Functional fluorocarbon derivatives via free radical reactions

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A THESIS

entitled

FUNCTIONAL FLUOROCARBON DERIVATIVES VIA FREE-RADICAL REACTIONS

Submitted by

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MEMORANDUM

The work described in this thesis was carried out at the University of Durham between January 1977 and October 1979. 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 the following publication:

R.D. Chambers, N. Kelly, J.W. Emsley, and W.G.M. Jones, J. Fluorine Chem., 1979, 13, 49.

NOMENCLATURE

The following nomenclature is used in this thesis:-

1. A capital F at the beginning of a chemical name means that the compound referred to is totally fluorinated. For example, F-cyclobutene is equivalent to hexafluorocyclobutene.
2. A capital F in the middle of a name means that all the substituents, apart from those named before the F, are fluorine. For example, 1,2-dichloro-F-cyclobutane is equivalent to 1,2-dichlorohexafluorocyclobutane.
3. The presence of an F in the middle of a ring means that all unmarked substituents are fluorine. For example, F-cyclobutene and 1,2-dichloro-F-cyclobutane are represented as follows:-

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ABSTRACT

Gamma-ray and benzoyl peroxide initiated addition of the functional hydrocarbons, methanol, acetaldehyde, and dimethyl ether, to perfluorocycloalkenes generally resulted in mixtures of geometric isomers. The exception was the addition of acetaldehyde to perfluorocyclohexene which gave stereospecific cis addition with the acyl group positioned equatorial and the hydrogen axial. The assignment of structures to the geometric isomers was based on a simple correllation with the ^{19}F nuclear magnetic resonance chemical shifts of the fluorine atoms geminal to the substituents.

Additions to tetra-F-alkyl ethenes gave adducts, one of which underwent a remarkable cyclization: pyrolysis of the dihydrofuran product provided a novel furan synthesis. Further, reaction with dimethyl ether favoured a two-to-one rather than a one-to-one adduct and an intramolecular rearrangement is proposed to account for this process.

A preliminary study of the effect of substituents on carbon-hydrogen bond reactivity has shown that an aromatic nucleus causes deactivation. Otherwise, a methoxy group tends to react readily under free-radical conditions but the reactivity of a methylene is more dependent on the nature of the substituents.

Many of the reactions of the functional fluorocarbon derivatives were found to be influenced by the fluorine-containing substituent. The main effects were steric and electron-withdrawing inductive effects. Chlorination of a methyl ether derivative resulted mainly in substitution at the least expected carbon-hydrogen bond.

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CHAPTER X EXPERIMENTAL TO CHAPTER V

INTRODUCTION

CHAPTER I

FREE-RADICAL ADDITIONS TO FLUOROALKENES

I.A INTRODUCTION

Reactions involving free-radicals are extremely varied and regular surveys[1] of the literature and reviews[2-6] by several authors have been carried out over the years. Radical additions to hydrocarbon alkenes have been investigated in depth and were the subject of early reviews[7,8]. This review considers the addition of organic molecules to fluoroalkenes.

I.B FREE-RADICAL ADDITION CHAIN MECHANISM

The overall reaction in which a molecule R-H is added across a double bond occurs through a sequence of steps. These steps may be indicated as follows:-

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

(2) $R\cdot + \rangle C{=}C\langle \longrightarrow R\text{-}\overset{\backslash}{\underset{/}{C}}\text{-}\overset{/}{\underset{\backslash}{C}}\cdot$ Propagation

(3) $R\text{-}\overset{\backslash}{\underset{/}{C}}\text{-}\overset{/}{\underset{\backslash}{C}}\cdot + R\text{-}H \longrightarrow R\text{-}\overset{\backslash}{\underset{/}{C}}\text{-}\overset{/}{\underset{\backslash}{C}}\text{-}H + R\cdot$ Chain Transfer

Where the alkene is homopolymerisable step (4) may compete with step (3):

(4) $R\text{-}\overset{\backslash}{\underset{/}{C}}\text{-}\overset{/}{\underset{\backslash}{C}}\cdot + \rangle C{=}C\langle \longrightarrow R\text{-}\left[\overset{\backslash}{\underset{/}{C}}\text{-}\overset{/}{\underset{\backslash}{C}}\right]_2\cdot$ Telomerisation

Succesive additions of alkene are followed by step (5) to give a telomer molecule:

(5) $R\text{-}\left[\overset{\backslash}{\underset{/}{C}}\text{-}\overset{/}{\underset{\backslash}{C}}\right]_n\cdot + R\text{-}H \longrightarrow R\text{-}\left[\overset{\backslash}{\underset{/}{C}}\text{-}\overset{/}{\underset{\backslash}{C}}\right]_n\text{-}H + R\cdot$ Chain Transfer

The chains are terminated by radical-radical combination reactions.

