140.0.	Overlapping AB's	10	a, b, c, d, f, g

M.Wt. 416 No.107

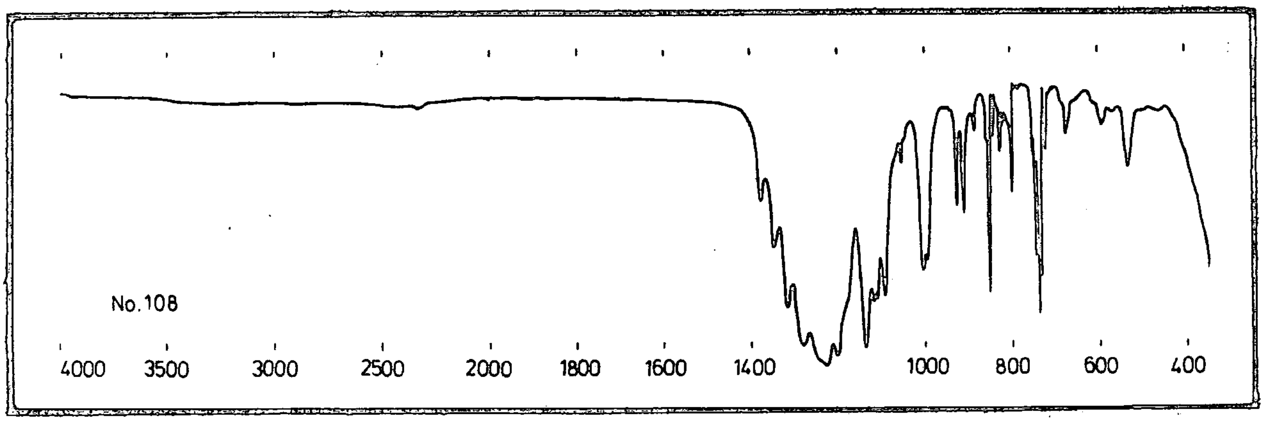


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	8.69	36	247.89	2.54
2	30.91	1.00	37	258.90	2.70
3	32.02	1.62	38	280.92	0.96
4	47.08	2.83	39	296.91	1.46
5	50.94	0.54	40	308.87	5.70
6	68.96	100.00	41	346.90	3.33
7	69.91	1.16	42	396.82	6.99
8	92.97	0.62	43	397.91	0.75
9	96.98	22.00			
10	97.96	0.58			
11	99.87	7.28			
12	108.91	0.96			
13	111.96	0.50			
14	113.00	1.04			
15	118.97	31.45			
16	119.95	0.79			
17	127.99	0.54			
18	130.93	84.73			
19	131.96	3.29			
20	142.92	0.62			
21	146.94	6.36			
22	149.89	12.98			
23	150.94	2.37			
24	158.94	0.67			
25	161.97	0.50			
26	168.95	17.01			
27	169.92	0.62			
28	180.93	11.31			
29	181.98	0.62			
30	196.90	0.96			
31	199.86	0.92			
32	218.95	3.45			
33	230.91	8.36			
34	231.92	0·62	35	246·87	47·96

No.108

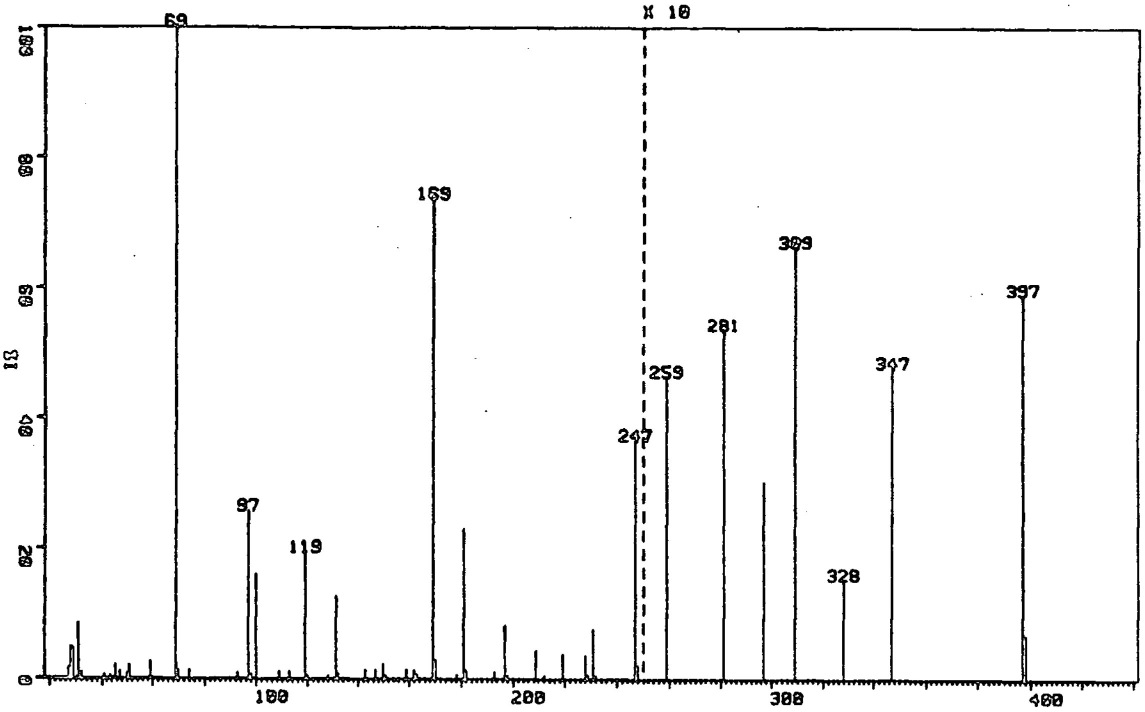


Perfluoro 2-methyl-2-propyloxolane (189).

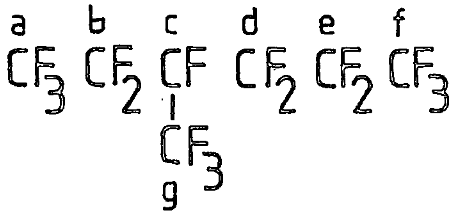


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
73.8	M	3	h
82.1, 88.0	AB, J_{FF}=141	2	d
83.8	M (T)	3	g
115.5	M	2	b, c, e, f
118.7, 120.3	M	2	
126.0	M	2	
129.1, 133.0	AB, J_{FF}=248	2	

M.Wt. 416 No.108



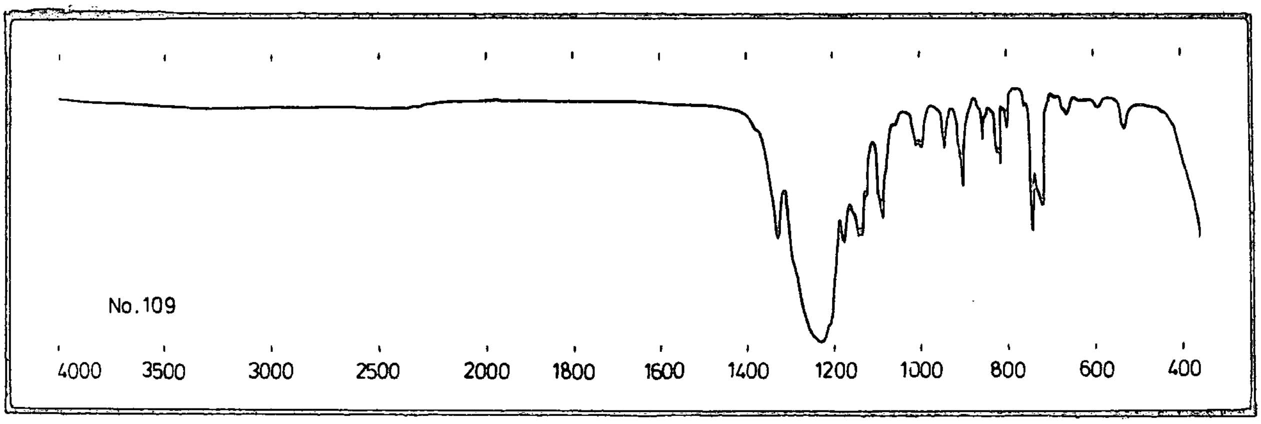
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.26	1.58	36	177.95	0.68
2	28.13	4.92	37	180.90	23.06
3	29.02	4.51	38	181.94	1.26
4	30.93	8.44	39	192.92	1.13
5	32.02	1.04	40	196.90	8.17
6	40.99	0.54	41	197.96	0.54
7	43.11	0.50	42	208.84	4.38
8	45.17	2.03	43	211.94	0.54
9	47.08	1.17	44	218.99	3.79
10	49.87	0.81	45	227.97	3.52
11	50.93	2.03	46	228.99	0.59
12	59.03	2.57	47	230.94	7.54
13	68.97	100.00	48	232.00	0.45
14	69.91	1.31	49	246.90	36.60
15	74.12	1.40	50	247.89	2.12
16	92.94	0.99	51	258.90	4.65
17	96.95	25.77	52	280.92	5.37
18	97.93	0.77	53	296.86	3.02
19	99.84	16.06	54	308.91	6.63
20	108.89	1.17	55	327.92	1.53
21	113.01	1.17	56	346.91	4.78
22	118.96	19.45	57	396.82	5.91
23	119.96	0.54	58	397.92	0.68
24	127.99	0.50			
25	130.94	12.68			
26	131.97	0.77			
27	142.93	1.49			
28	146.95	1.40			
29	149.89	2.35			
30	150.97	0.50			
31	158.95	1.44			
32	161.95	1.35			
33	162.97	0.59			
34	168.93	73.65	35	169.93	2.84



$\overset{a}{CF_3}\,\overset{b}{CF_2}\,\overset{c}{CF}(\underset{g}{CF_3})\,\overset{d}{CF_2}\,\overset{e}{CF_2}\,\overset{f}{CF_3}$

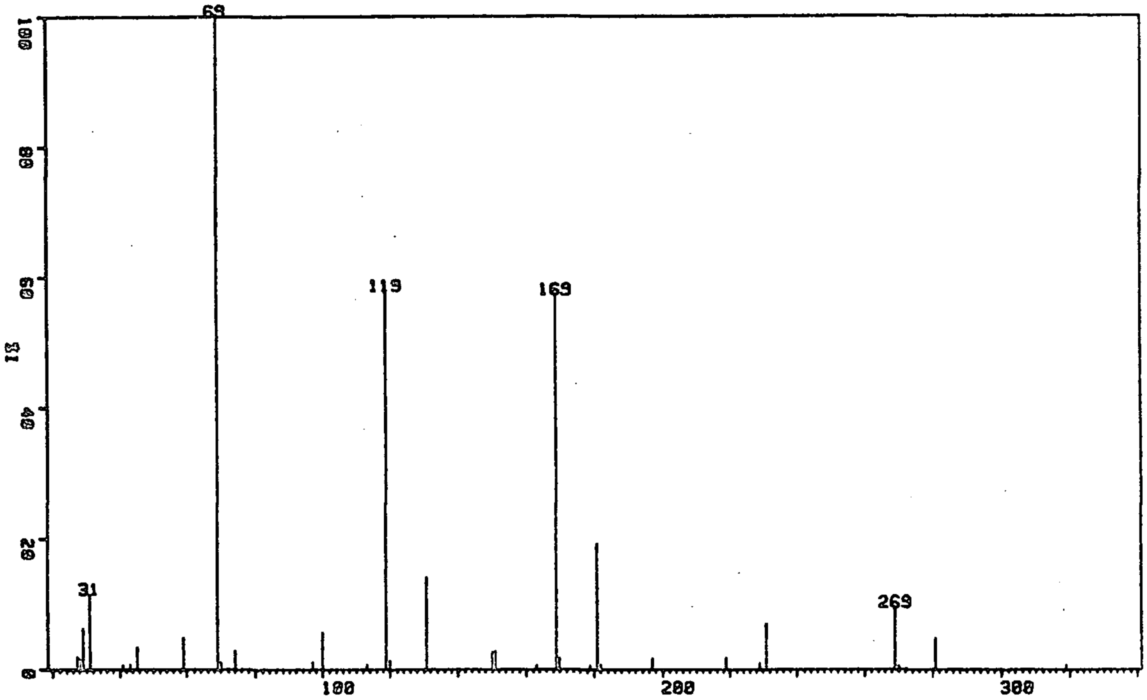
No.109

Perfluoro 3-methylhexane (109).

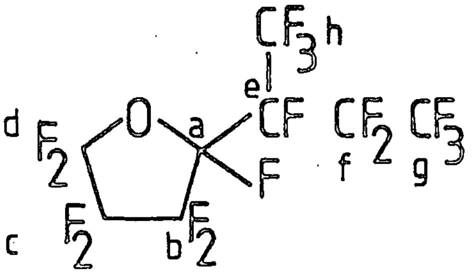


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
73.7	M	3	g
83.5	M	3	a
84.2	M	3	f
115.8	M	2	d
118.9	M	2	b
126.8	M	2	e
187.0	M	1	c

M.Wt. 388 No.109

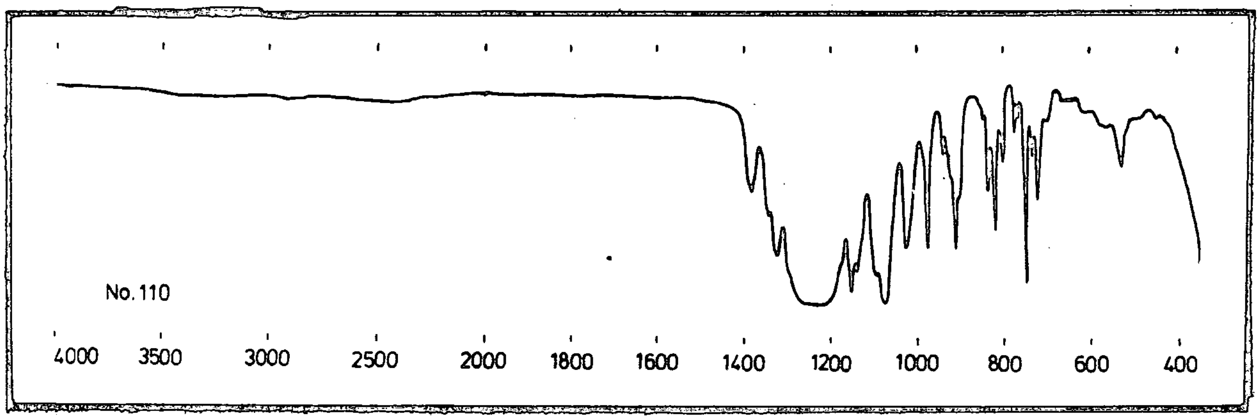


PEAK NO.	MASS	%HT. BASE
1	27.25	1.98
2	28.13	1.55
3	29.02	6.24
4	30.92	11.57
5	40.99	0.68
6	43.11	0.82
7	45.16	3.48
8	59.01	4.84
9	68.95	100.00
10	69.89	1.11
11	74.15	2.90
12	97.00	1.16
13	99.89	5.71
14	113.04	0.82
15	118.96	58.03
16	119.92	1.31
17	130.94	14.13
18	149.92	2.61
19	150.95	2.76
20	163.00	0.68
21	168.91	57.45
22	169.90	1.79
23	178.93	0.58
24	180.91	19.22
25	181.94	0.82
26	196.97	1.74
27	218.86	1.79
28	228.95	1.06
29	230.95	7.02
30	268.93	9.54
31	269.92	0.63
32	280.91	4.79
33	318.89	0.73



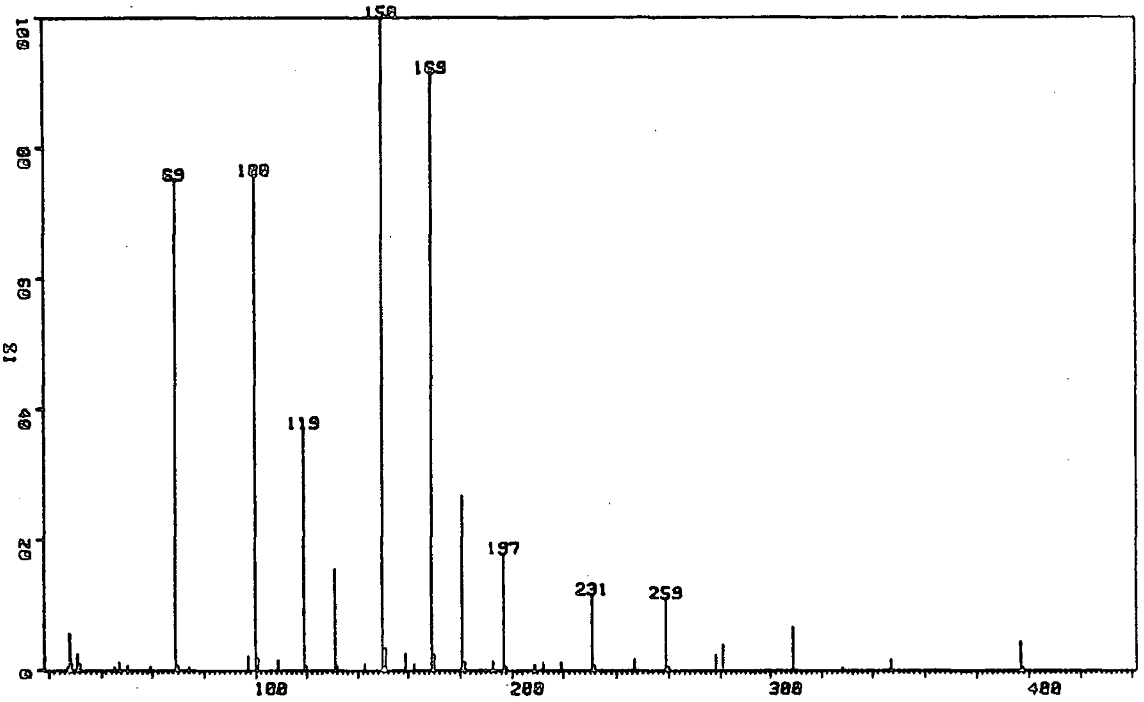
No.110

Perfluoro 2-(1-methylpropyl)oxolane (192).

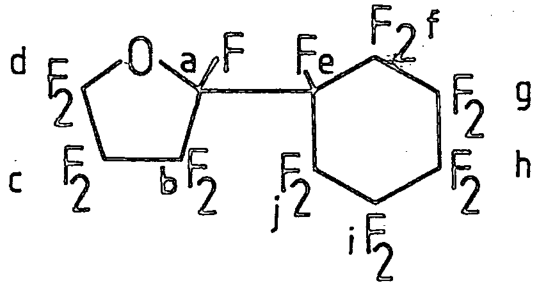


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
73.3	M	3	h
74.5	M		
83.8	M	3	g
85.5, 86.8, 87.7, 89.5, 90.0, 92.0,	Overlapping M's	2	d
117.8	M	3	a , f
126.2, 126.7, 128.0, 128.8, 130.2, 133.2, 136.0, 137.8, 140.5, 142.5.	Overlapping AB's	4	b , c
185.3	M	1	e

M.Wt. 416 No. 110

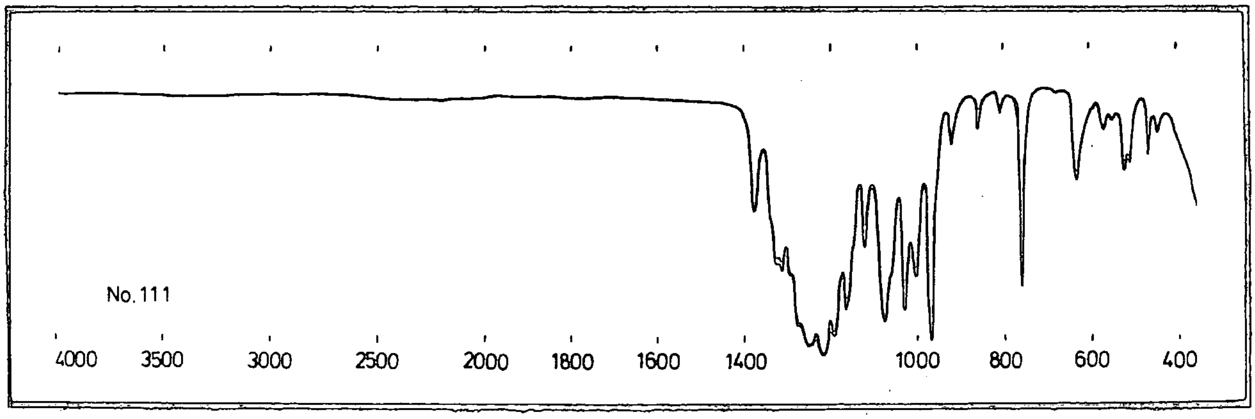


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.26	0.54	36	230.94	11.71
2	28.13	5.65	37	231.96	0.79
3	29.03	1.12	38	246.94	1.83
4	30.92	2.57	39	258.88	11.09
5	32.02	1.04	40	259.89	0.66
6	45.18	0.62	41	277.96	2.45
7	47.10	1.33	42	280.94	4.07
8	49.88	0.75	43	308.90	6.60
9	59.05	0.62	44	327.97	0.50
10	68.99	75.08	45	346.97	1.79
11	69.93	0.91	46	396.91	4.44
12	74.16	0.58	47	397.89	0.62
13	96.97	2.28			
14	99.88	75.87			
15	100.95	1.95			
16	108.92	1.62			
17	118.99	37.13			
18	119.97	0.75			
19	130.96	15.57			
20	131.99	0.79			
21	142.96	1.04			
22	149.89	100.00			
23	150.95	3.45			
24	158.95	2.62			
25	161.98	1.04			
26	168.96	91.49			
27	169.96	2.49			
28	180.95	26.79			
29	181.97	1.33			
30	192.95	1.45			
31	196.92	17.98			
32	197.90	0.62			
33	208.87	0.96			
34	211.93	1.25	35	219.02	1.33



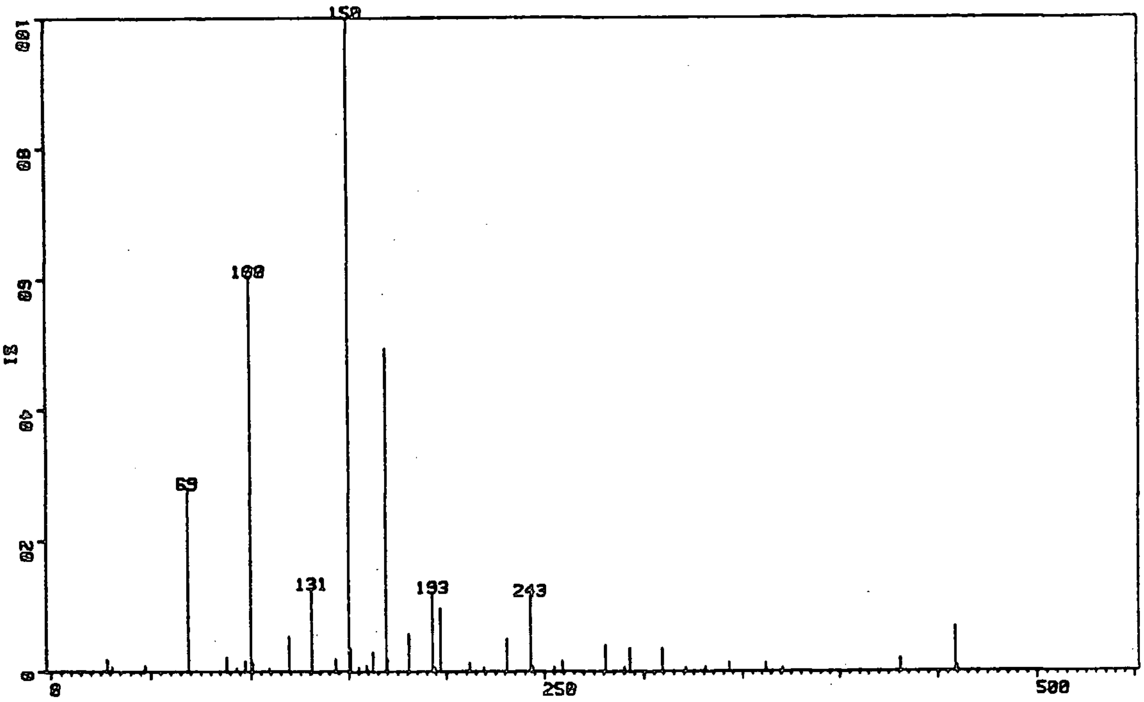
No.111

Perfluoro 2-cyclohexyloxolane (193).



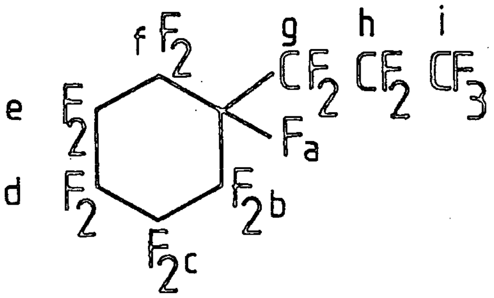
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
83.3, 87.7	AB, J_{FF}=136	2	d
113.7, 114.3, 115.0, 116.8, 117.3, 122.2, 124.3, 127.2, 128.7, 130.2, 130.7, 131.3, 131.8, 132.3, 133.0, 134.0, 136.7, 138.7, 140.0, 142.5, 143.0, 145.0, 147.7.	Overlapping AB's	15	a, b, c, f, g, h, i, j.
186.7	M	1	e

M.Wt. 478 No. 111

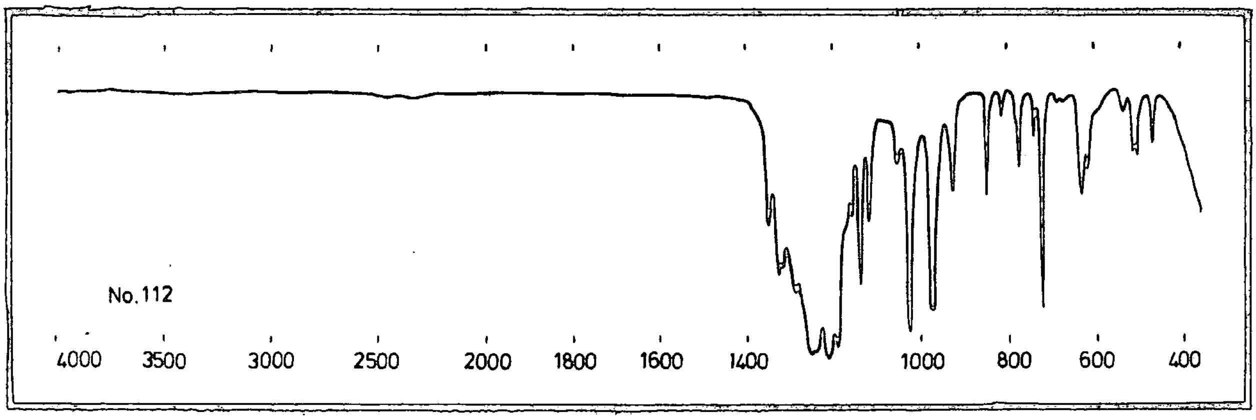


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	1.91	36	320.97	0.70
2	30.91	0.70	37	330.95	0.74
3	47.09	0.88	38	342.93	1.44
4	68.98	27.98	39	361.99	1.40
5	87.96	2.09	40	370.99	0.61
6	93.04	0.51	41	430.92	2.00
7	97.04	1.63	42	458.89	6.84
8	99.94	60.47	43	459.95	0.88
9	100.98	1.30			
10	109.00	0.56			
11	118.98	5.35			
12	130.99	12.62			
13	143.03	1.91			
14	149.95	100.00			
15	150.99	3.45			
16	155.04	0.70			
17	158.99	0.93			
18	162.01	2.98			
19	168.98	49.44			
20	169.97	1.96			
21	180.96	5.77			
22	193.01	12.01			
23	194.06	0.70			
24	197.01	9.59			
25	211.98	1.35			
26	218.99	0.61			
27	230.98	4.98			
28	242.99	11.55			
29	244.02	0.74			
30	255.00	0.74			
31	258.97	1.68			
32	281.00	4.05			
33	289.95	0.70			
34	292.95	3.58			
35	308.93	3.54			

No.112

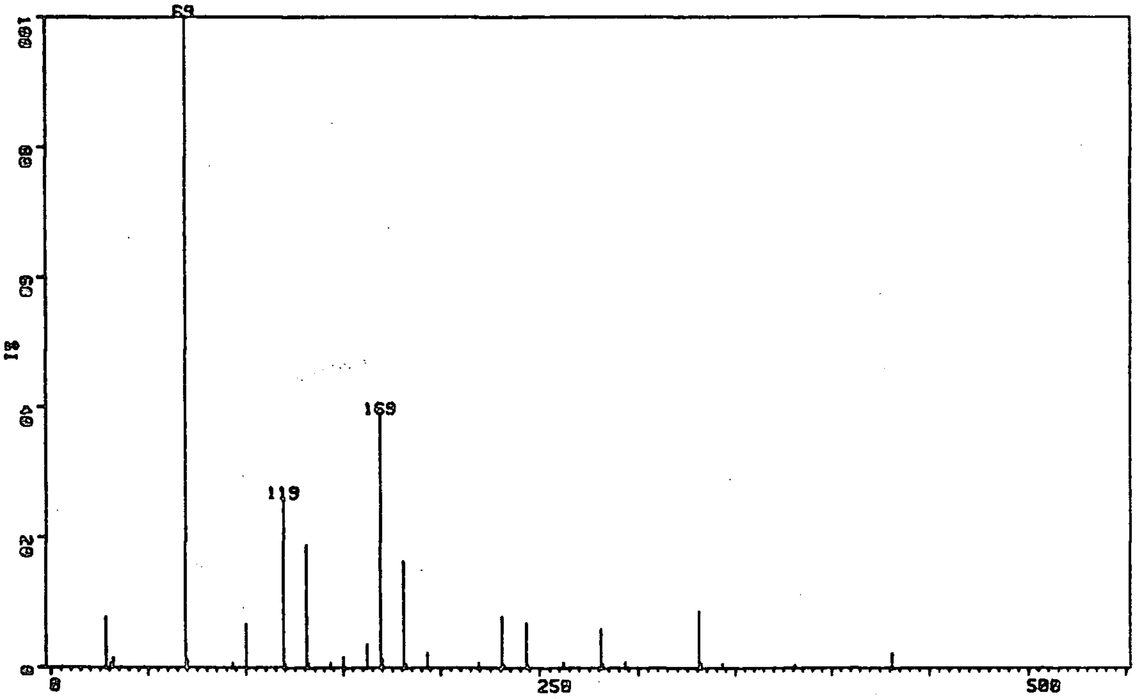


Perfluoropropylcyclohexane (194).

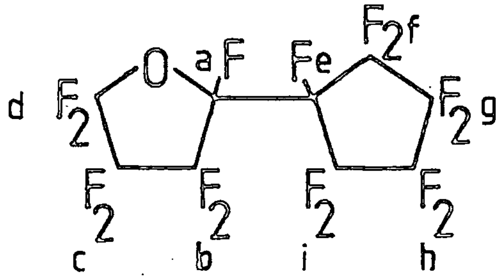


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
84.6	M	3	i
117.4, 121.1, 124.6, 126.5, 128.1, 130.1, 132.1, 135.7, 141.8, 144.5, 145.3, 147.9.	Overlapping AB's	14	b, c, d, e, f, g, h.
190.6	M	1	a

M.Wt. 450 No. 112

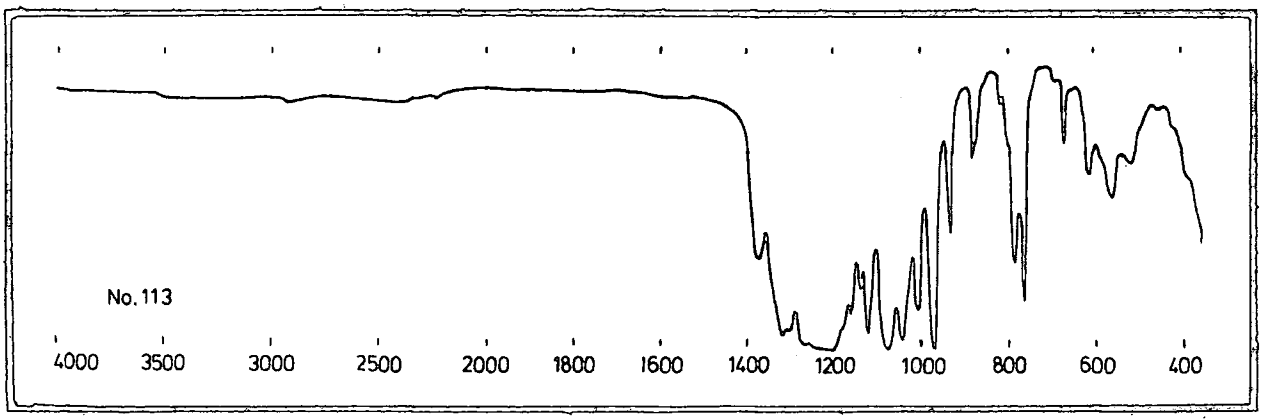


PEAK NO.	MASS	%HT. BASE
1	28.13	7.72
2	30.92	0.72
3	32.02	1.54
4	69.03	100.00
5	69.97	1.20
6	93.12	0.79
7	99.99	6.66
8	119.07	26.06
9	120.05	0.51
10	131.10	18.75
11	132.11	0.68
12	143.12	0.85
13	150.04	1.74
14	162.12	3.62
15	169.05	39.04
16	170.00	1.33
17	181.06	16.26
18	182.15	0.51
19	193.12	2.36
20	219.06	0.89
21	231.11	7.89
22	232.15	0.38
23	243.10	6.97
24	244.06	0.48
25	262.08	0.92
26	281.14	5.98
27	282.15	0.58
28	293.09	0.96
29	331.08	8.67
30	332.14	0.79
31	343.10	0.75
32	381.12	0.48
33	431.14	2.42



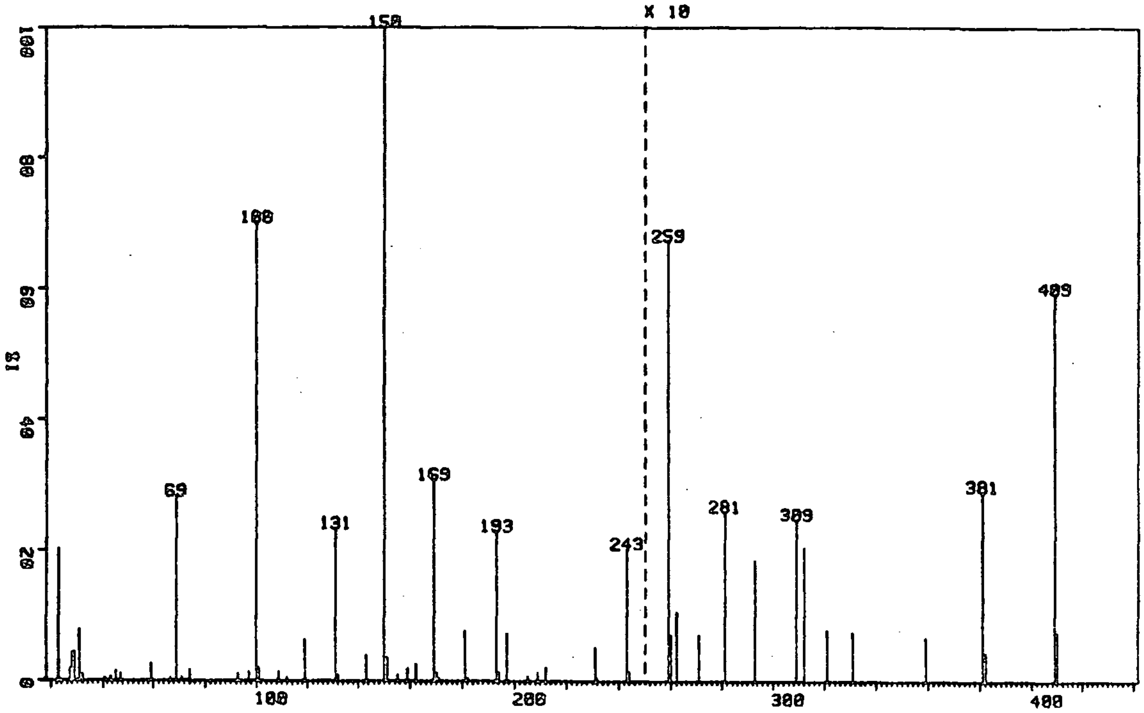
No.113

Perfluoro 2-cyclopentyloxolane (195).