1. Initiation of Homolytic Bond Cleavage

(a) Methods of Initiation

Homolytic bond cleavage can be brought about in several ways. Conventional techniques include ultraviolet radiation and the thermal decomposition of chemical initiators. High-energy radiation also effects covalent bond homolysis and the use of one particular source of high-energy radiation, cobalt-60, will be discussed in detail in Chapter II.

(i) Thermolysis

Thermolysis of all organic compounds at sufficiently high temperature (ca. 800°C) produces radicals capable of reacting with metallic mirrors. In solution, molecules with relatively weak bonds (bond dissociation energy less than 160 kJ $mole^{-1}$) dissociate at a useful rate at temperatures below 150°C and provide a convenient method of producing radicals which serve as a chain addition reaction initiator. Two chief types of compounds particularly susceptible to homolysis are organic peroxides and azobisnitriles. Their chemistry is discussed elsewhere[9].

(ii) Photolysis

The fission of chemical bonds by radiation is a direct method of producing free-radicals. The bonds between atoms can often be broken by ultraviolet, X- or gamma-ray irradiation and the minimum energy required is determined by the strength of the bond itself. Most bond strengths are less than 500 kJ $mole^{-1}$ [10,11]. The energy associated with light of a particular wavelength can be calculated from Planck's equation

$$E = \frac{hc}{\lambda}$$

where h is Planck's constant, c is the speed of light and λ the wavelength. When converted to kJ per einstein[12] (per mole of quanta) it can be seen in the first part of Table 1 that the energies associated with short wavelength ultraviolet light are sufficient to bring about the rupture of most single covalent bonds into radicals.

However the actual production of radicals from photoexcited molecules is a multi-step process. Absorption of energy results in the excitation of n or π electrons to the excited π^* state in which the electrons are paired. This excited state normally contains an excess of vibrational energy which is rapidly dissipated and thereafter one of the following processes takes place: (a) radiation is emitted

Table 1 Relationship of Wavelength of Electromagnetic Radiation and Energy[12]

Wavelength	Energy, kJ/einstein
470 nm.	254
420 nm.	285
300 nm.	397
280 nm.	426
200 nm.	598
1.24 nm.[a] (1 keV)	10^5
1.24 pm.[b] (1.2 MeV)	10^8
1.24 fm.[c] (1 TeV)[d]	10^{11}

a A photon of wavelength 124 nm. has an energy of 1 eV.

b $p = 10^{-12}$

c $f = 10^{-15}$

d $T = 10^9$

(fluorescence) and the molecule returns to the ground state; (b) energy can be lost by collision with the solvent; (c) the excited singlet may undergo intersystem crossing to an excited triplet state, provided that the particular compound has a triplet state of appropriate energy; (d) homolysis can occur, giving a radical pair in which the electron spins are anti-parallel. The triplet may undergo homolysis, in which case radicals with unpaired spins would be produced.

In photolysis, as opposed to thermolysis, energy of a particular value i.e. quantized is supplied to the molecule and thus the energy necessary for the onset of radical production can often be determined by simply varying the wavelength of the incident illumination. The method

depends on the ability of the molecule to absorb energy and promote an electron to an excited state.

(iii) High-Energy Radiation

Homolysis can also be brought about by the energy supplied by high-energy sources of radiation e.g. gamma-rays, X-rays and high-energy electrons. The energies available from these sources are very much higher than from ultraviolet radiation. The high energies associated with such high frequency electromagnetic radiation are often quoted in electron volt (eV) units and they range from 1 keV to 1000 MeV i.e. 10^8 to 10^{14}J per einstein (see second part of Table 1). As will be seen in Chapter II, gamma-ray photons emitted by cobalt-60 have energies of around 1.2 MeV, corresponding to a wavelength of 10^{-15}m. Their interaction with matter and mode of radical production is discussed in Chapter II.

(b) Effect of Substituents on Bond Dissociation Energy

In general the strength of the bond R-X which has to be broken depends on the nature of both R and X. For a given R, bond strength decreases in the order X = H > Cl > Br > I[13]. Changes in bond strength for a given X, viz. a carbon - hydrogen bond, depend on the nature of the substituents attached to the carbon atom.

The energy required to cleave the bond (the bond dissociation energy, B.D.E.) is related to the heats of formation of the constituent radicals by the equation

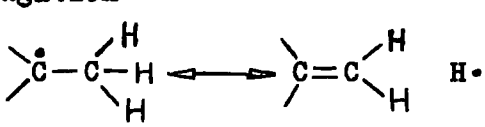
$$B.D.E.(R\text{-}H) = \Delta H_f^\circ (R\cdot) + \Delta H_f^\circ (H\cdot) - \Delta H_f^\circ (RH)$$

The heats of formation of many organic molecules, radicals, and atoms are known and the carbon - hydrogen bond dissociation energy has been calculated for a range of molecules from the information tabulated by Benson[11]. These are shown in Table 2. It can be seen that, with the exception of trifluoromethane, when a hydrogen atom in methane is replaced the carbon - hydrogen bond dissociation energy decreases. This

Table 2 Bond Dissociation Energies of C-H Bonds in Different Environments.[11]

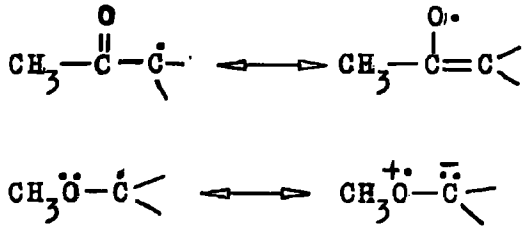
R-H	Bond Dissociation Energy, kJ mole^{-1}.
H_3C-H	434
F_3C-H	434
Ph-H	431
C_2H_5-H	410
Cl_3C-H	402
Me_2CH-H	395
$CH_3C(OH)H$-H	389
$HOCH_2$-H	389
CH_3OCH_2-H	385
Me_3C-H	380
HOOC-H	376
CH_3CO-H	366
CH_2=$CHCH_2$-H	356
$PhCH_2$-H	356
Ph_3C-H	313

indicates that the substituents stabilise the radical R· with respect to methyl . Alkyl groups, for instance, are able to stabilise radicals due to hyperconjugation



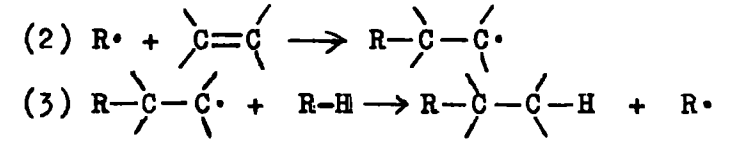
This is supported by e.s.r. studies which show that alkyl groups withdraw spin from a radical centre.[14] Tedder[15] suggested that radical formation should be favoured by α-substituents with π electrons (e.g. ketone , ester, alkene) or non-bonded p electrons (e.g. halogen, alkoxy)

because of the possibilities of radical delocalisation e.g.,



2. Propagation and Chain Transfer

The overall addition reaction is in general exothermic. In order for steps (2) and (3)



to form part of a rapid chain reaction they must both be low activation energy processes. The energy must be suitably divided between the two steps, or at least the balance should not be so that one is significantly endothermic. Substituents which stabilise the intermediate radical formed in step (2) lead to a lowering of the activation energy for this step. At the same time, the stabilised intermediate radical will be less reactive, having gained in resonance energy and the activation energy for step (3) will thus be increased.

Considering step (2) in more detail it is clear that its rate will depend on the reactivity of both R· and the alkene. It has been argued[16] that if the transition state of the addition reaction resembles the reactants rather than the products, then the reactant properties will have the greatest influence on the orientation and rate of the reaction. Thus polar and steric interactions between R· and the alkene would be decisive and factors like the stability of the addend radical would be of minor importance. Theoretical calculations[17] support an early transition state but it was pointed out that this conclusion could not be generalised to all radical additions and that partial charge transfer induced by electronegativity differences between the radical and the alkene is important in determining the position and character

of the transition state.

(a) Structure and Reactivity of the Chain-Carrying Radical

The addition step (2) is exothermic for simple alkyl and substituted alkyl radicals reacting with mono-alkenes. It can become endothermic if the radical contains highly electron-withdrawing substituents so that the new carbon - carbon bond is weak, or in additions to conjugated alkenes, aromatic compounds etc. when resonance is lost in forming the intermediate radical.