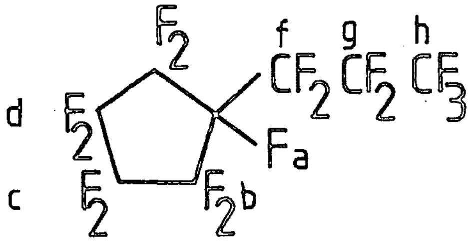
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
85.7, 87.6	AB, J_{FF}=130	2	d
118.0	M	1	a
121.7, 126.5, 126.9, 127.5, 128.3, 129.2, 130.7, 131.8, 133.2, 135.3, 136.0, 136.5, 140.8.	Overlapping AB's	12	b, c, f, g, h, i.
184.0	M	1	e

M.Wt. 428 No. 113

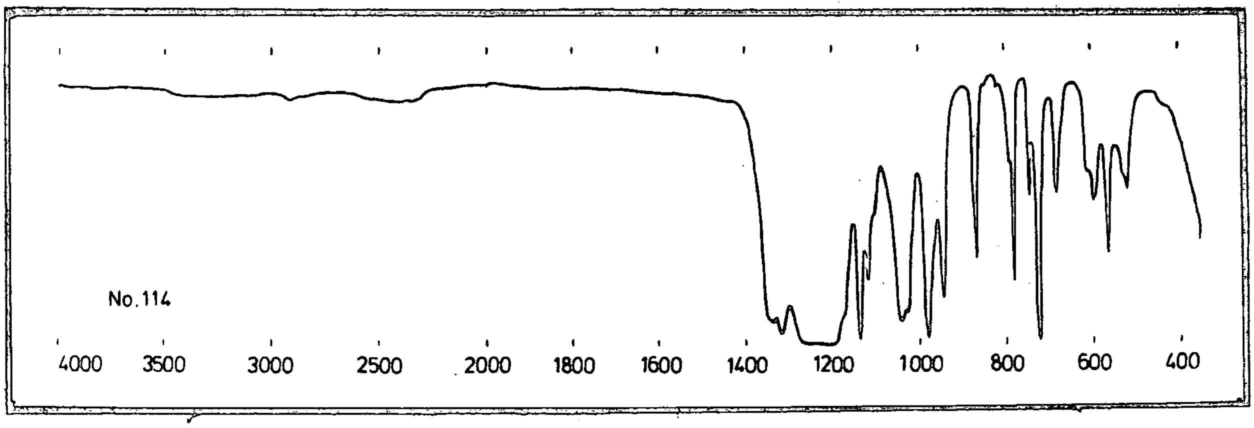


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	22.93	20.17	36	193.10	23.01
2	27.26	1.77	37	194.11	1.42
3	28.14	4.26	38	197.07	7.29
4	29.03	4.37	39	205.13	0.75
5	30.94	7.72	40	208.99	1.30
6	32.03	0.99	41	212.07	2.13
7	41.02	0.43	42	231.04	5.16
8	43.15	0.67	43	232.07	0.43
9	45.20	1.54	44	243.11	20.33
10	47.11	1.10	45	244.11	1.38
11	59.07	2.60	46	259.03	6.74
12	66.83	0.43	47	260.03	0.71
13	69.01	28.25	48	262.07	1.06
14	71.07	0.59	49	271.09	0.71
15	74.18	1.62	50	281.05	2.60
16	93.05	1.14	51	293.07	1.85
17	97.05	1.38	52	309.09	2.48
18	99.95	70.17	53	312.12	2.05
19	101.00	2.01	54	321.08	0.79
20	109.01	1.50	55	331.11	0.75
21	112.05	0.51	56	359.04	0.67
22	119.05	6.26	57	381.08	2.92
23	131.04	23.40	58	382.10	0.43
24	132.08	0.99	59	409.15	5.95
25	143.09	3.90	60	410.12	0.75
26	150.03	100.00			
27	151.07	3.59			
28	155.13	0.95			
29	159.03	1.89			
30	162.08	2.52			
31	169.06	30.89			
32	170.07	1.22			
33	171.09	0.39			
34	181.04	7.68	35	182.09	0.43

No.114

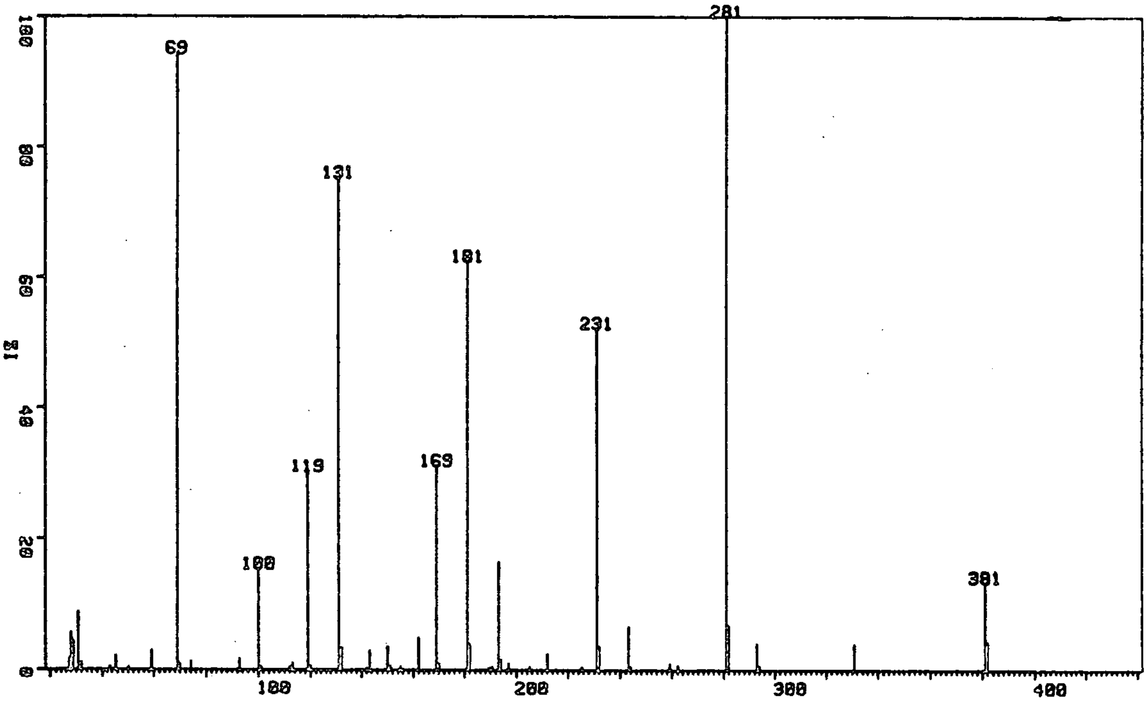


Perfluoropropylcyclopentane (196).

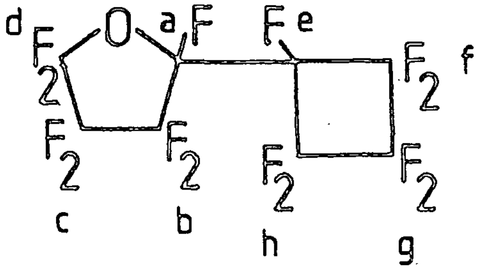


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
84.0	M (T J=10)	3	h
118.7, 122.5, 127.5, 129.5, 133.0, 134.0, 138.8.	Overlapping AB's	12	b, c, d, e, f, g.
187.5	M	1	a

M.Wt. 400 No. 114

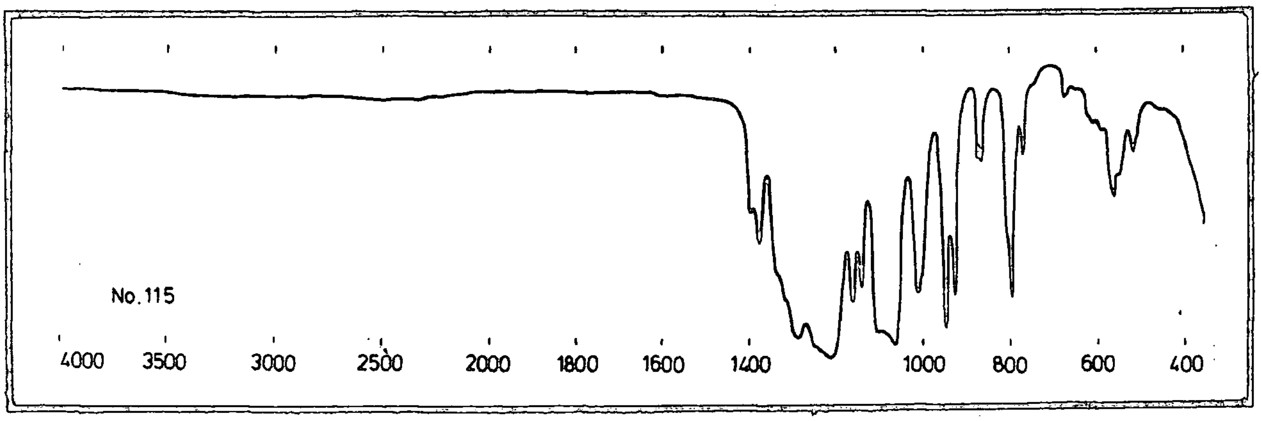


PEAK NO.	MASS	%HT. BASE
1	27.26	1.68
2	28.14	5.71
3	29.03	4.36
4	30.93	8.78
5	32.03	1.13
6	43.13	0.48
7	45.19	2.12
8	49.90	0.40
9	59.06	2.96
10	69.01	94.33
11	69.95	0.99
12	74.16	1.32
13	93.02	1.68
14	99.94	15.45
15	100.99	0.48
16	112.04	0.55
17	113.06	1.10
18	119.03	30.34
19	120.00	0.66
20	131.02	75.29
21	132.04	3.37
22	141.86	0.33
23	143.07	2.96
24	150.01	3.62
25	151.05	0.66
26	155.14	0.59
27	162.03	4.83
28	169.04	31.15
29	170.01	0.95
30	181.01	62.45
31	182.03	3.92
32	189.52	0.33
33	190.68	0.51
34	193.04	16.43
35	194.06	1.57
36	197.04	1.02
37	205.10	0.59
38	212.06	2.45
39	225.17	0.44
40	231.07	52.27
41	232.10	3.70
42	243.09	6.59
43	244.12	0.55
44	259.08	0.99
45	262.12	0.73
46	281.01	100.00
47	281.92	6.81
48	293.08	4.06
49	294.17	0.70
50	331.05	3.88
51	381.09	13.43
52	381.80	4.36



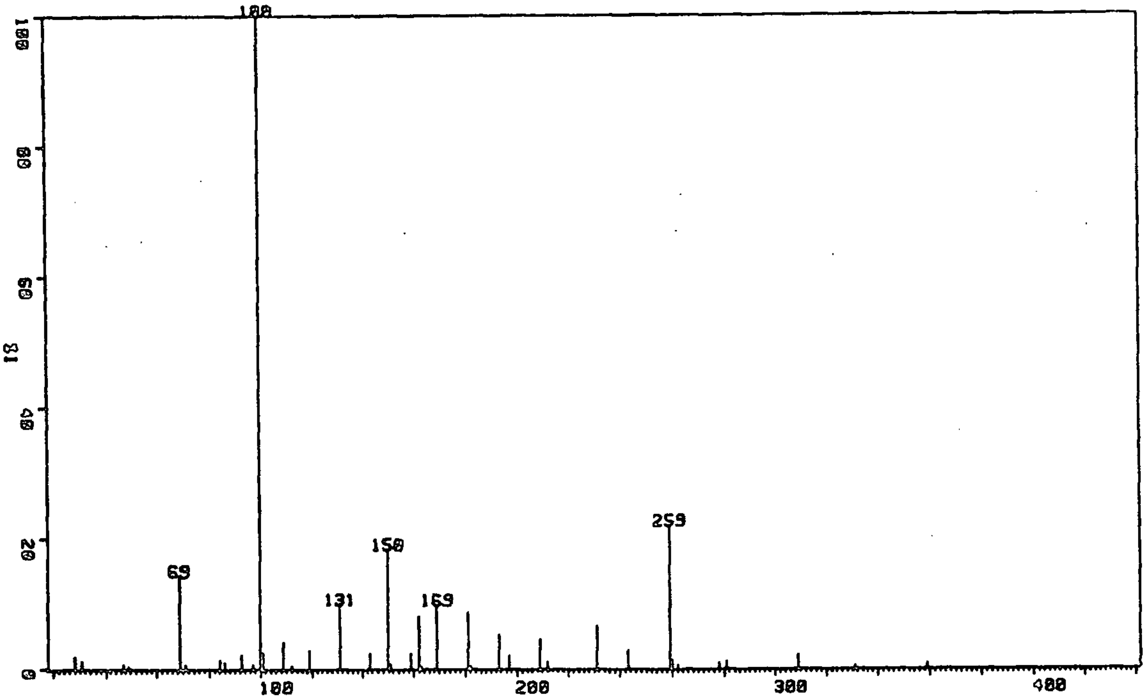
No. 115

Perfluoro 2-cyclobutyloxolane (197).

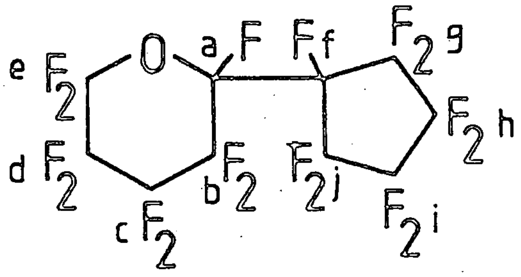


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
84.3, 88.5	AB, J_{FF}=132	2	d
120.7	M	1	a
124.0, 127.7, 128.7, 129.7, 130.3, 130.8, 132.0, 133.7, 134.5, 135.2, 135.7, 140.2.	Overlapping AB's	10	b, c, f, g, h.
191.7	M	1	e

M.Wt. 378 No. 115

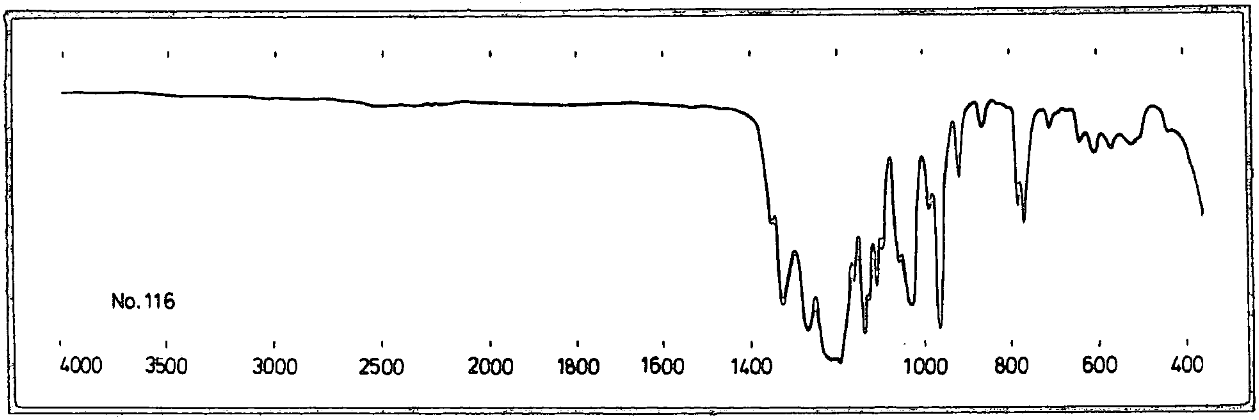


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	2.00	36	281.02	1.27
2	30.91	1.23	37	309.04	2.29
3	47.09	0.81	38	331.14	0.68
4	48.96	0.42	39	359.05	0.93
5	69.00	14.23			
6	71.04	0.72			
7	84.01	1.44			
8	86.00	1.10			
9	93.06	2.34			
10	97.07	0.76			
11	99.97	100.00			
12	101.01	2.51			
13	109.00	4.20			
14	112.06	0.64			
15	119.04	2.97			
16	131.06	9.98			
17	143.11	2.55			
18	150.00	18.34			
19	151.04	0.81			
20	159.01	2.46			
21	162.05	8.20			
22	163.05	0.38			
23	169.03	9.81			
24	181.03	8.70			
25	182.08	0.55			
26	193.08	5.35			
27	197.06	2.17			
28	209.01	4.71			
29	212.07	1.15			
30	231.04	6.62			
31	243.10	3.06			
32	259.05	21.87			
33	260.08	1.40			
34	262.13	0.64			
35	278.07	1.02			



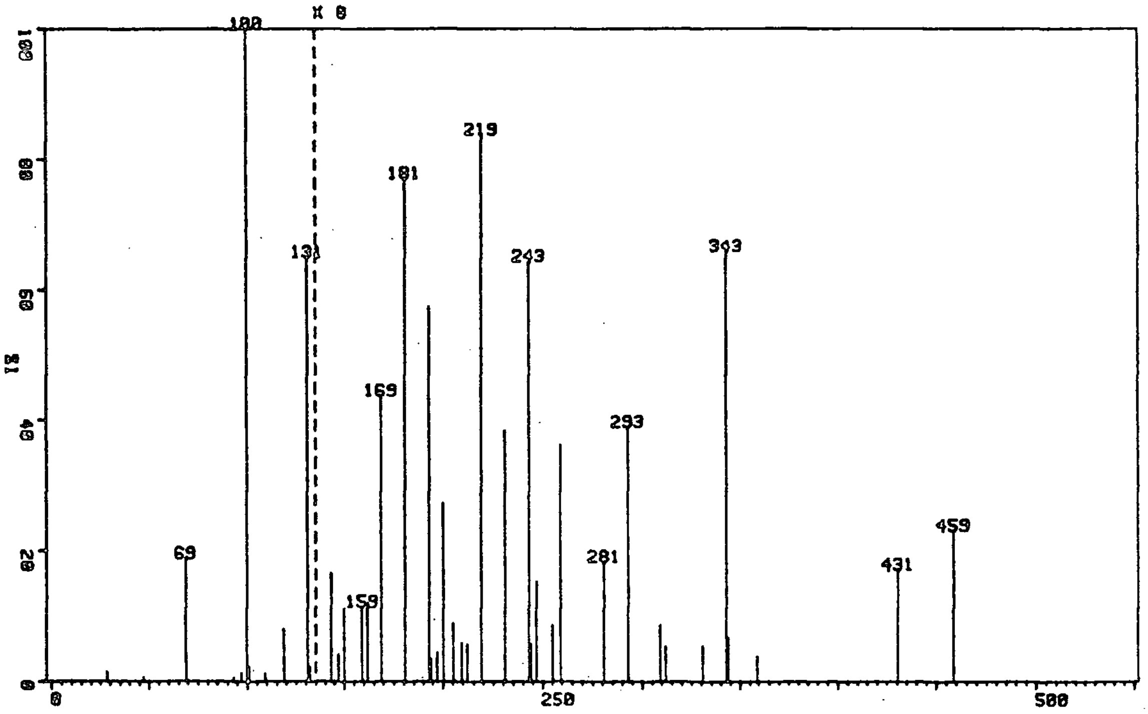
No. 116

Perfluoro 2-cyclopentyloxane (198).