Relating alkene and radical structure to their reactivity in the addition reaction is a subject of continuing investigation. Experimentally the main technique has been to react one radical with a series of alkenes exhibiting various structural features and then attempt to correlate the relative alkene reactivities with the radical and alkene properties. Competitive techniques enable the addition reaction to be compared with an abstraction of known rate or alternatively measuring the addition step (2) relative to the radical combination rate. By the application of this kind of method the relative rates of addition of several alkyl radicals to series of alkenes have been determined. It is much more difficult to measure the reactivity of a series of radicals with an alkene, mainly because details of the reaction mechanism change from one system employing one radical to another. Nevertheless the rates of addition of a number of radicals to ethylene, a convenient reference alkene in gas-phase work, have been determined and are shown in Table 3. There is a degree of uncertainty in the absolute values of the rates and Arrhenius parameters of addition quoted but their relative rates are fairly precise. It can be seen that the rate of addition varies little from radical to radical, which is to be expected since the strength of the bond formed, polar and steric effects, and the stabilities of the addend radicals will be similar in all cases. The rate of addition of unsubstituted alkyl

Table 3 Arrhenius Parameters for the Addition of Alkyl Radicals to Ethene[18, 19]

$$R_3C\cdot + CH_2{=}CH_2 \longrightarrow R_3CCH_2CH_2\cdot$$

Radical	Log k (164°C) (l/mole/s)	log A (l/mole/s)	E (kJ/mole)
$CF_3\cdot$	7.2	8.4	10.1
$CCl_3\cdot$	5.3	8.3	26.4
$CH_2F\cdot$	5.4	7.6	18.1
$CH_3\cdot$	4.6	8.1	29.4
$C_2H_5\cdot$	4.4	8.2	31.9
$n\text{-}C_3H_7\cdot$	4.8	7.4	21.4
$i\text{-}C_3H_7\cdot$	4.7	8.2	29.0
$n\text{-}C_4H_9\cdot$	4.0	7.3	28.1
3-Methylbutyl	4.3	7.5	26.9

radicals shows very little variation since bond strength differences, polar effects, etc., will be in this case minimal. However there is a tendency for the activation energy to decrease and thus the rate to increase as the radical becomes more electrophilic e.g. trifluoromethyl radical addition is much faster than methyl radical addition.

When the relative rates of addition of some alkyl radicals to hydrocarbon and halo-substituted alkenes are compared, the radicals fall into two groups (see Table 4). Firstly, with trichloromethyl, trifluoromethyl and heptafluoropropyl, the rate tends to increase with increasing number of alkyl substituents on the alkene but decreases as the number of halogen substituents on the alkene increases. The nucleophilic methyl radical, however, shows the reverse trends, i.e. the relative rate decreases with increasing alkyl substitution but increases with halogen substitution on the alkene. In general the

Table 4 Relative Rates[a] of Addition of Alkyl Radicals to Alkenes[16].

Alkene	$CH_3\cdot$ [b]	$CCl_3\cdot$ [c]	$CF_3\cdot$ [d]	$C_3F_7\cdot$ [e]
$CH_2=CH_2$	1.00	1.00	1.00	1.00
$MeCH=CH_2$	0.67	1.47	1.25[f]	-
$EtCH=CH_2$	0.42	-	1.52[f]	-
cis-$MeCH=CHMe$	0.18	-	3.54[f]	-
trans-$MeCH=CHMe$	0.28	-	2.24[f]	-
$Me_2C=CH_2$	1.03	-	3.80[f]	-
$Me_2C=CHMe$	0.24	-	3.47[f]	-
$Me_2C=CMe_2$	0.08	-	7.08[f]	-
$ClCH=CH_2$	-	0.94	0.49	-
$MeCF=CH_2$	-	0.66	0.42	-
$CHF=CH_2$	-	0.69	0.09	0.54
$CF_2=CH_2$	-	0.17	-	0.20
$CF_2=CHF$	-	0.13	-	0.08
$CF_2=CF_2$	11.4	0.06	0.12	0.20
$CF_3CF=CF_2$	15.5	0.02	-	-

a The relative rates are the combined rates for addition at both ends of the alkene.

b Methyl radicals in gas phase at 180°C.

c Trichloromethyl radicals in gas phase at 100°C.

d Trifluoromethyl radicals in gas phase at 65°C.

e Heptafluoropropyl radicals in gas phase at 164°C.

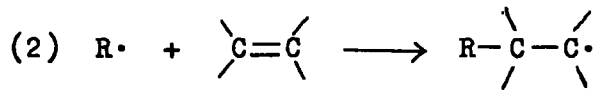
f Solution phase results.

reactivity of radicals with electron-withdrawing groups increases with alkenes of increasing electron supply and vice versa for alkenes with

electron-withdrawing substituents.