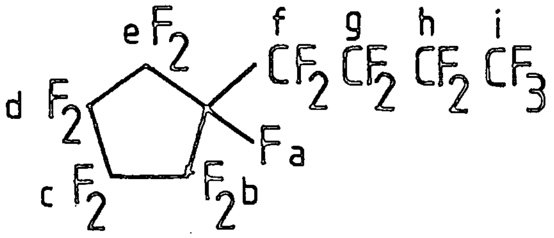


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
79.4, 93.5	AB, J_{FF}=160	2	e
116.8, 121.2, 122.0, 124.7, 125.5, 126.2, 129.8, 130.7, 131.2, 131.5, 131.8, 134.3, 134.8, 138.5, 138.8, 140.2, 143.5, 145.2.	Overlapping AB's	15	a, b, c, d, g, h, i, j.
184.0	M	1	f

M.Wt. 478 No. 116

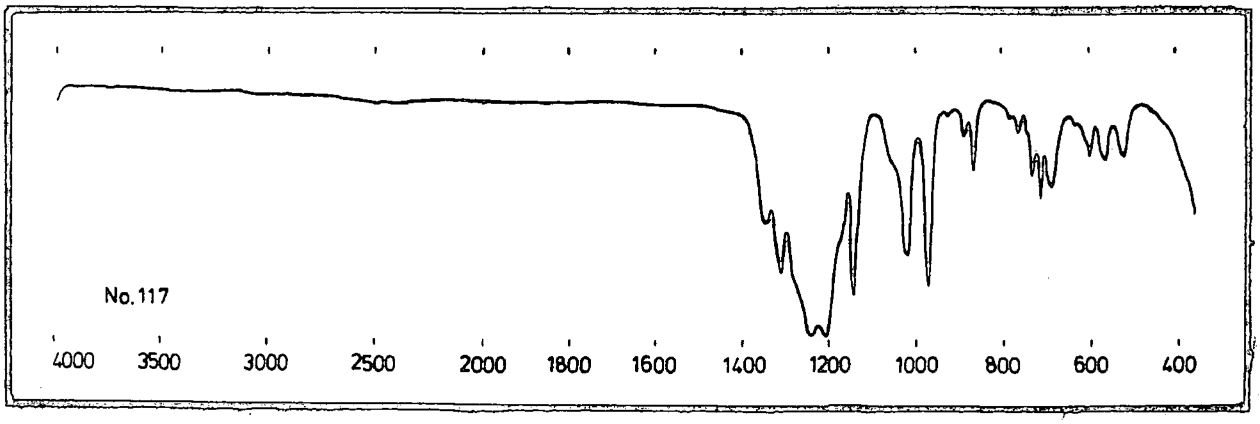


PEAK NO.	MASS	%HT. BASE
1	28.13	1.47
2	47.09	0.60
3	68.95	18.86
4	92.99	0.60
5	96.99	1.27
6	99.89	100.00
7	100.96	2.26
8	108.96	1.19
9	118.93	8.06
10	130.93	65.11
11	131.97	2.34
12	142.96	2.06
13	146.94	0.52
14	149.91	1.39
15	158.91	1.43
16	161.93	1.51
17	168.90	5.48
18	180.89	9.65
19	192.96	7.19
20	193.98	0.44
21	196.97	0.56
22	199.88	3.41
23	204.99	1.11
24	208.94	0.75
25	211.94	0.71
26	218.89	10.48
27	230.92	4.80
28	242.92	8.06
29	243.95	0.71
30	246.90	1.91
31	254.91	1.07
32	258.88	4.53
33	280.96	2.30
34	292.90	4.88
35	308.87	1.07
36	311.91	0.67
37	330.84	0.67
38	342.91	8.26
39	343.94	0.83
40	358.91	0.48
41	430.69	2.14
42	458.71	2.90



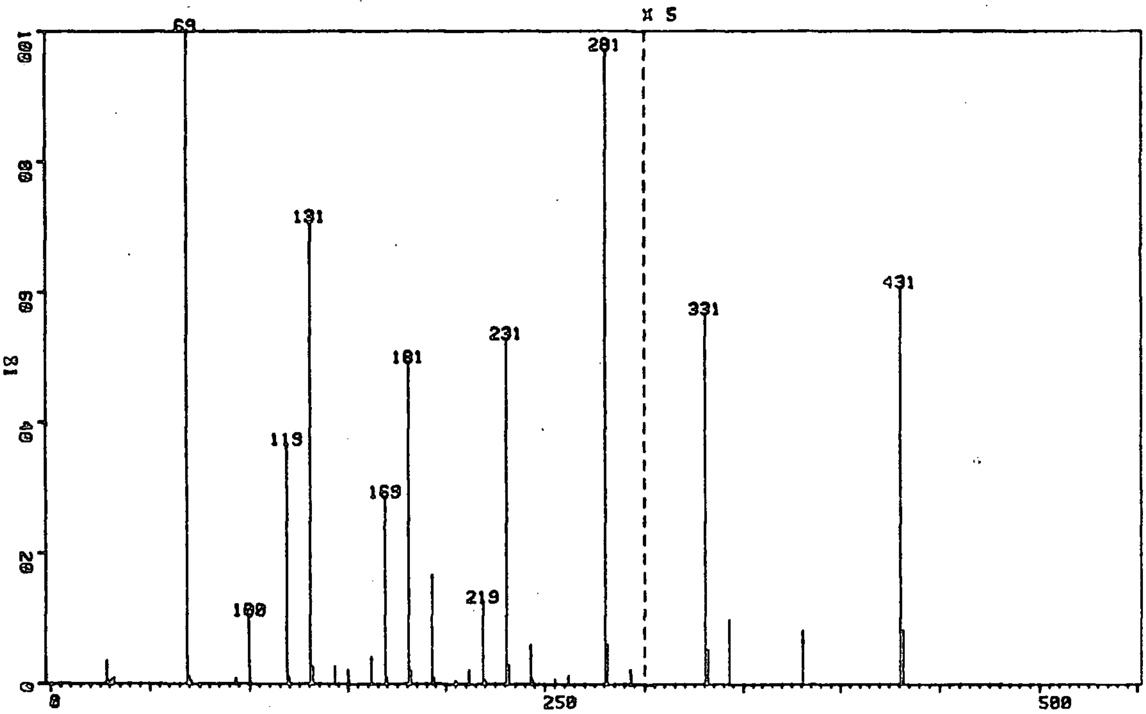
No.117

Perfluorobutylcyclopentane (199).

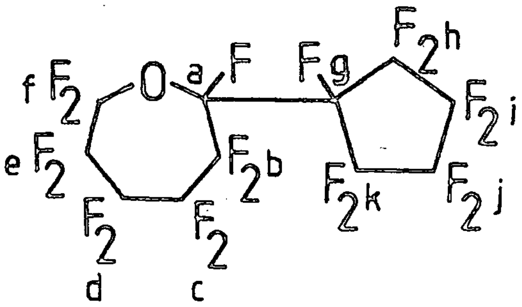


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
83.3	T, J=11	3	i
117.0, 121.7, 123.0, 126.3, 127.8, 128.5, 132.2, 133.3, 137.8.	Overlapping AB's	14	b, c, d, e, f, g, h.
186.3	M	1	a

M.Wt. 450 No.117

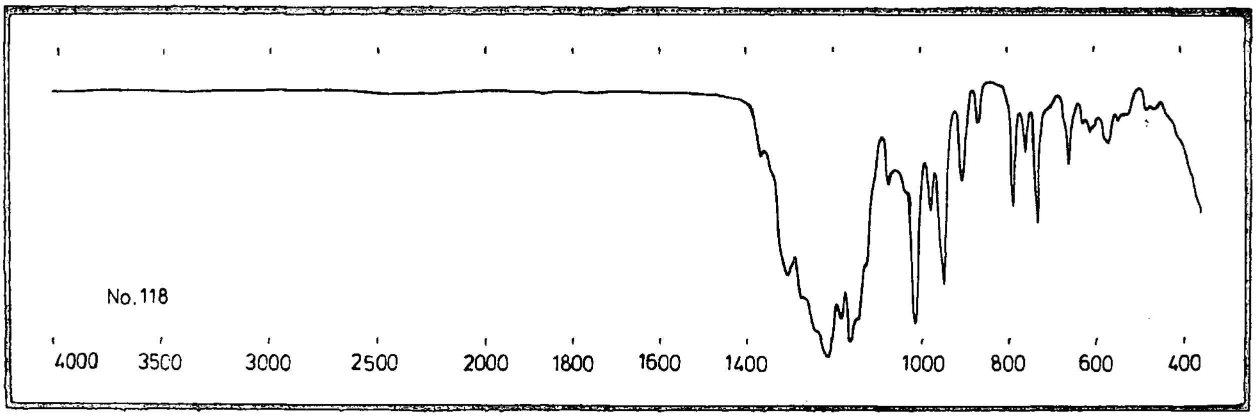


PEAK NO.	MASS	%HT. BASE
1	28.13	3.47
2	29.03	0.44
3	30.92	0.69
4	32.02	0.97
5	68.95	100.00
6	69.88	1.21
7	71.01	0.57
8	92.99	0.89
9	99.90	10.55
10	118.94	36.69
11	119.91	0.93
12	130.91	70.91
13	131.95	2.51
14	142.94	2.63
15	149.88	2.26
16	161.91	4.08
17	168.90	28.69
18	169.89	0.93
19	180.92	49.33
20	181.94	2.02
21	192.96	16.69
22	193.95	0.97
23	204.96	0.57
24	211.95	2.10
25	218.89	12.57
26	219.92	0.61
27	230.93	52.97
28	231.95	2.83
29	242.88	6.10
30	243.94	0.57
31	254.91	0.85
32	261.91	1.37
33	280.84	97.21
35	292.97	2.30
34	281.78	6.14
36	330.82	11.35
37	331.93	1.05
38	342.90	1.98
39	380.91	1.66
40	430.69	12.16
41	431.75	1.66



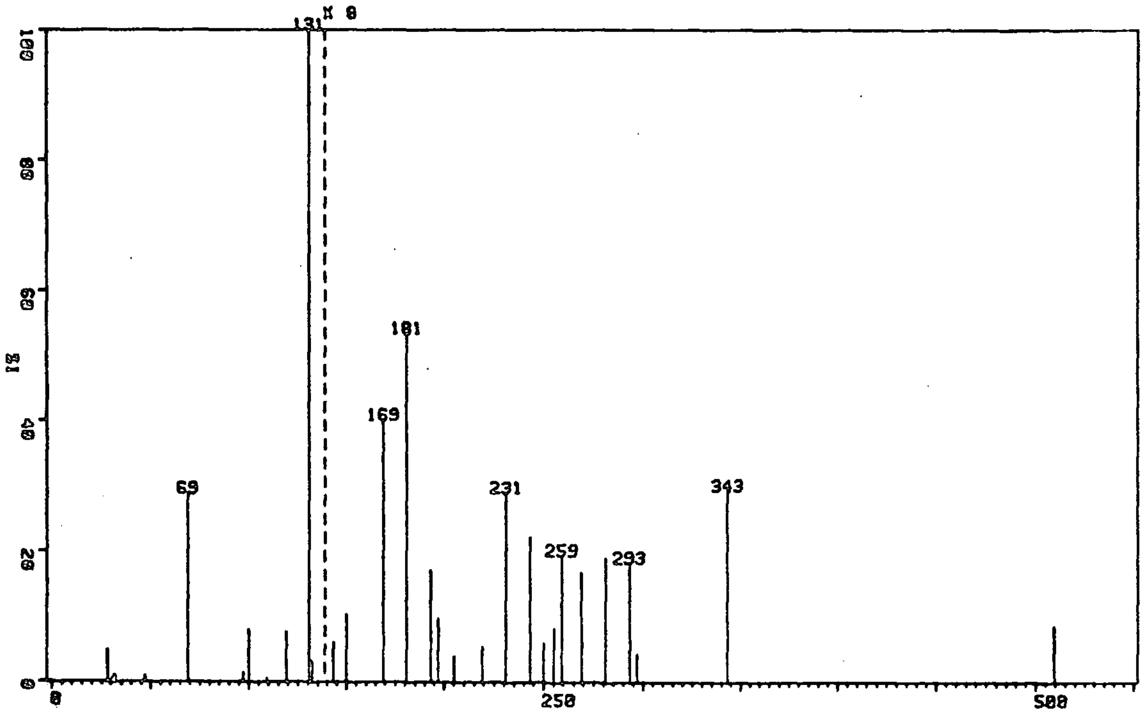
No.118

Perfluoro 2-cyclopentyloxepane (200).

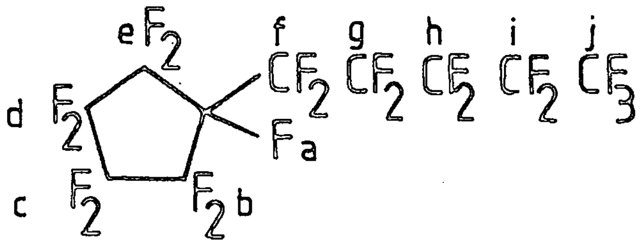


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
81.3	M	2	f
122.2, 123.5, 125.8, 126.8, 127.7, 130.3, 131.0, 132.0, 133.3, 134.3, 135.2, 136.0, 136.5, 141.0.	Overlapping AB's	17	a, b, c, d, e, h, i, j, k.
183.7	M	1	g

M.Wt. 528 No.118

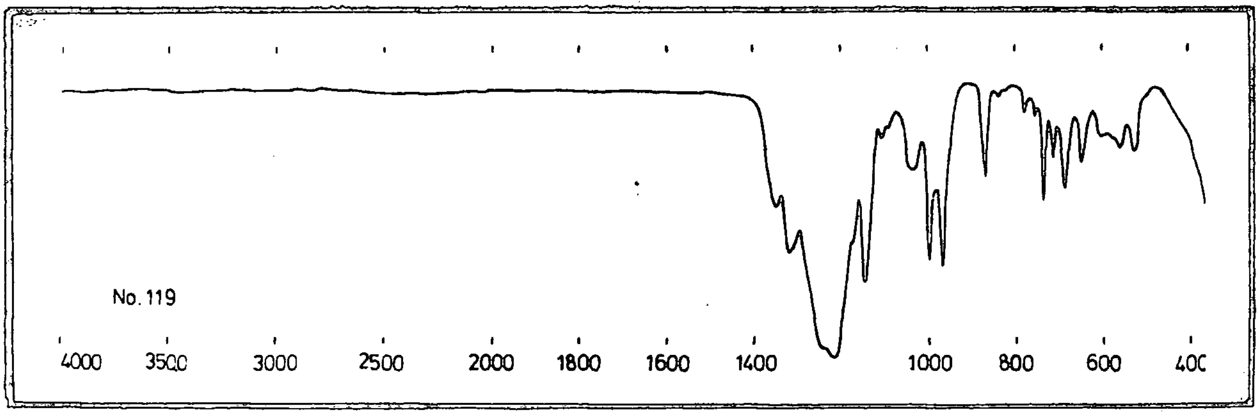


PEAK NO.	MASS	%HT. BASE
1	28.13	4.89
2	30.92	0.58
3	32.02	1.03
4	47.10	0.99
5	69.01	28.87
6	97.13	1.39
7	100.00	8.07
8	109.09	0.54
9	119.05	7.58
10	131.09	100.00
11	132.13	3.18
12	143.11	0.76
13	150.04	1.30
14	169.10	5.02
15	181.09	6.68
16	193.17	2.15
17	197.10	1.21
18	205.10	0.49
19	219.09	0.67
20	231.15	3.63
21	243.15	2.78
22	250.12	0.76
23	255.11	1.03
24	259.04	2.42
25	269.06	2.11
26	281.11	2.38
27	293.15	2.29
28	297.10	0.54
29	343.13	3.68
30	509.31	1.08



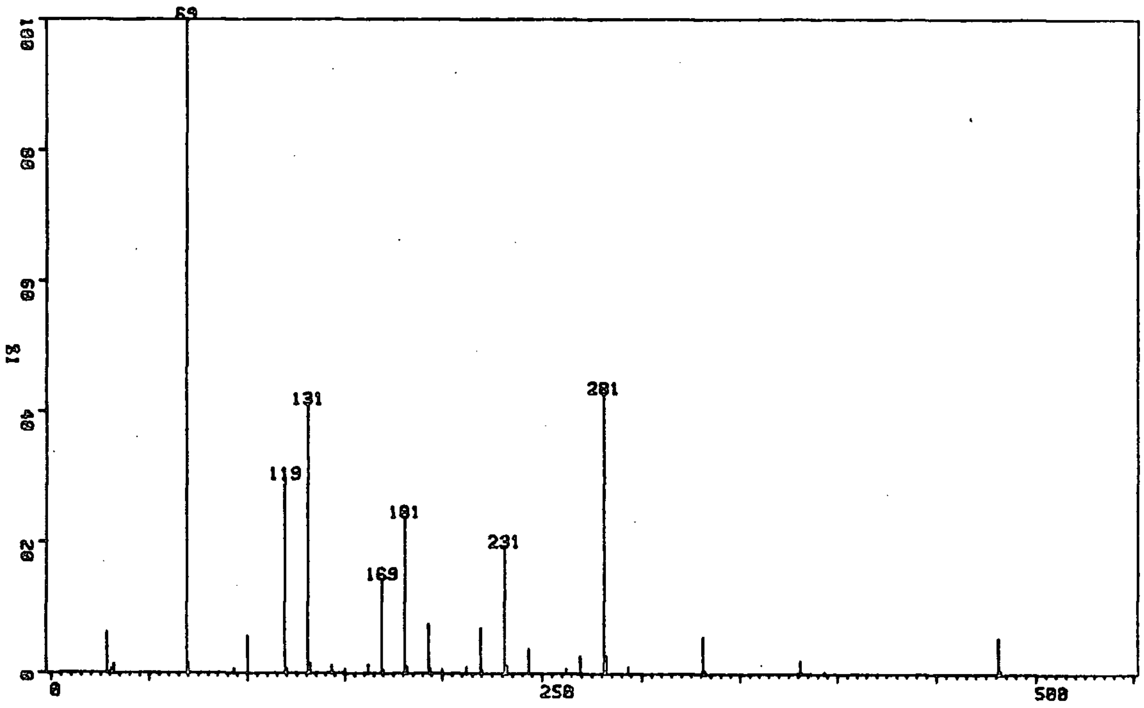
No.119

Perfluoropentylcyclopentane (201).



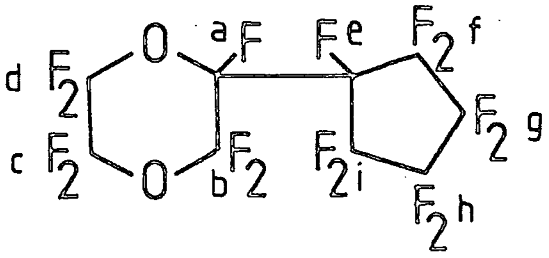
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
84.3	M (T J=10)	3	j
117.7, 122.8, 124.8, 127.2, 128.7, 129.2, 133.0, 134.2, 138.7.	Overlapping AB's	16	b, c, d, e, f, g, h, i.
187.0	M	1	a

M.Wt. 500 No.119

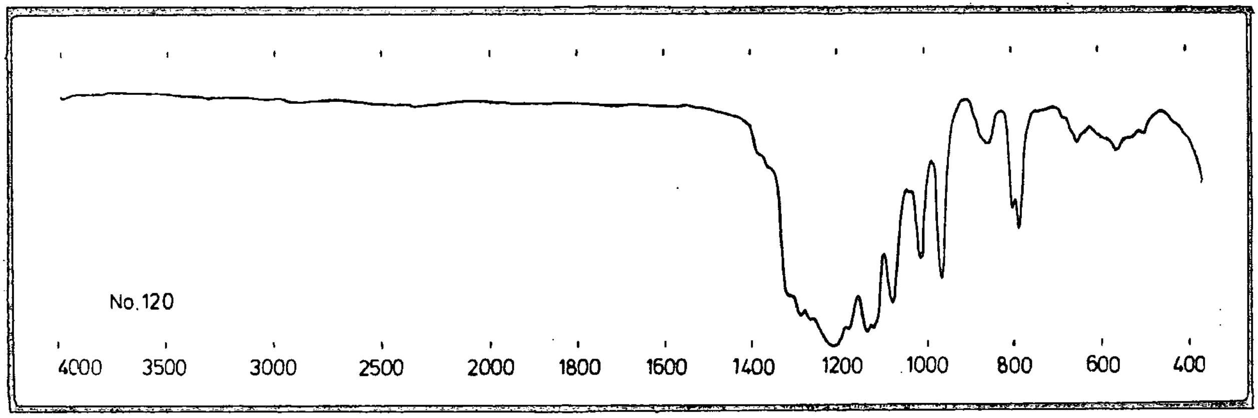


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	6.22	36	393.20	0.34
2	30.92	0.64	37	481.25	5.46
3	32.02	1.41	38	482.27	0.52
4	69.03	100.00			
5	69.96	1.50			
6	93.12	0.64			
7	100.01	5.67			
8	119.05	29.73			
9	120.03	0.77			
10	131.10	41.28			
11	132.13	1.44			
12	143.12	1.20			
13	150.04	0.74			
14	162.12	1.41			
15	169.07	14.40			
16	170.08	0.46			
17	181.12	23.87			
18	182.11	1.01			
19	193.11	7.45			
20	194.09	0.64			
21	200.03	0.64			
22	212.07	1.01			
23	219.07	6.86			
24	220.10	0.40			
25	231.13	19.40			
26	232.12	1.23			
27	243.10	3.74			
28	262.10	0.77			
29	269.06	2.70			
30	281.11	42.97			
31	282.09	2.67			
32	293.15	1.13			
33	331.12	5.61			
34	332.15	0.46	35	281.17	1.96

No.120

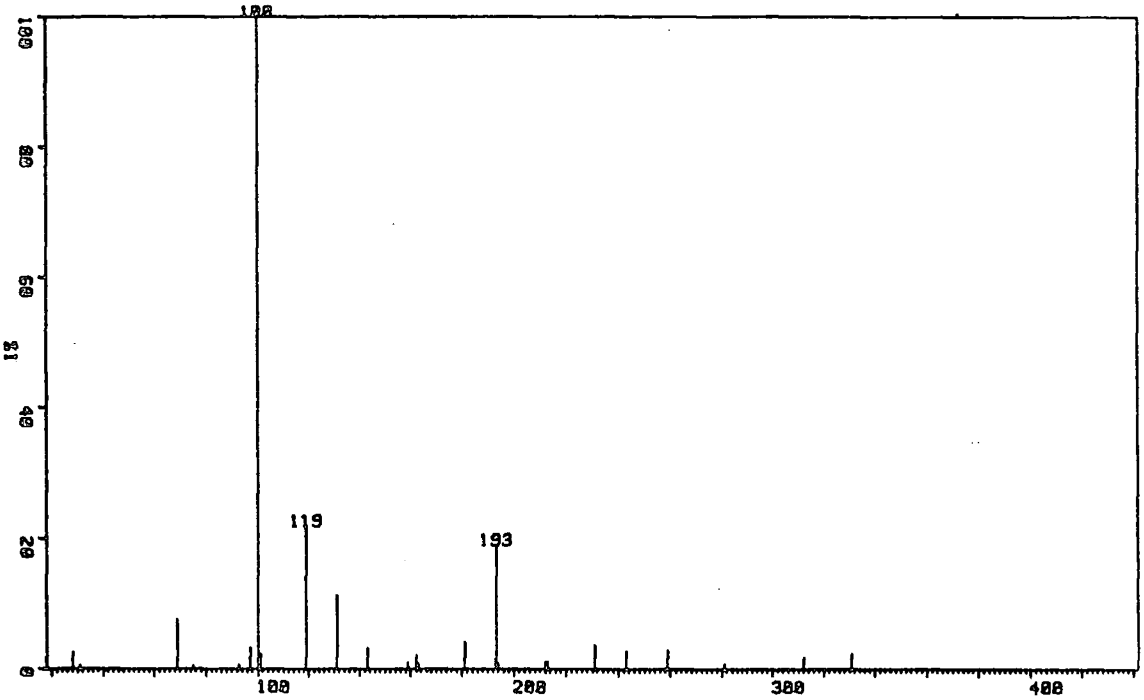


Perfluoro 2-cyclopentyl-1,4-dioxan (202).