(b) Structure and Reactivity of the Alkene

Steric hindrance affects radical reactions, particularly in the addition step (2):-



(2) $R\cdot + \text{>C=C<} \longrightarrow R-\text{C}-\text{C}\cdot$

Thus non-terminal alkenes generally undergo addition reactions less readily than terminal alkenes. In fact the usual direction of addition in radical reactions, in which the radical R· adds to the less substituted end of the double bond, is largely a steric effect although it is also aided by the greater resonance stabilisation of the resulting radical.

An example of the influence of steric hindrance was described by Swarc and co-workers[20] who compared the affinity of methyl radical for 1-substituted ethenes with its affinity for those bearing an additional 2-substituent. The results (Table 5) show that, whereas substituents in

Table 5 Affinity of Methyl Radical for Substituted Ethenes[20]

Alkene	Methyl Affinity[a]
$PhCH=CH_2$	1630
$PhMeC=CH_2$	1890
$Ph_2C=CH_2$	2240
trans-PhCH=CHPh	205
$Ph_2C=CHPh$	85
$Ph_2C=CPh_2$	<25

a Benzene = 1

the 1-position increase reactivity, further substituents in the 2-position decrease reactivity through steric hindrance even though they would otherwise have a stabilising effect. The steric effect is thus working

in opposition to possible resonance stabilisation. Reactivity can also be decreased through steric inhibition of resonance. For example, cis-1,2-diphenylethene is only half as reactive as the trans isomer[20]. This is because only one phenyl at a time can assume the coplanarity with the double bond necessary for resonance stabilisation. Steric hindrance effects have been found for other substituents[21] and is probably the main reason for the decreased reactivity of internal alkenes, including cycloalkenes, as compared with terminal alkenes.

The polar effects arising from the presence of electron-withdrawing or electron-supplying substituents on the alkene cannot always be clearly distinguished from the accompanying resonance and steric effects. Experimental evidence[7,22] indicates that alkenes with electron-withdrawing groups show enhanced reactivity with radicals containing electron-supplying substituents and vice versa; such groups on the alkene reduce the electron density at the double bond. Electron-supplying substituents on the alkene decrease reactivity through increased coulombic repulsion. Since fluorine and fluoroalkyl groups are examples of electron-withdrawing substituents, it is to be expected that fluoroalkenes will be especially reactive with nucleophilic radicals. Acyl radicals (from aldehydes) and α-hydroxyalkyl radicals (from alcohols) are considered to belong to this class since they give particularly good yields of adducts with fluoroalkenes (see Section I.C).

(c) Orientation of Addition

A complete understanding of the factors which control the rate and orientation of free-radical addition to alkenes has not been reached. Early qualitative work by Kharasch and co-workers was compiled by Walling[2] and the quantitative data were collated by Kerr and Parsonage[19]. Tedder and Walton[22] have more recently given an account of the kinetic and orientation information available.

Free-radical addition is seldom completely specific to one carbon of the double bond but the predominant direction of attack can nearly

always be predicted by the simple empirical rule that it will occur preferentially at the "least substituted" carbon atom. This rule is illustrated in Table 6 for the case of addition of a selection of

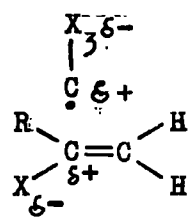
Table 6 Orientation of Electrophilic Radical Addition to Alkenes[23]

Alkene	$CF_3\cdot$	$CCl_3\cdot$	$C_3F_7\cdot$
$CH_2=CHF$	1:0.12[a]	1:0.077	1:0.050
$CH_2=CF_2$	1:0.0	1:0.012	1:0.009
$CH_2=CHCl$	1:0.0	1:0.0	-
$CH_2=CHCH_3$	1:0.12	1:0.071	-
$CH_2=CFCH_3$	-	1:0.007	-
$CHF=CF_2$	1:0.48	1:0.29	1:0.25
$CHF=CHCF_3$	1:0.33	-	-
$CHCl=CF_2$	1:11.5	1:25	-
$CHCl=CCl_2$	-	1:0.033	-
$CH_3CH=CF_2$	1:0.0	-	-
$CF_3CH=CF_2$	1:0.67	-	-
$CH_3CH=CHCF_3$	1:0.25	-	-
$CF_2=CFCl$	1:0.25	1:0.0	-
$CF_2=CFBr$	-	1:0.03	-
$CF_2=CFCF_3$	1:0.25	1:0.0	-
$CF_2=CCl_2$	-	1:0.2	-

a The ratio refers to the relative proportion of attack at each end of the double bond.

The value zero is given in cases where addition was apparently exclusive at the other end of the double bond and none of the adduct was detected.

radicals to a series of alkenes. Where comparison is possible the radicals show the same orientation in addition to a given alkene. The exception is 1,1-difluorochloroethene where $CF_3\cdot$ and $CCl_3\cdot$ radicals react faster at the difluoromethylene end. The orientation data in Table 6 can be rationalised in terms of four factors. (i) The strength of the bond being formed i.e. the radical attaches itself preferentially to the end of the alkene which leads to the strongest bond. (ii) Steric hindrance i.e. the radical avoids crowded sites, either because the approach of the radical is hindered and/or because the bond being formed is weakened by steric interactions in the addend radical. (iii) Polar effects e.g. radicals containing halogen atoms may be polarised as shown



i.e. they will be electrophilic. When the alkene contains electron-withdrawing substituents e.g. halogen, fluoroalkyl groups, electrostatic repulsion may be expected. Salem and co-workers[24] have developed a theory of radical reactions which forecasts that partial ionic character in the incipient bond is important in controlling the orientation of addition. (iv) Stability of the addend radicals i.e. the radical attaches itself at the end of the alkene which leads to the more stable product radical. The stability of the addend radical is usually measured by the extent to which the unpaired electron is delocalised.

It has been shown previously (Section B.1(c)) that α-substituents weaken a bond. Thus $X_3C{-}CHR$ would be weaker than $X_3C{-}CH_2\cdot$. Hence the observed predominant addition at $=CH_2$ in the first group of alkenes in Table 6 can be simply accounted for in terms of the relative strengths of the bonds that can be formed. Further the addend radicals formed by addition at the methylene are the more stable product radicals

of the two possibilities. In each case addition at the $=CH_2$ end leads to the stronger bond being formed.

Steric and polar factors must also be invoked when considering the middle group of alkenes in Table 6. In general the orientation ratios show that the attacking radical avoids the more sterically crowded site. Consideration of polar effects leads to a similar rationalisation of the data: when an electrophilic radical attacks a halogen-substituted alkene, the polar force is repulsive and addition occurs at the less halogenated end of the alkene. The most interesting example of this group is 1,1-difluorochloroethene. Although the strength of the bond formed at $=CF_2$ might well be less than that at =CHCl and the $=CF_2$ end is more substituted and causes greater polar repulsion, the steric effect of the chlorine atom overrides and addition is preferred at the difluoromethylene end.

In the final group of fully substituted alkenes in Table 6, differences in the strengths of the bonds being formed are minor and polar effects are similar at both ends of the double bond. Thus the direction of attack is decided by steric factors and the predominant site of addition is, as expected, the least sterically crowded difluoromethylene position.

The orientation of addition to a given alkene also depends on the nature of the attacking radical. The adduct ratios for addition of a variety of radicals to trifluoroethene are shown in Table 7. If the relative orientation were governed solely by the stabilities of the addend radicals (1) and (2) then no change in the orientation should be

$CX_3CFHCF_2\cdot$ (1) $\qquad$ $CX_3CF_2CFH\cdot$ (2)

observed when a different radical is used since the unpaired electron is still situated on CF_2 or CHF. In fact there is quite a change in

Table 7 Orientation of Radical Addition to Trifluoroethene[22,25]

Radical	$CFH=CF_2$
$CH_3\cdot$	1 : 7.26
$CH_2F\cdot$	1 : 2.04
$CHF_2\cdot$	1 : 0.95
$CF_3\cdot$	1 : 0.50
$CF_2Cl\cdot$	1 : 0.40
$CF_2Br\cdot$	1 : 0.47
$CFBr_2\cdot$	1 : 0.37
$CCl_3\cdot$	1 : 0.30
$CBr_3\cdot$	1 : 0.24
$C_3F_7\cdot$	1 : 0.25

the adduct ratio as the attacking radical changes. The change in the orientation ratios for the series of radicals $CF_3\cdot$, $CF_2H\cdot$, $CFH_2\cdot$, and $CH_3\cdot$, where the radicals are in decreasing order of electronegativity, suggests that polar forces play a significant role. Evidence for a steric effect can be seen in the series $CF_3\cdot$, $CF_2Br\cdot$, $CFBr_2\cdot$, and $CBr_3\cdot$, where, although the change in electronegativity is small, the ratio changes as the number of bromine atoms increases. The bulk of the bromine atoms appears to be causing steric repulsion.

3. Reactions Competing with Chain Propagation

Complications in addition reactions can arise from a variety of competing side reactions.