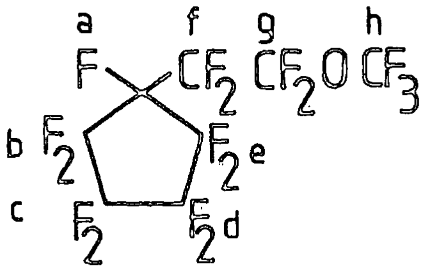
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
78.2, 81.0, 82.5, 84.8, 85.3, 87.8, 92.0, 95.0, 97.8.	Overlapping AB's	6	b, c, d
121.2, 122.3, 124.8, 125.7, 127.0, 130.8, 132.0, 132.7, 135.7, 140.2.	Overlapping AB's	9	a, f, g, h, i.
185.5	M	1	e

M.Wt. 444 No.120

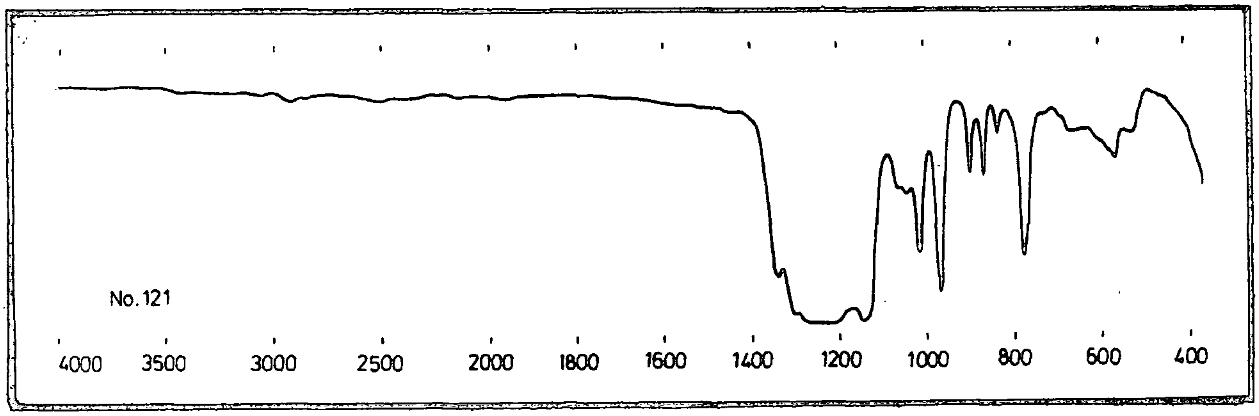


PEAK NO.	MASS	%HT. BASE
1	28.13	2.60
2	30.91	0.54
3	68.98	7.52
4	75.09	0.54
5	93.05	0.66
6	97.06	3.22
7	99.95	100.00
8	101.00	2.25
9	119.00	21.91
10	131.02	11.28
11	143.06	3.22
12	159.01	1.12
13	162.04	2.06
14	163.06	0.89
15	180.99	4.15
16	193.05	19.00
17	194.06	0.97
18	212.01	1.20
19	213.02	1.20
20	230.98	3.64
21	242.99	2.68
22	258.93	2.91
23	281.05	0.85
24	312.00	1.90
25	330.95	2.37

No.121

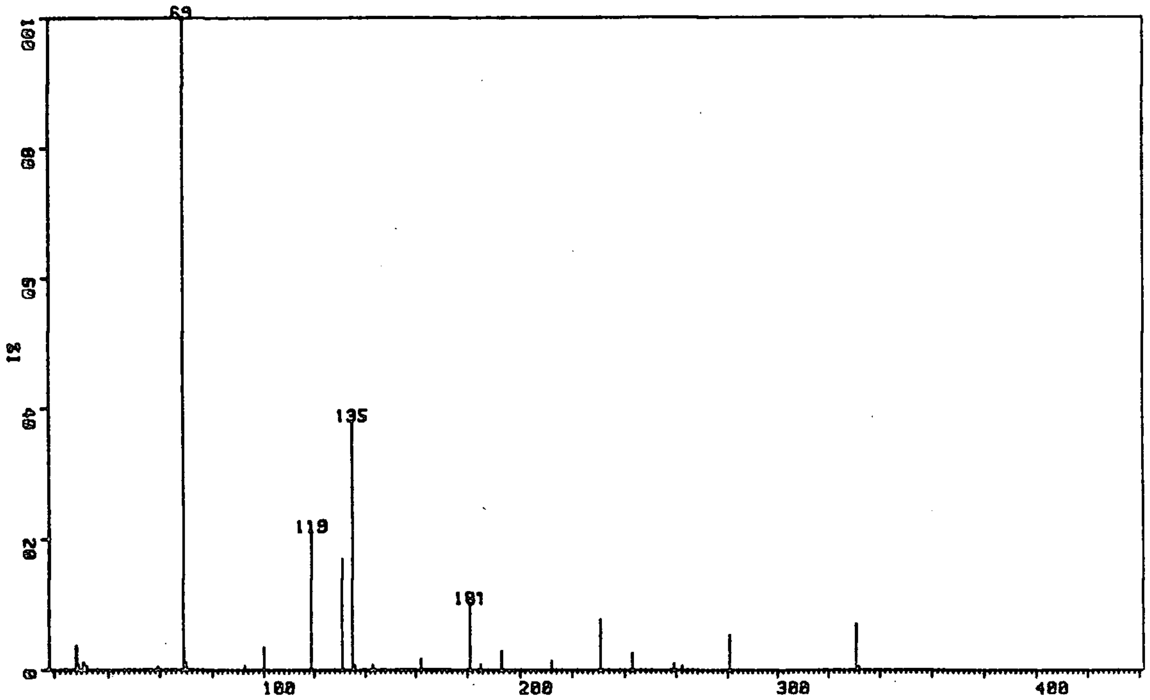


Perfluoro 2-cyclopentylethyl methyl ether (203).



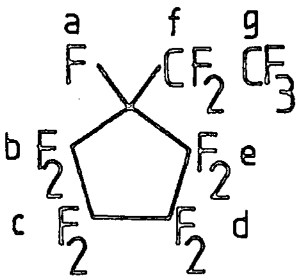
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
58.8	M	3	h
88.3	M	2	g
122.2, 127.3, 130.3, 132.0, 133.3, 135.0, 138.0.	Overlapping AB's	10	b, c, d, e, f.
188.0	M	1	a

M.Wt. 416 No.121

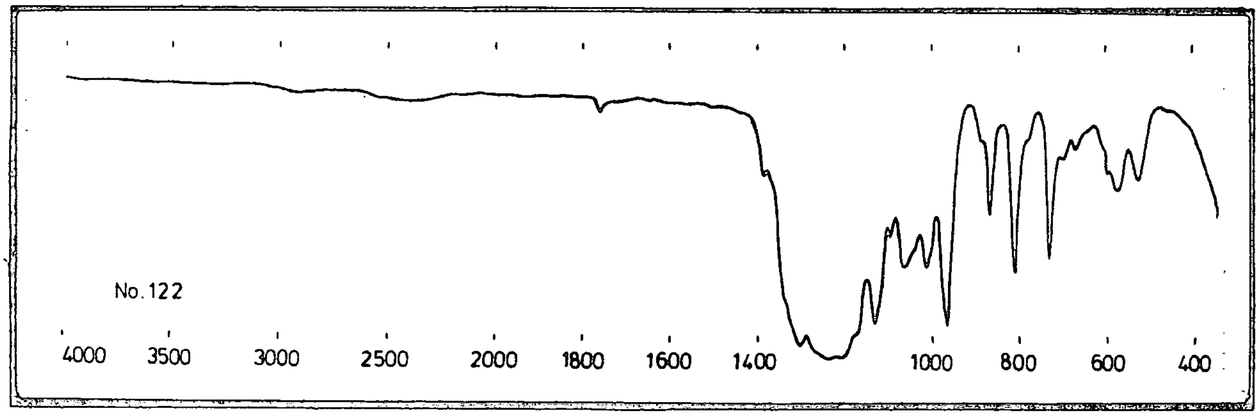


PEAK NO.	MASS	%HT. BASE
1	28.13	3.67
2	29.03	0.85
3	30.93	1.16
4	32.02	0.62
5	59.04	0.50
6	68.98	100.00
7	69.92	1.08
8	93.04	0.69
9	99.95	3.47
10	119.00	21.20
11	130.99	17.03
12	135.06	38.11
13	136.07	0.73
14	143.06	0.81
15	162.01	1.62
16	180.99	10.15
17	185.03	0.89
18	193.05	2.90
19	212.05	1.47
20	230.98	7.68
21	242.99	2.63
22	258.97	1.00
23	261.96	0.73
24	281.00	5.37
25	330.95	7.07
26	331.95	0.54

No.122

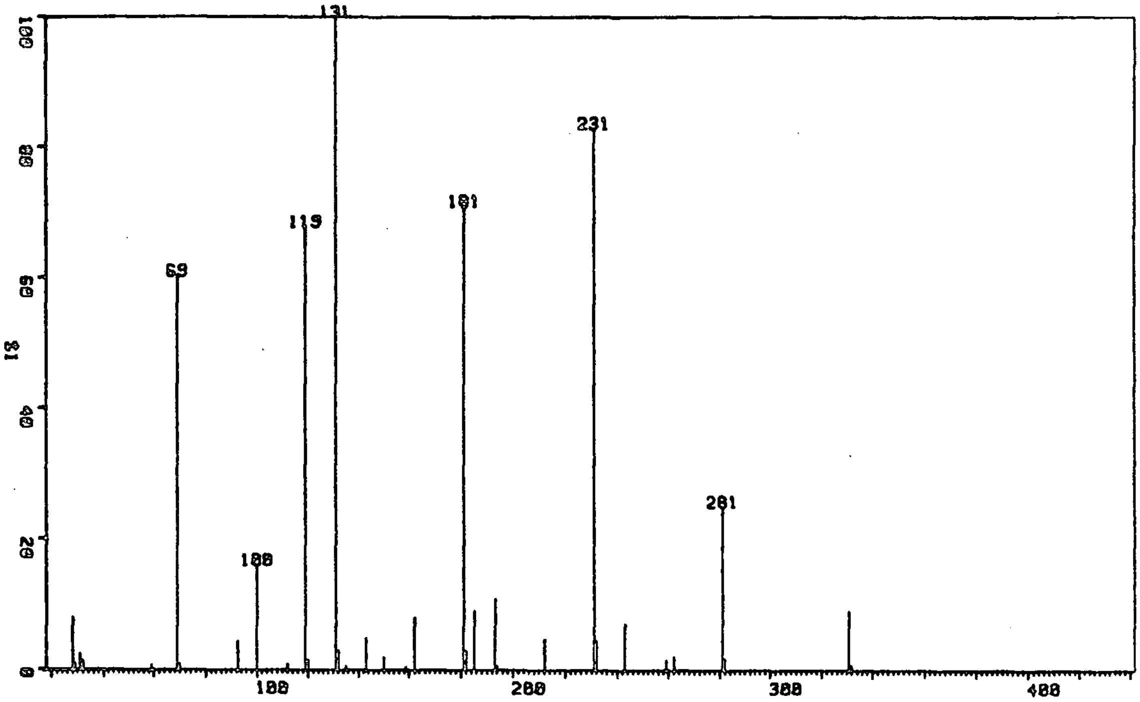


Perfluoroethylcyclopentane (204).



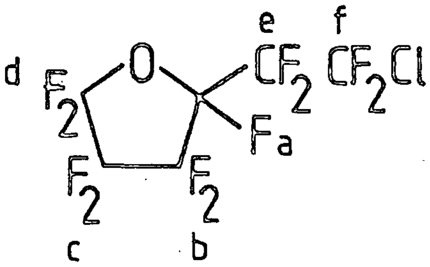
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
84.5	M	3	g
122.8, 127.5, 130.3, 132.0, 133.3, 138.0.	Overlapping AB's	10	b, c, d, e, f.
188.3	M	1	a

M.Wt. 350 No. 122

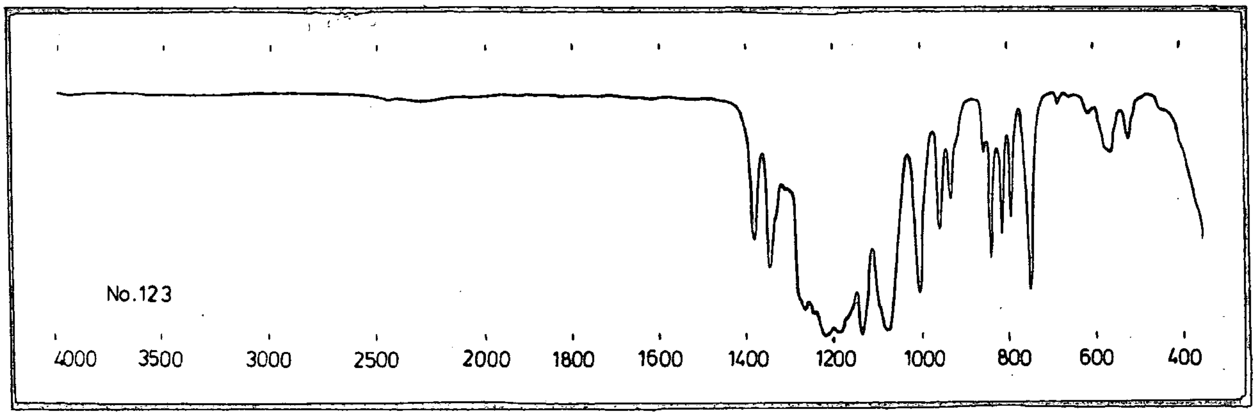


PEAK NO.	MASS	%HT. BASE
1	28.13	8.00
2	29.03	0.98
3	30.93	2.36
4	32.03	1.30
5	59.05	0.75
6	68.99	60.22
7	69.93	0.87
8	93.05	4.29
9	99.95	16.03
10	112.07	0.98
11	119.02	67.82
12	119.98	1.34
13	131.02	100.00
14	132.05	2.95
15	135.08	0.59
16	143.06	4.92
17	150.00	1.93
18	159.01	0.43
19	162.04	8.03
20	180.99	70.93
21	182.05	3.03
22	185.03	9.06
23	193.05	10.79
24	194.10	0.63
25	212.05	4.69
26	231.02	82.87
27	232.05	4.29
28	243.03	7.05
29	259.02	1.54
30	262.01	2.05
31	281.05	24.93
32	282.09	1.73
33	330.95	9.02
34	332.01	0.83

No.123

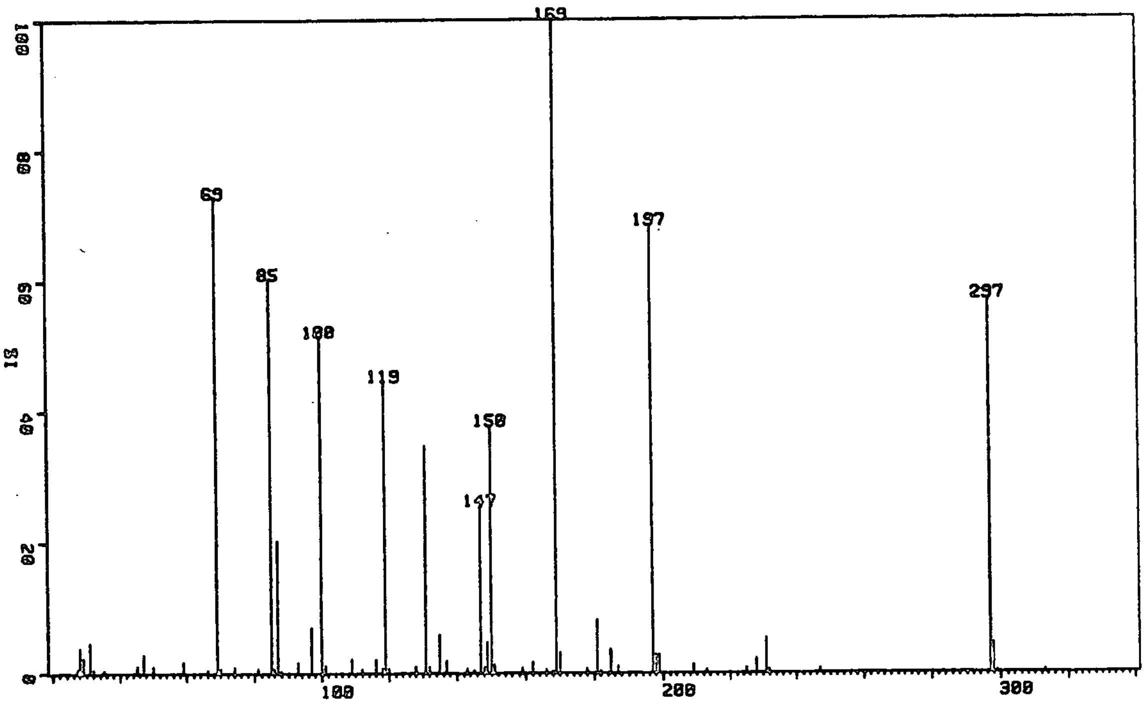


Perfluoro 2-(2-chloroethyl)oxolane (205).



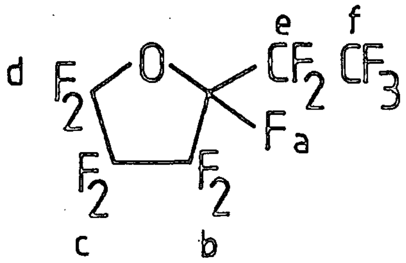
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
70.5	M	2	f
85.2, 87.4	AB, J_{FF}=136	2	d
125.2	M	1	a
119.8, 124.7	AB, J_{FF}=282	2	b, c, e
129.0, 139.4	AB, J_{FF}=260	2	
131.3	M	2	

M.Wt. 332·5 No.123

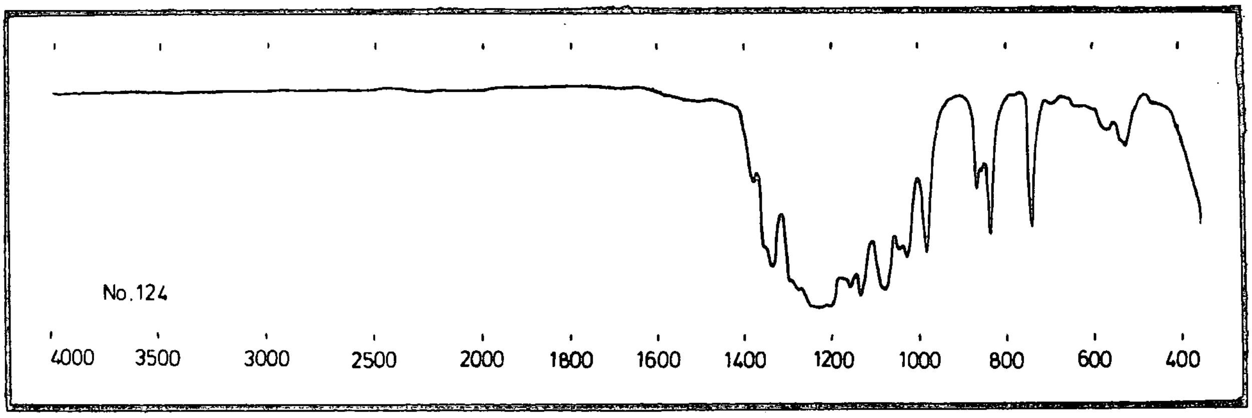


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.25	0.73	36	145.02	0.44
2	28.13	3.90	37	146.94	25.60
3	29.03	2.38	38	147.93	1.01
4	30.92	4.69	39	148.88	4.72
5	32.02	0.63	40	149.93	37.90
6	35.16	0.54	41	150.96	1.43
7	45.17	1.27	42	158.94	0.89
8	47.09	2.85	43	161.96	1.74
9	49.87	1.14	44	166.00	0.60
10	59.01	1.90	45	167.93	0.41
11	66.05	0.60	46	168.92	100.00
12	68.96	72.72	47	169.92	3.17
13	69.90	0.86	48	177.95	0.73
14	74.13	1.01	49	180.93	8.17
15	80.92	0.86	50	181.95	0.41
16	84.97	60.30	51	184.93	3.64
17	85.97	0.86	52	186.92	1.11
18	86.94	20.31	53	196.95	68.57
19	87.93	0.41	54	197.93	2.88
20	92.96	1.68	55	198.88	2.82
21	96.96	7.00	56	208.96	1.33
22	99.87	51.55	57	212.94	0.54
23	100.95	1.17	58	224.94	0.86
24	108.95	2.31	59	227.94	2.25
25	111.97	0.73	60	230.92	5.32
26	115.98	2.19	61	231.95	0.44
27	117.95	0.82	62	246.90	0.76
28	118.95	44.71	63	296.91	57.22
29	119.92	0.86	64	297.74	4.47
30	127.97	1.05	65	298.94	0.41
31	130.93	34.79	66	312.97	0.38
32	131.96	1.05			
33	134.97	5.99			
34	136.95	2.00	35	142.96	0.86

No. 124

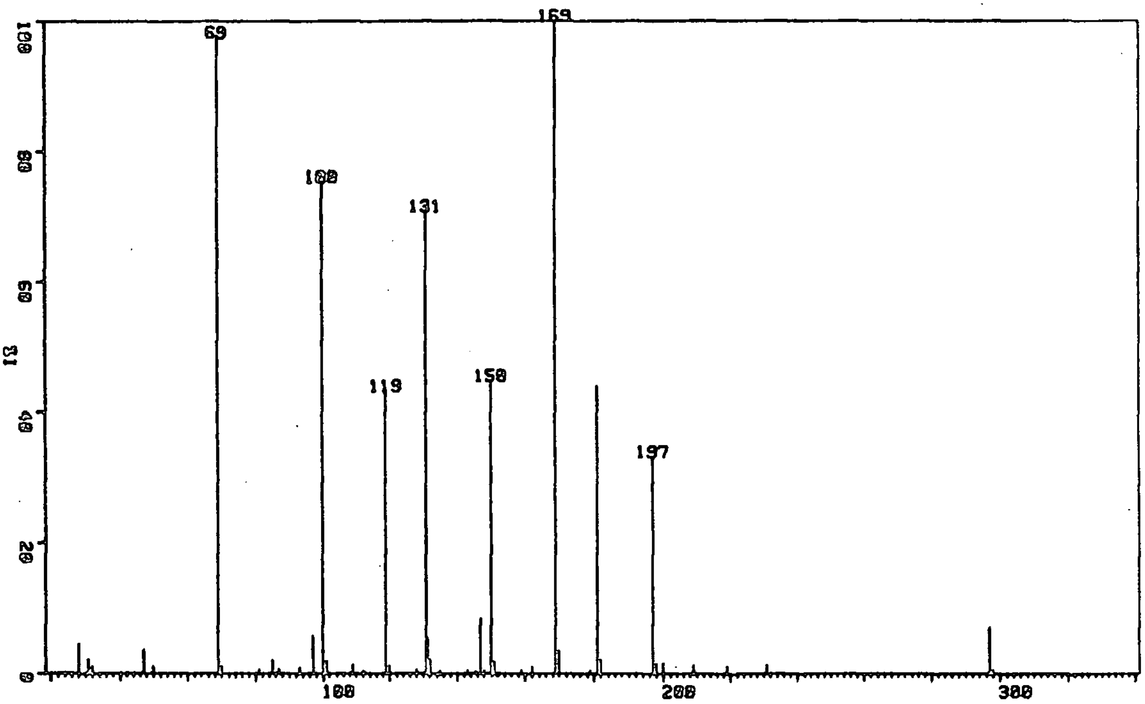


Perfluoro 2-ethyloxolane (<u>206</u>).

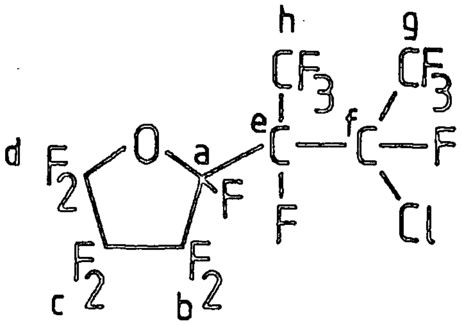


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
85.2	M	3	f
86.9, 88.8	AB, J_{FF}=130	2	d
127.7	M	1	a
127.7, 131.6	AB, J_{FF}=294	2	b, c, e
130.5, 140.7	AB, J_{FF}=243	2	
132.7	M	2	

M.Wt. 316 No.124

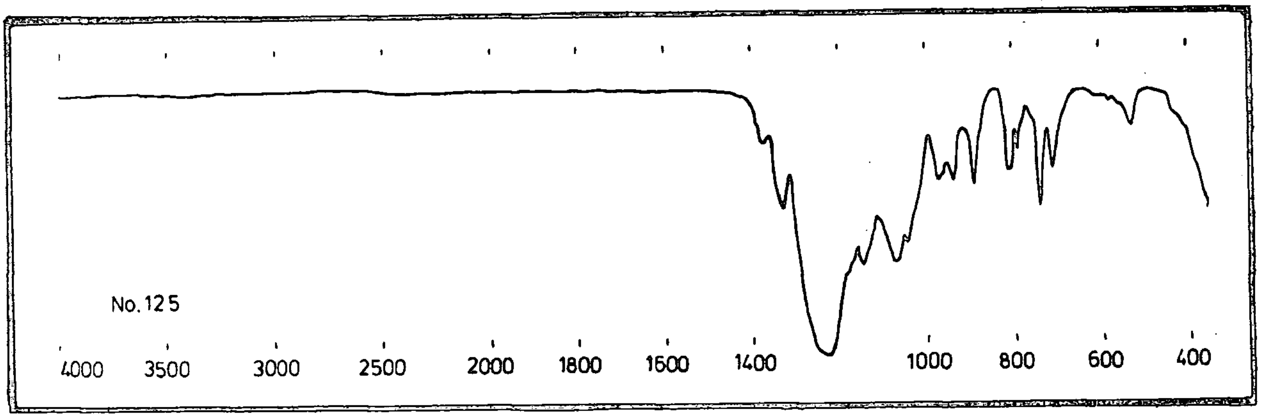


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	4.53	36	181.95	2.13
2	30.91	2.10	37	196.97	33.18
3	32.02	1.02	38	197.96	1.52
4	47.09	3.60	39	199.92	1.58
5	49.86	1.08	40	208.92	1.23
6	68.96	97.54	41	218.91	1.14
7	69.90	1.17	42	230.93	1.32
8	80.94	0.67	43	296.87	7.04
9	85.00	2.02	44	297.89	0.50
10	86.99	0.67			
11	93.01	0.99			
12	97.01	5.76			
13	99.90	75.30			
14	100.94	1.93			
15	108.96	1.40			
16	111.99	0.50			
17	118.95	43.23			
18	119.92	1.20			
19	127.97	0.61			
20	130.95	70.83			
21	131.13	5.32			
22	131.95	2.08			
23	134.98	0.38			
24	142.95	0.53			
25	145.31	0.32			
26	146.93	8.36			
27	147.95	0.38			
28	149.89	44.81			
29	150.93	1.78			
30	158.95	0.56			
31	161.95	1.05			
32	168.92	100.00			
33	169.88	3.48			
34	178.94	0.47	35	180.92	44.02



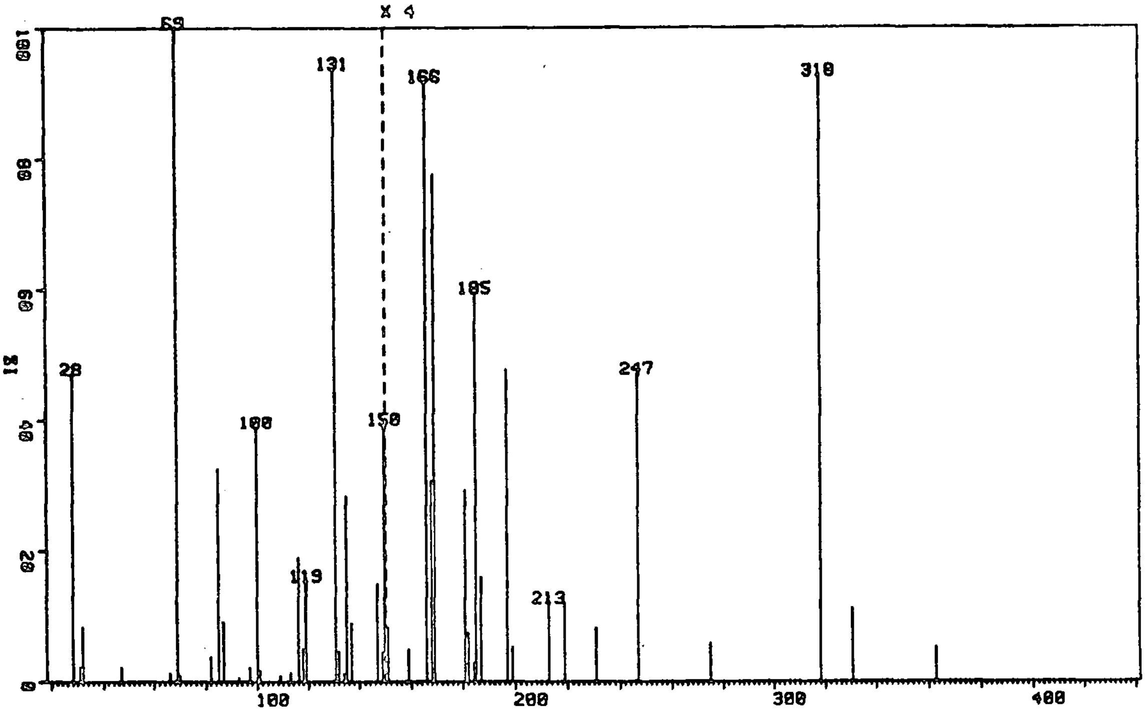
No.125

Perfluoro 2-(2-chloro-1-methylpropyl)oxolane (207).



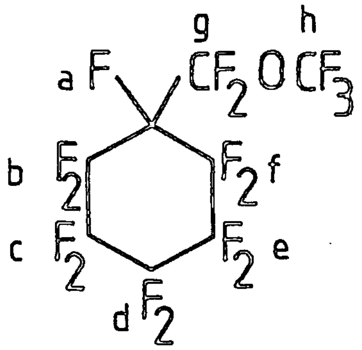
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
70.7, 71.7, 72.5, 73.8, 75.7, 77.0, 78.7, 79.7, 83.7, 85.2, 86.2, 87.2, 88.8, 91.3, 94.0, 96.2.	Overlapping M's	8	d, g, h
106.7, 111.0, 112.3, 113.8, 115.8, 117.3, 119.7, 124.2, 127.2, 128.0, 129.5, 131.7, 134.7, 135.5, 136.2, 137.3, 139.3, 140.5, 141.7.	Overlapping AB's	6	a, b, c, f
175.0 and 184.7	M and M	1	e

M.Wt. 432·5 No.125

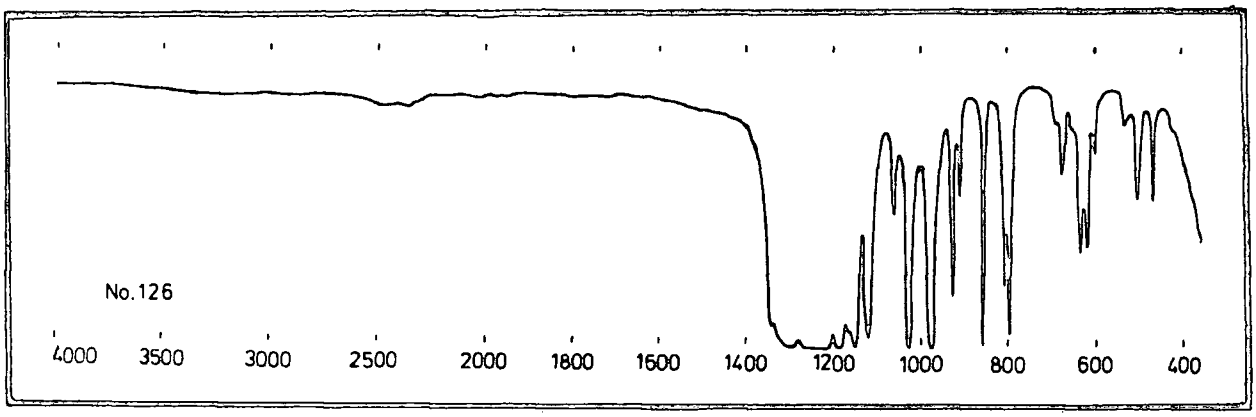


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	47.11	36	184.93	14.87
2	30.92	2.24	37	186.92	3.97
3	32.02	8.37	38	196.94	11.91
4	47.08	2.15	39	198.90	1.31
5	66.04	1.35	40	212.89	3.00
6	68.95	100.00	41	218.93	3.00
7	69.89	0.93	42	230.94	2.07
8	81.99	3.84	43	246.92	11.79
9	85.00	32.53	44	274.92	1.48
10	86.99	9.04	45	318.08	23.15
11	93.02	0.59	46	330.80	2.79
12	97.00	2.24	47	362.90	1.31
13	99.91	38.91			
14	100.95	1.73			
15	108.96	0.93			
16	113.00	1.48			
17	115.98	18.93			
18	117.96	4.99			
19	118.95	15.42			
20	130.93	93.75			
21	131.92	4.60			
22	133.93	1.31			
23	134.97	28.35			
24	136.96	9.00			
25	146.94	15.00			
26	148.91	4.52			
27	149.90	39.33			
28	150.93	2.07			
29	158.91	1.23			
30	165.94	22.94			
31	167.90	7.65			
32	168.95	19.39			
33	180.92	7.31			
34	181.92	1.86	35	183.93	0.72

No.126

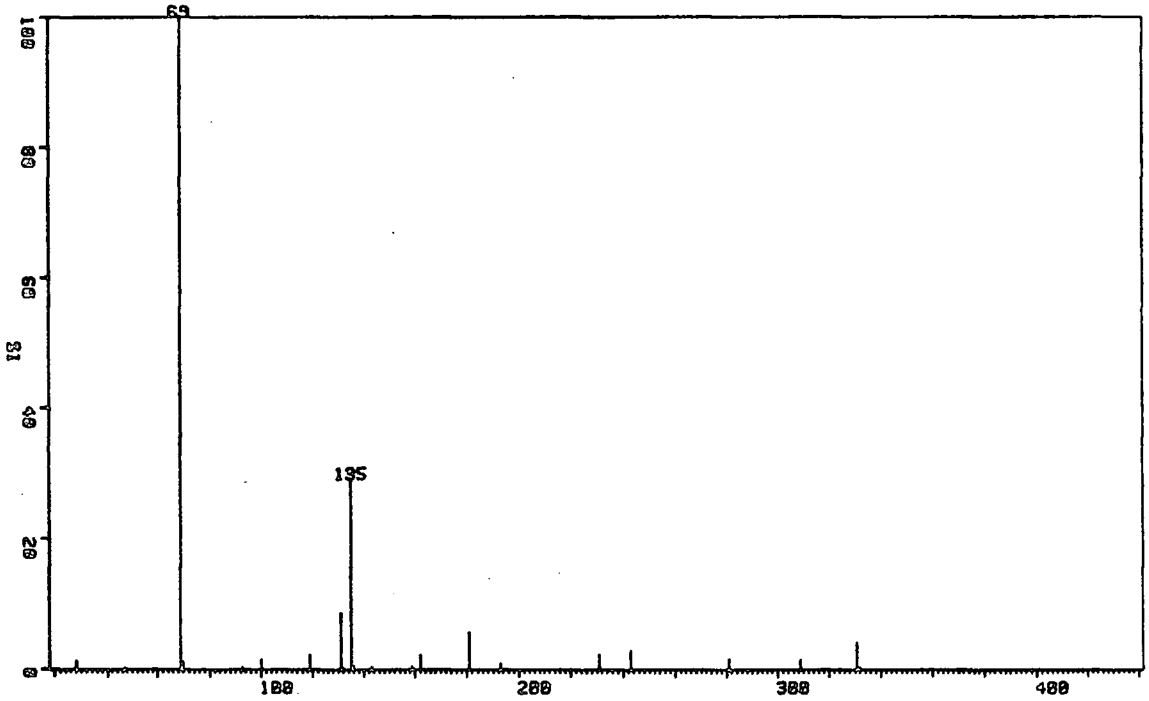


Perfluoromethoxymethylcyclohexane (<u>208</u>).