(a) Reaction of R· with the Initiator

It has been found on occasion that the added chemical initiator reacts preferentially with the first formed radical R· and the free-radical chain addition to the alkene is not initiated. For example,

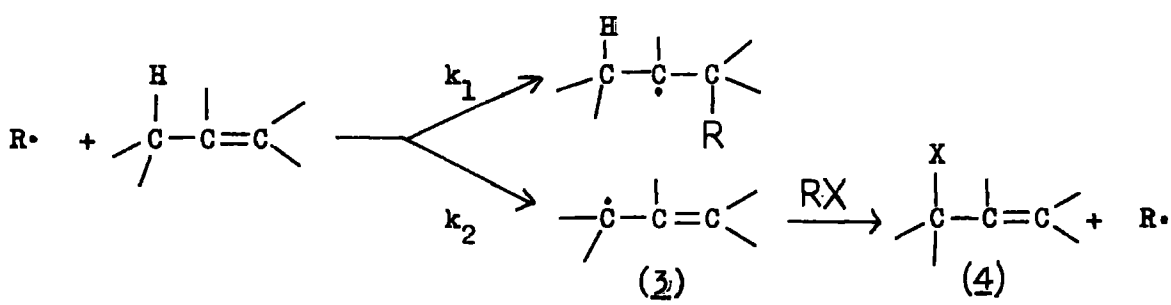
alkyl peroxides are effective initiation reagents for the addition of alcohols to hydrocarbon alkenes but diacyl peroxides are not.[26] Benzoyl peroxide has been shown to decompose rapidly in alcohols[27] by attack of the α-hydroxyalkyl radical on the peroxide e.g.

$$RR'\dot{C}OH + (PhCOO)_2 \longrightarrow RR'C(OH)OCOPh + PhCOO\cdot$$

Thus the α-hydroxyalkyl radical prefers to react with the peroxide rather than with the hydrocarbon alkene even though the former is in relatively low concentration. This is probably due to some extent to polar effects since, as will be seen later, alcohol additions to fluoroalkenes can be initiated by benzoyl peroxide to give high yields of adducts. The α-hydroxyalkyl radicals therefore have a greater affinity for fluoroalkenes than for benzoyl peroxide.

(b) Allylic Attack

A second complication in radical addition processes arises from the possibility of competition between the desired addition and hydrogen abstraction to give an allyl radical (3) in alkenes with one or more



hydrogen atoms on the α-carbon. Unless the allyl radical is too stable to continue the chain, reaction with the addendum leads to allylic substitution products (4). The importance of the reaction depends obviously on the ratio of the rate constants k_1/k_2 and can be neglected altogether for the case of perfluoroalkenes.

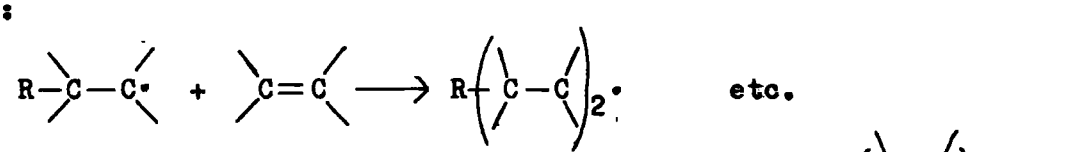
(c) Rearrangements

The rearrangements that sometimes accompany radical additions may be classified into various types: 1,2 shifts, ring opening and closure

and a miscellaneous group. Detailed discussions of radical rearrangements in general are available[28,29] and examples of the various types of rearrangements mentioned are described elsewhere[7].

4. Telomerization[36]

An important process which interferes with the formation of the one-to-one adduct is telomerization. The adduct radical may add to another alkene molecule instead of abstracting from the starting material:



A series of products containing 2,3 etc., alkene units, $R\text{-}(C\text{-}C)_n\text{-}H$, is is eventually formed. These materials, known as telomers, are usually undesirable by-products in a synthesis of the one-to-one adduct but their formation can usually be reduced or suppressed by using a high ratio of addend to alkene or by working at higher temperatures.

I.C ADDITIONS OF FUNCTIONAL COMPOUNDS TO FLUOROALKENES

Free-radical additions to fluoroalkenes can be conveniently divided into two groups; (i) those that lead to carbon-carbon bond formation and (ii) those that lead to carbon-heteroatom bond formation. Attention herein is focussed on additions to fluorocycloalkenes but reactions of acyclic fluoroalkenes are also considered although in less detail.