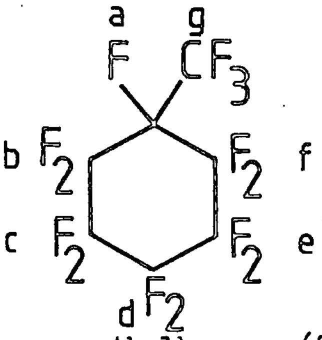
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
<u>^{19}F</u>			
58.7	M, J=9	3	h
73.0	M	2	g
119.1, 122.8, 124.5, 127.8, 129.5, 132.3, 137.6, 141.3, 143.3, 146.5, 148.7.	Overlapping AB's	10	b, c, d, e, f.
189.7	M	1	a

M.Wt. 416 No. 126

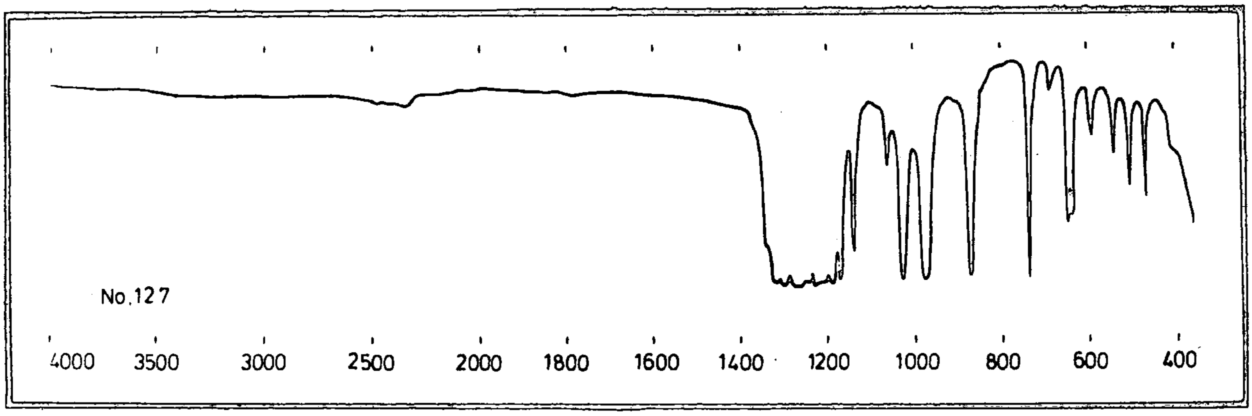


PEAK NO.	MASS	%HT. BASE
1	28.13	1.25
2	47.09	0.33
3	68.97	100.00
4	69.91	1.20
5	93.02	0.36
6	99.94	1.50
7	118.98	2.28
8	130.97	8.68
9	132.01	0.33
10	135.03	29.18
11	136.03	0.64
12	143.03	0.39
13	158.96	0.53
14	161.99	2.25
15	180.93	5.73
16	192.98	0.97
17	230.94	2.39
18	242.91	2.81
19	280.95	1.67
20	308.88	1.53
21	330.87	4.09
22	331.91	0.33

No.127

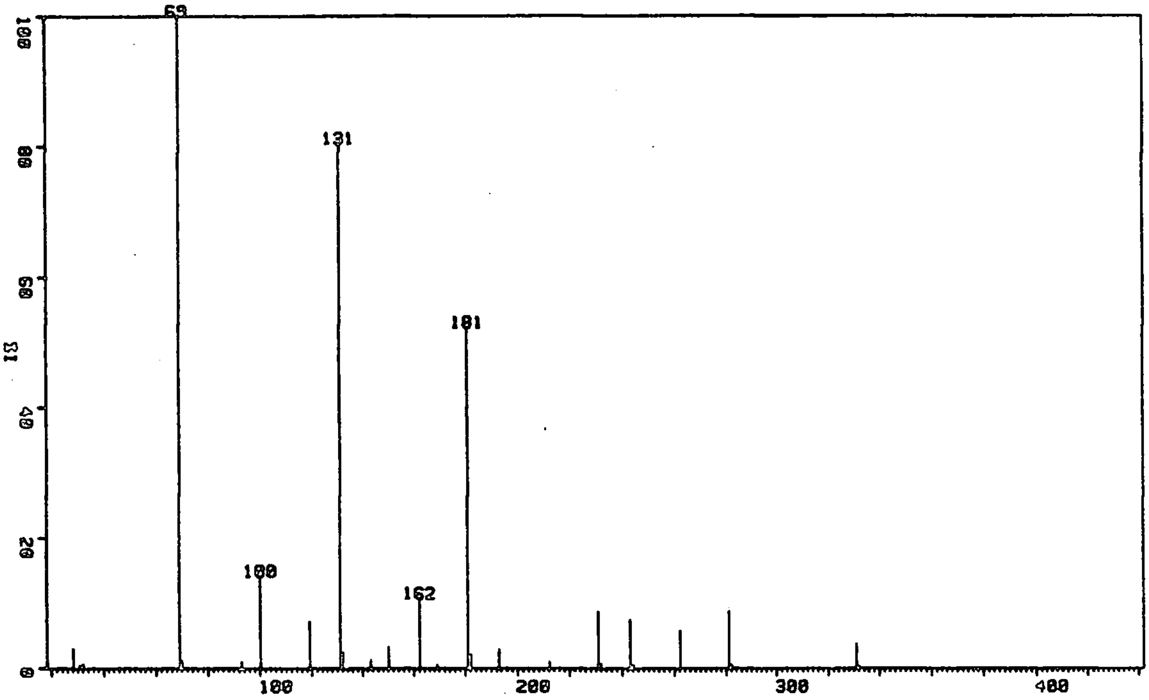


Perfluoromethylhexane (209).



SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{19}F			
72.8	M	3	g
119.7, 122.7, 124.8, 127.8, 129.3, 132.8, 138.2, 141.2, 143.2, 146.3, 148.5.	Overlapping AB's	10	b, c, d, e, f.
191.2	M	1	a

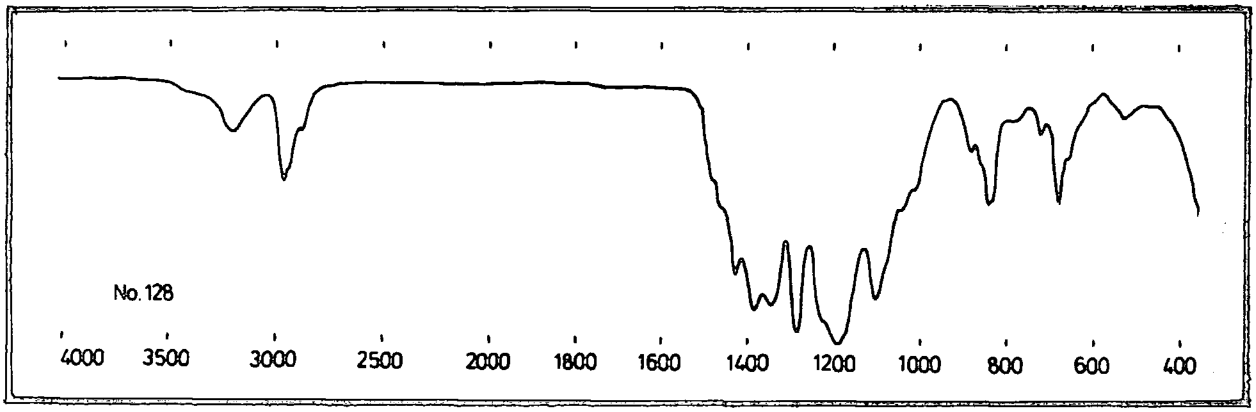
M. Wt. 350 No.127



PEAK NO.	MASS	%HT. BASE
1	28.13	2.58
2	30.93	0.46
3	68.98	100.00
4	69.91	1.04
5	93.02	1.00
6	99.94	14.77
7	118.98	6.91
8	130.99	78.86
9	132.01	2.70
10	143.03	1.37
11	149.95	3.37
12	162.01	10.45
13	163.01	0.58
14	169.00	0.79
15	180.96	51.77
16	181.99	2.29
17	193.01	3.33
18	211.98	1.21
19	230.98	9.11
20	232.05	0.54
21	242.95	7.82
22	244.02	0.54
23	261.96	5.37
24	280.95	7.99
25	282.00	0.67
26	330.89	4.24

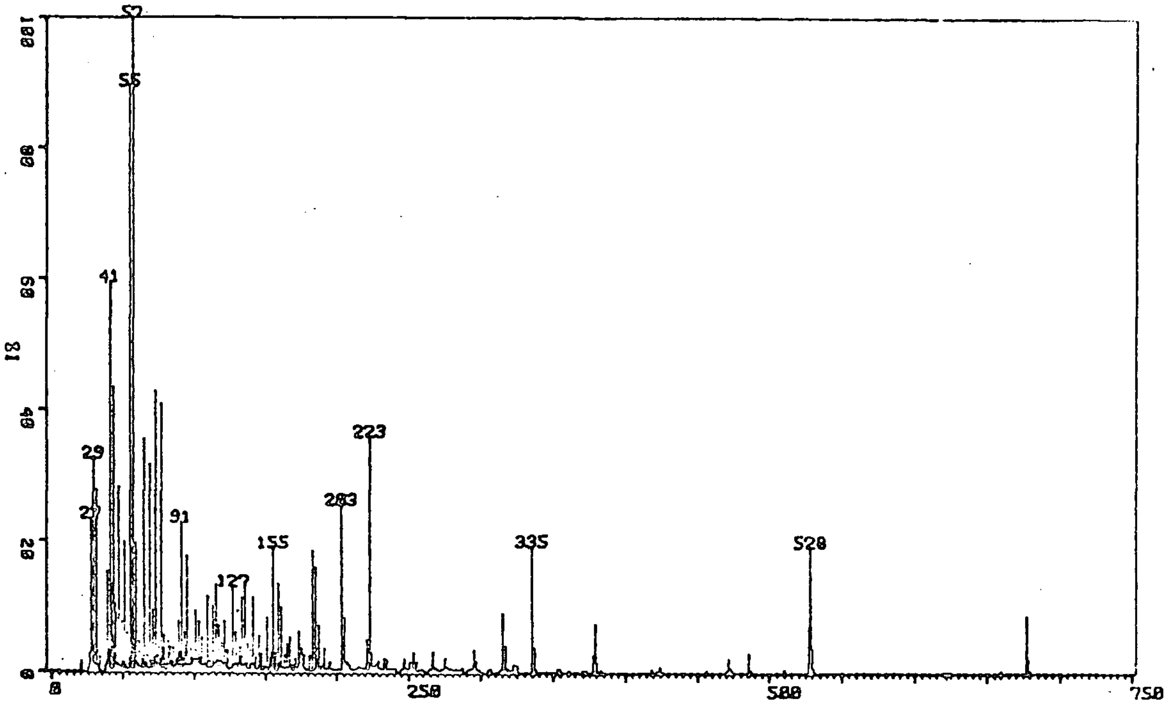
No.128

Adduct of tributyl borate and hexafluoropropene (<u>69</u>).



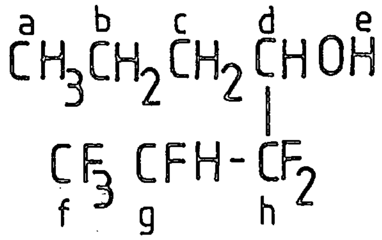
SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
1.05	M(broad)	2.4	$CH_3CH_2CH_2$
1.47	M(broad)		
1.97	M(broad)		
3.82	M(broad)	1	CHO and CHF.
4.50	M(broad)		
5.10	M(broad)		
^{19}F			
75.7	M	3	CF_3
109.5, 117.0, 120.7, 122.0, 125.0.	Series of M's	2	CF_2
211.5	M	1	CFH
213.0	M		

M. Wt. 680 No. 128



PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
4	27.41	23.46	96	120.95	7.81
5	28.26	9.31	102	126.96	13.19
6	29.11	32.64	104	128.89	6.26
9	30.98	27.82	108	132.96	11.29
14	38.91	15.43	110	134.99	13.93
16	40.86	59.61	116	140.88	11.55
17	41.95	13.30	120	144.95	5.60
18	43.00	43.56	126	150.86	8.46
19	44.02	10.42	130	154.95	19.11
20	45.02	8.94	133	158.86	13.64
22	47.00	28.25	135	160.88	9.99
24	48.89	7.76	141	167.02	5.41
26	50.85	19.95	147	173.01	6.28
28	52.99	6.14	155	182.92	18.51
30	55.05	89.56	156	184.82	16.05
31	56.05	71.41	158	186.94	7.22
32	57.04	100.00	171	202.91	25.62
34	58.93	19.78	173	204.93	8.35
40	64.99	35.64	186	220.85	5.12
44	68.87	31.73	187	222.87	36.06
46	70.94	9.37	241	314.75	9.00
48	73.00	42.88	250	334.75	19.33
52	76.95	40.87	260	378.84	7.56
54	78.86	5.58	274	510.46	0.54
64	88.93	7.84	275	527.18	7.10
66	90.93	22.87	276	528.33	19.33
68	92.97	6.03	277	529.37	3.82
70	94.97	17.80	278	530.41	0.71
76	100.91	9.34	279	621.90	0.28
78	102.96	7.84	280	623.81	0.25
80	104.99	5.32	281	659.75	0.42
84	108.89	11.63	282	677.20	8.92
88	112.93	10.05	283	678.55	2.15
90	114.95	13.39	284	679.61	0.37

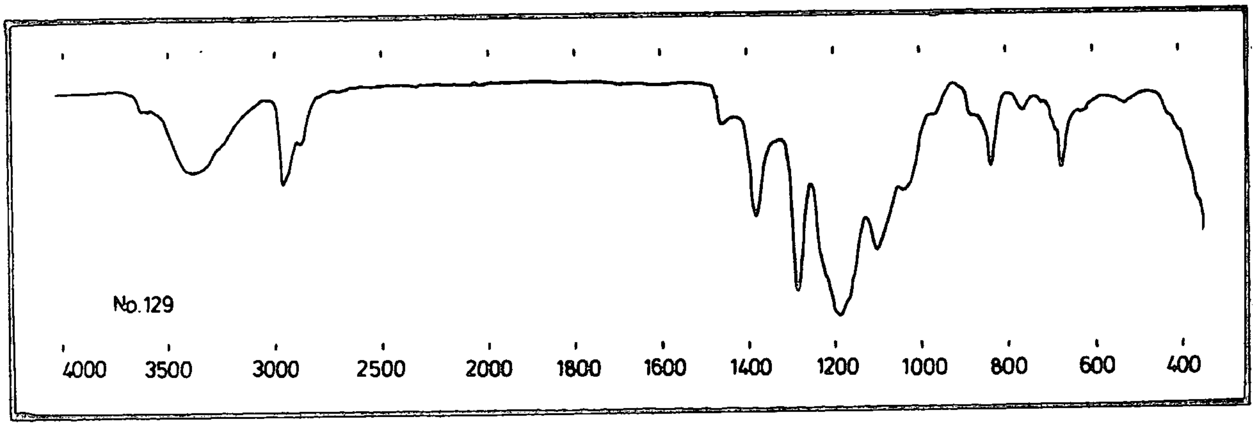
92 116.98 7.16



$CH_3CH_2CH_2CH(OH)CF_2CFHCF_3$

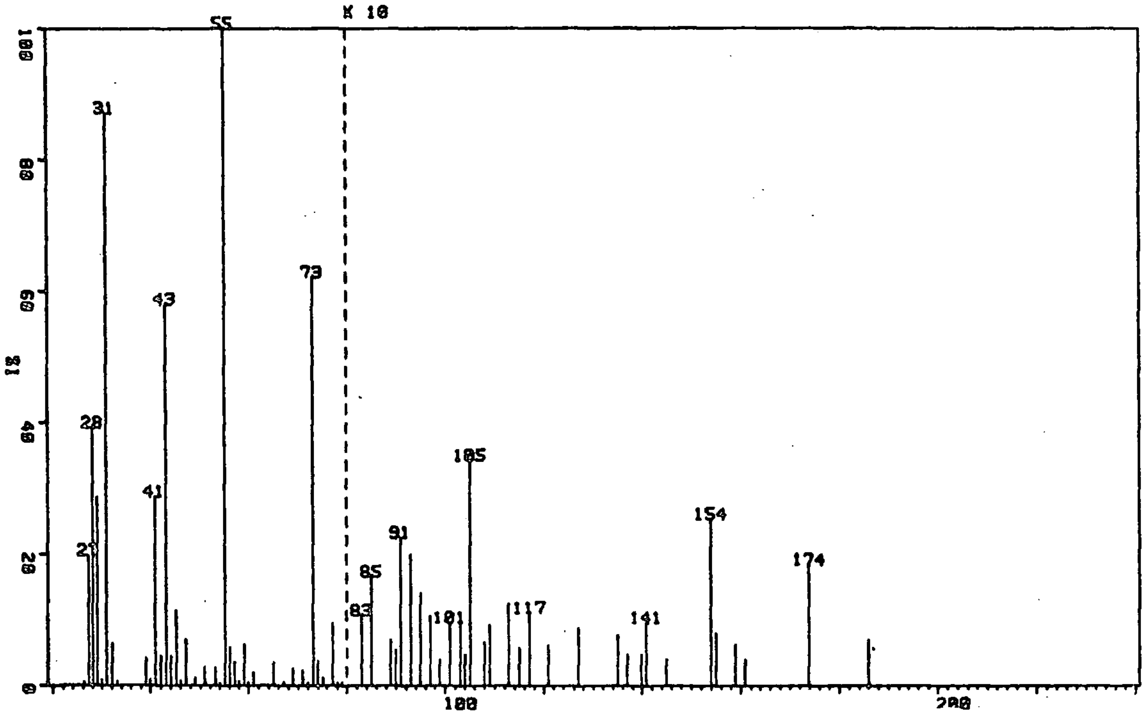
No.129

1,1,1,2,3,3,-Hexafluoroheptan-4-ol (70).

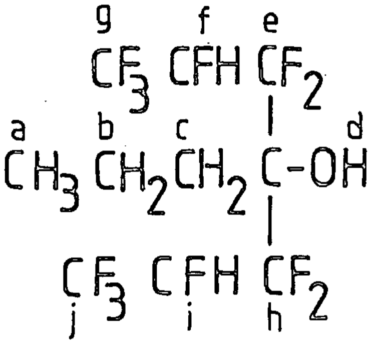


SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^1H			
0.9	M(broad)	3	a
1.4	M(broad)	4	b , c
3.6	M(broad)	2	d , e
4.1	M(broad)		
5.1	M(broad)	1	g
^{19}F			
76.3	M	3	f
111.2, 116.1, 117.3, 118.6, 123.3, 125.1, 128.5, 130.1, 134.2.	Overlapping AB's	2	h
198.8, 200.4, 201.9, 203.3.	Series of M's	1	g

M.Wt. 224 No.129

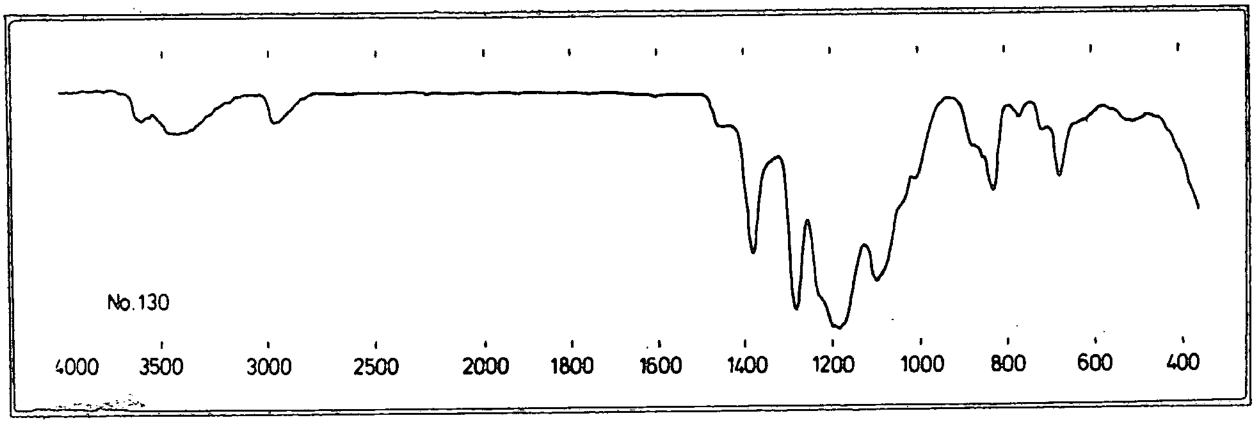


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	26.31	0.55	36	75.07	1.22
2	27.25	19.82	37	77.01	9.45
3	28.14	39.28	38	77.98	0.55
4	29.01	28.68	39	78.93	0.55
5	29.85	0.96	40	83.02	1.07
6	30.92	87.08	41	85.03	1.66
7	32.02	6.46	42	88.92	0.70
8	33.13	0.70	43	89.89	0.55
9	38.99	4.25	44	90.94	2.25
10	39.87	1.07	45	92.98	1.99
11	40.97	28.72	46	95.00	1.40
12	42.06	4.54	47	97.01	1.07
13	43.12	58.07	48	98.96	0.41
14	44.14	4.54	49	100.91	0.96
15	45.16	11.44	50	102.98	0.76
16	46.15	0.85	51	104.01	0.48
17	47.10	7.09	52	105.00	3.43
18	48.95	1.14	53	107.94	0.66
19	50.92	2.92	54	108.91	0.92
20	53.07	2.84	55	112.91	1.26
21	54.10	0.48	56	114.98	0.59
22	55.13	100.00	57	116.97	1.11
23	56.14	5.91	58	120.90	0.63
24	57.09	3.58	59	126.94	0.89
25	58.05	0.74	60	134.95	0.78
26	58.99	6.31	61	136.97	0.48
27	59.92	0.48	62	139.85	0.48
28	60.98	1.96	63	140.85	0.96
29	65.09	3.51	64	144.97	0.41
30	67.05	0.55	65	153.92	2.55
31	68.95	2.62	66	154.95	0.81
32	70.97	2.36	67	158.88	0.63
33	72.04	0.41	68	160.87	0.41
34	73.05	62.13	69	173.92	1.85
35	74.07	3.80	70	185.93	0.70



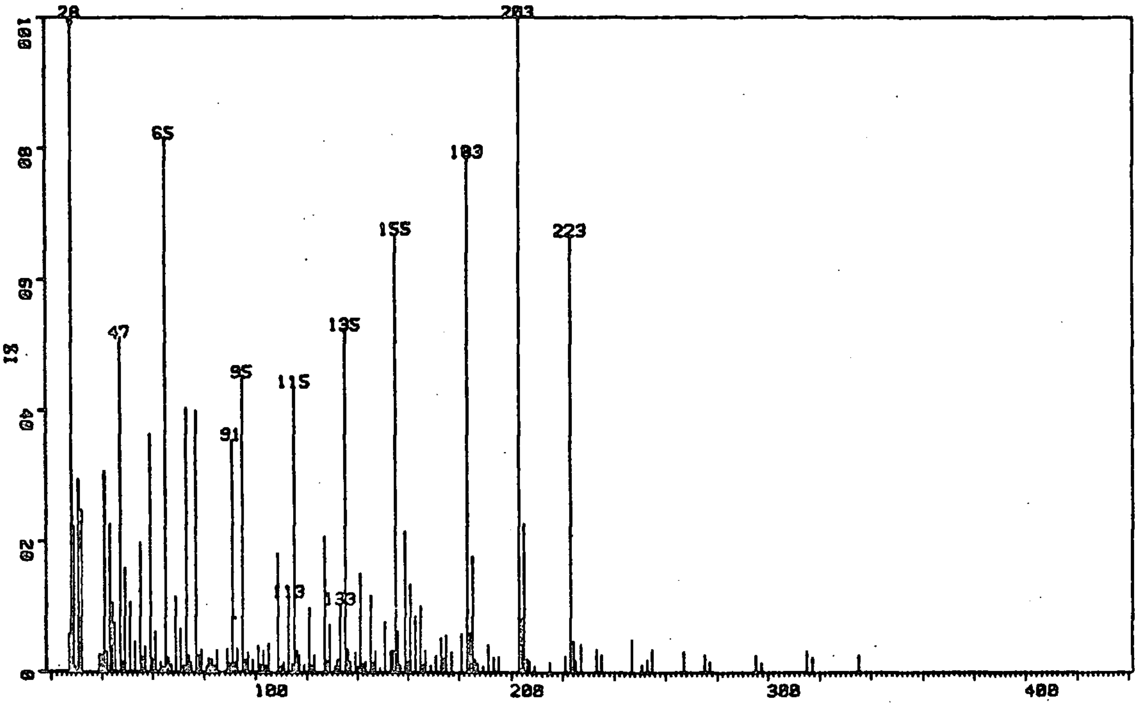
No.130

1,1,1,2,3,3-Hexafluoro-4-(1,1,2,3,3,3-hexafluoropropyl)heptan-4-ol (71).



SHIFT (p.p.m)	FINE STRUCTURE COUPLING CONSTANTS (Hz)	RELATIVE INTENSITY	ASSIGNMENT
^{1}H			
1.00	M(broad)	3	a
1.73	M(broad)	4	b , c
3.80	M(broad)	3	d
4.70	D of M(broad), J=44		f , i
^{19}F			
73.7	M	3	g , j
116.7, 118.7, 121.7, 124.0, 127.5, 129.0,	Series of M's	2	e , h
210.7	M	1	f , i
213.0	M		

M.Wt. 374 No. 130



PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.25	4.98	63	115.06	36.86	123	208.97	0.86
2	28.13	100.00	64	116.07	2.80	124	215.06	1.32
3	29.01	18.72	67	120.98	8.30	125	221.04	2.12
5	30.93	24.90	70	127.03	17.52	126	223.09	56.27
6	32.02	20.89	72	128.97	6.18	127	224.11	4.06
9	40.99	25.93	75	133.03	8.82	128	225.11	1.55
10	42.08	2.69	76	135.08	44.25	129	227.01	3.61
11	43.14	19.06	77	136.09	2.98	130	233.05	2.98
12	44.16	8.93	79	138.99	2.69	131	235.05	2.29
13	45.19	6.35	81	140.99	12.82	132	247.06	4.24
14	47.14	43.22	84	145.04	9.90	133	251.06	0.97
16	48.99	13.39	86	147.06	2.80	134	253.10	1.66
17	50.96	8.99	88	150.99	6.53	135	255.06	2.92
18	53.13	3.95	89	153.07	2.80	136	267.07	2.69
19	55.18	16.66	90	154.11	2.92	137	275.08	2.29
21	57.14	3.26	91	155.07	56.55	138	277.11	1.32
22	59.03	30.74	92	156.05	5.27	139	295.13	2.18
24	61.05	5.21	94	158.99	18.20	140	297.12	1.26
27	65.09	68.86	96	160.98	11.39	141	315.04	2.75
30	68.96	9.79	97	163.06	7.33	142	317.03	1.95
31	70.99	5.67	98	165.08	8.53	143	335.12	2.18
33	73.08	34.12	101	167.08	2.80			
36	77.02	33.71	104	173.07	4.46			
38	78.97	2.92	106	175.07	4.87			
43	85.08	2.86	107	177.03	2.69			
44	88.96	3.03	108	181.03	5.04			
46	90.98	30.05	109	183.08	66.46			
48	93.04	3.09	110	184.10	5.09			
49	95.05	38.07	111	185.04	15.00			
51	97.07	2.58	115	191.03	3.55			
53	100.99	3.49	118	203.02	84.43			
55	103.08	2.86	119	204.05	7.04			
57	105.14	3.72	120	205.05	19.23			
58	109.00	15.40	121	206.05	1.72			
61	113.02	9.79	122	207.01	1.49			

COLLOQUIA AND CONFERENCES.

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

(a) all research colloquia, research seminars, and lectures arranged by the Department of Chemistry and the Durham University Chemical Society during the period of the writer's residence as a postgraduate student;

(b) details of the first-year postgraduate induction course; and

(c) all research conferences attended and papers read out by the writer of the thesis, during the period when the research for the thesis was carried out.

A. RESEARCH COLLOQUIA, SEMINARS, AND LECTURES.

1. Durham University Chemistry Department Colloquia.

Academic Year 1979-1980.

21 November. Dr. J. Müller (University of Bergen), "Photochemical reactions of ammonia".

28 November. Dr. B. Cox (University of Stirling), "Macrobicyclic cryptate complexes: dynamics and selectivity".

5 December. Dr. G.C. Eastmand (University of Liverpool), "Synthesis and properties of some multicomponent polymers".

12 December. Dr. C.I. Radcliffe, "Rotor motions in solids".

18 December. Dr. K.E. Newman (University of Lausanne), "High pressure multinuclear N.M.R. in the elucidation of mechanism of fast simple inorganic reactions".

30 January. Dr. M.J. Barrow (University of Edinburgh), "The structures of some simple inorganic compounds of silicon and germanium - pointers to structural trends in group IV".

6 February.	Dr. J.M.E. Quirke (University of Durham), "Degredation of Chlorophyll-a in sediments".
23 April.	Mr. B. Grievson (University of Durham), "Halogen radio-pharmaceuticals".
14 May.	Dr. R. Hutton (Waters Associates), "Recent developments in multi-milligram and multi-gram scale preparative high performance liquid chromatography".
21 May.	Dr. T.W. Bentley (University of Swansea), "Medium and structural effects on solvolytic reactions".
10 July.	Prof. D. DesMarteau (University of Heidelberg), "New developments in organonitrogen fluorine chemistry".

Academic Year 1980-1981.

7 October.	Prof. T. Fehlner (Notre Dame University, Indiana), "Metalloboranes- cages or co-ordination compounds".
15 October.	Dr. R. Alder (University of Bristol), "Doing chemistry inside cages- medium ring bicyclic molecules".
12 November.	Dr. M. Gerloch (University of Cambridge), "Magneto-chemistry is about chemistry".
19 November.	Dr. T. Gilchrist (University of Liverpool), "Nitroso-olefines as synthetic intermediates".
3 December.	Dr. J.A. Connor (University of Manchester), "Thermochemistry of transition metal compounds".
18 December.	Dr. R.F. Evans (University of Brisbane), "Some recent communications to the Australian Journal of Failed Chemistry".
18 February.	Prof. S.F.A. Kettle (University of East Anglia), "Variations in the molecular dance at the crystal ball".
25 February.	Dr. K. Bowden (University of Essex), "The transmission of polar substituent effects".

4 March.	Dr. S. Cradock (University of Edinburgh), "Pseudo-linear pseudohalides".
18 March.	Dr. P.J. Smith (Int. Tin Research Institute), "Organotin compounds- a versatile class of organometallic derivatives".
6 May.	Prof. M. Szwarc, F.R.S., "Ions and ion pairs".
8 May.	Prof. H.F. Koch (Bathaca College, U.S.A.), "Proton-transfer during elimination reactions".
13 May.	Prof. H. Fritzer (University of Graz), "Simple methods to construct representations for discrete symmetry groups".
14 May.	Prof. H. Fritzer (University of Graz), "The interplay of permutational and geometrical symmetry of certain electronic systems".
10 June.	Dr. J. Rose (I.C.I. Plastics Division), "New engineering plastics".
17 June.	Dr. P. Moreau (University of Montpellier), "Recent results in perfluoro-organometallic chemistry".
24 June.	Dr. S.A.R. Knox (University of Bristol), "Coordination and reactivity of organic species at dinuclear metal centres".
26 June.	Prof A.P. Schaap (U.S. Office of Naval Research, London) "Mechanism of chemiluminescence and photooxygenation".

Academic Year 1981-1982.

14 October.	Prof. E. Kluk (University of Katowice), "Chemo-luminescence and photo-oxidation".
28 October.	Dr. R.J.H. Clark (University College, London), "Resonance Raman spectroscopy".
6 November.	Dr. W. Moddeman (Monsanto Research Labs., St. Louis, Missouri), "High energy materials".

18 November.	Prof. M.J. Perkins (Chelsea College, London), "Spin trapping and nitroxide radicals".
25 November.	Dr. M. Baird (University of Newcastle), "Intramolecular reactions of carbenes and carbinoids".
2 December.	Dr. G. Beamson (University of Durham), "Photoelectron spectroscopy in a strong magnetic field".
30 November.	Dr. B.T. Heaton (University of Kent), "N.M.R. studies of carbonyl clusters".
20 January.	Dr. M.R. Bryce (University of Durham), "Organic metals".
27 January.	Dr. D.L.H. Williams (University of Durham), "Nitrosation and nitrosoamines".
3 February.	Dr. D. Parker (University of Durham), "Modern methods of determining enantiomeric purity".
10 February.	Dr. D. Pethrick (University of Strathclyde), "Conformation of small and large molecules".
17 February.	Prof. R.D. Chambers (University of Durham), "Recent reactions of fluorinated internal olefins".
24 February.	Dr. L. Field (University of Oxford), "Applications of N.M.R. to biosynthetic studies on penicillin".
3 March.	Dr. P. Bamfield (I.C.I. Organics Division), "Computer aided design in synthetic organic chemistry".
17 March.	Prof. R.J. Haines (University of Natal), "Clustering around Ruthenium, Iron, and Rhodium".
7 April.	Dr. A. Pensak (DuPont, U.S.A.), "Computer aided synthesis".
5 May.	Dr. G. Tennant (University of Edinburgh), "Exploitation of the aromatic nitro-group in the design of new heterocyclisation reactions".

7 May.	Dr. C.D. Garner (University of Manchester), "The structure and function of Molybdenum centres in enzymes".
26 May.	Dr. A. Welch (University of Edinburgh), "Conformation patterns and distortion in carbometalloboranes".
14 June.	Prof. C.M.J. Stirling (University College of Wales, Bangor), "How much does strain affect reactivity?".
28 June.	Prof. D.J. Burton (University of Iowa), "Some aspects of the chemistry of fluorinated phosphoniun salts and their phosphonates".
2 July.	Prof. H.F. Koch (Ithaca College, U.S.A.), "Proton transfer to and elimination reactions from localized and delocalized carbanions".

2. Durham University Chemical Society Lectures.

Academic Year 1979-1980.

18 October.	Dr. G. Cameron (University of Aberdeen), "Synthetic polymers - Twentieth century polymers".
25 October.	Prof. P. Gray (University of Leeds), "Oscillatory combustion reactions".
1 November.	Dr. J. Ashby (I.C.I. Toxicological Lab.), "Does chemically-induced cancer make chemical sense?".
8 November.	Prof. J.H. Turnbull (Royal Military College, Shrivenham), "Luminescence of drugs".
15 November.	Prof. E.A.V. Ebsworth (University of Edinburgh), "Stay still you brute; the shape of simple silyl complexes".
24 January.	Prof. R.J.P. Williams (University of Oxford), "On looking into biology's chemistry".

14 February.	Prof. G. Gamlen (University of Salford), "A yarn with a new twist - fibres and their uses".
21 February.	Dr. M.L.H. Green (University of Oxford), "Synthesis of highly reactive organic compounds using metal vapours".
28 February.	Prof. S.F.A. Kettle (University of East Anglia), "Molecular shape, structure, and chemical blindness".
6 March.	Prof. W.D. Ollis (University of Sheffield), "Novel molecular rearrangements".

Academic Year 1980-81.

These lectures were organized by the author while President of the society for the year 1980-81.

16 October.	Dr. D. Maas (University of Salford), "Reactions a go-go".
23 October.	Prof. T.M. Sugden (University of Cambridge), "Some reactions of metals in high temperature flames".
30 October.	Prof. N. Grassie (University of Glasgow), "Inflammability hazards in commercial polymers".
6 November.	Prof. A.G. Sykes (University of Newcastle), "Metalloproteins: an inorganic chemists approach".
13 November.	Prof. N.N. Greenwood (University of Leeds), "Metalloborane chemistry".
4 December.	Rev. R. Lancaster (Kimbolton School, Cambridgeshire), "Fireworks".
22 January.	Prof. E.A. Dawes (University of Hull), "Magic and mystery through the ages".
29 January.	Mr. H.J.F. MacLean (I.C.I. Agricultural Division), "Managing in the chemical industry in the 1980's".

5 February.	Prof. F.G.A. Stone (University of Bristol), "Chemistry of carbon to metal triple bonds".
12 February.	Dr. I. Fleming (University Of Cambridge), "Some uses of silicon compounds in organic synthesis".
17 March.	Prof. W.P. Jencks (Brandeis University, Massachusetts) "When is an intermediate not an intermediate".
7 May.	Prof. M. Gordon (University of Essex), "Do scientists have to count?".

Academic Year 1981-1982.

22 October.	Dr. P.J. Corish (Dunlop Ltd.), "What would life be like without rubber?".
29 October.	Miss. J.M. Cronyn (University of Durham), "Chemistry in archaeology".
12 November.	Prof. A.I. Scott (University of Edinburgh), "An organic chemist's view of life in the N.M.R. tube".
19 November.	Prof. B.L. Shaw (University of Leeds), "Big rings and metal-carbon bond formation".
26 November.	Dr. W.O. Ord (Northumbrian Water Authority), "The role of the scientist in a regional water authority".
3 December.	Dr. R.E. Hester (University of York), "Spectroscopy with lasers".
28 January.	Prof. I. Fells (University of Newcastle), "Balancing the energy equation".
11 February.	Dr. D.W. Turner (University of Oxford), "Photoelectrons in a strong magnetic field".
18 February.	Prof. R.K. Harris (University of East Anglia), "N.M.R. in the 1980's".
25 February.	Prof. R.O.C. Norman (University of York), "Turning points and challenges for the organic chemist".

4 March. Dr. R. Whyman (I.C.I. Runcorn), "Making metal clusters work".

B. POSTGRADUATE INDUCTION COURSE.

In each part of the course, the uses and limitations of the various services available were explained by those reponsible for them.

Departmental organisation - Dr. E.J.F. Ross
Electrical appliances and infra red spectroscopy - Mr. R.N. Brown
Chromatography and microanalysis - Mr. T.F. Holmes
Atomic absorption spectrometry and inorganic analysis - Mr. R. Coult
Mass spectrometry - Dr. M. Jones
N.M.R. spectrometry - Dr. R.S. Matthews
Glassblowing techniques - Mr. W.H. Fettis and Mr. R. Hart
Safety matters - Dr. M.R. Crampton

C. RESEARCH CONFERENCES ATTENDED.

Annual Chemical Congress of the Chemical Society, Bristol, April 1979
Symposium in honour of Prof. J. Chatt, Cambridge, 1 April 1980.
Annual Chemical Congress of the Chemical Society, Durham, 9-11 April 1980
International Symposium: Metallo-organics in Organic Synthesis, Swansea, 14-17 July 1980.
7th European Symposium on Fluorine Chemistry, Venice, 15-19 September 1980
A paper was presented by the author titled "Free radical additions of ethers to fluorinated olefins", R.D. Chambers, B. Grievson, and N.M. Kelly.
Annual Chemical Congress of the Royal Society of Chemistry, Guildford, 7-9 April 1981.

Annual Chemical Congress of the Royal Society of Chemistry, Aston in Birmingham, 30 March - 2 April 1982.

Graduate Symposium, Durham, 21 April 1982.

A paper was presented by the author titled "Free radical addition to fluorinated alkenes. A probe for information on structure and reactivity in radicals and new syntheses".

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3. R.D. Chambers, 'Fluorine in Organic Chemistry', Wiley Interscience, London, 1973.

4. R.E. Banks, 'Fluorocarbons and their Derivatives', Macdonald, London, 1970.

5. 'Organofluorine Chemicals and their Industrial Applications', ed. R.E. Banks, Ellis Horwood, Chichester, 1979.

6. 'Preparation, Properties, and Industrial Applications of Organofluorine Compounds', ed. R.E. Banks, Ellis Horwood, Chichester, 1982.

7. N.M. Kelly, PhD Thesis, University of Durham, 1979.

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