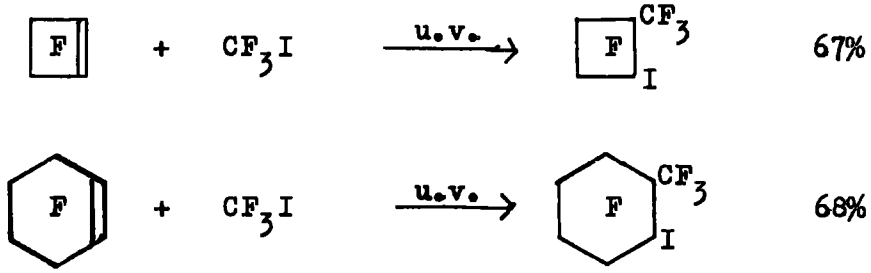
1. Carbon-Carbon Bond Formation

(a) Haloalkanes

Additions of haloalkanes have been widely studied[7,22]. On photolysis, they readily yield haloalkyl radicals which, in adding, as described earlier (Section I.B), provide information in kinetic and orientation studies of the addition reaction.

F-cyclo-butene and -hexene reacted slowly with trifluoroiodomethane on exposure to ultraviolet light to give the corresponding 1-iodo-

2-trifluoromethyl perfluorocycloalkanes[30].



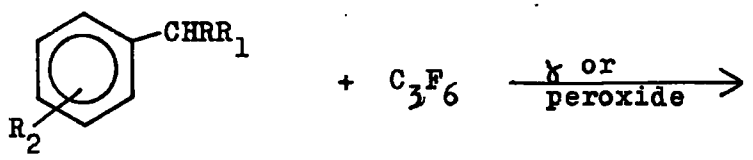
[30]

(b) Alkyl Benzenes

The reaction of F-propene with toluene has been reported[31] to give

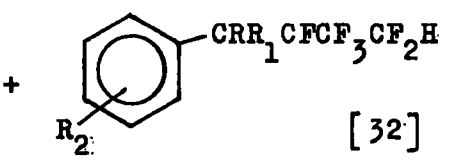
$$PhCH_3 + C_3F_6 \xrightarrow{450^oC} PhCH_2CF_2CFHCF_3 \quad (5) \qquad [31]$$

the one-to-one adduct (5) at 450°C but no proof of structure was given. Peroxide and gamma-ray initiated addition of a range of alkyl benzenes (6 a-i) to F-propene was also found[32] to give mainly the one-to-one



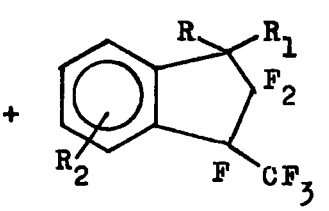
(6) (7)

	R	R_1	R_2
a;	H	H	H
b;	H	H	o-CH_3
c;	H	H	m-CH_3
d;	H	H	p-CH_3
e;	H	H	p-Cl
f;	H	H	p-OCH_3
g;	H	CH_3	H
h;	CH_3	CH_3	H
i;	H	C_2H_5	H



[32]

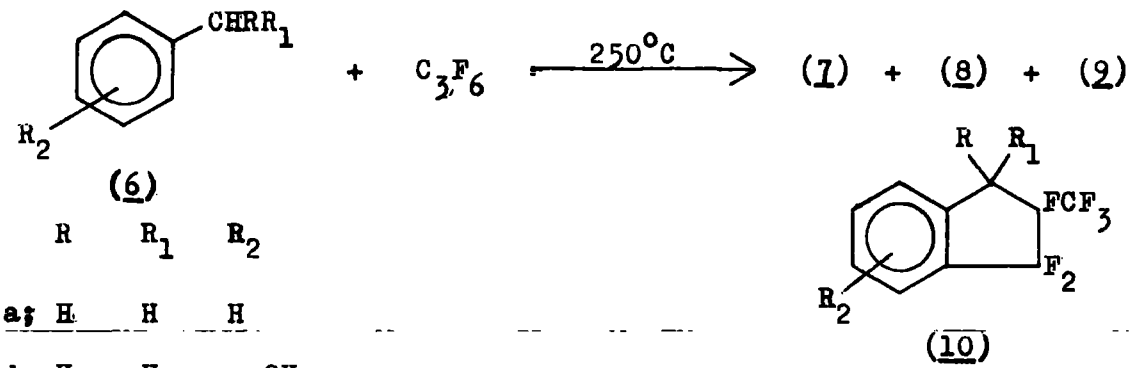
(8)



(9)

adduct (7) but also a small quantity of (8) formed by addition at the other end of the double bond: (6h) did not react. It was also found that (6 a, g, and h) gave low yields (1 - 3%) of the indanes (9). By

changing the reaction conditions, the amount of (9) produced was increased [33,34] making the synthesis of such fluorinated indanes a useful proposition. Thermal reaction (ca. 250°C) of (6a, d, e, g, and i) was found to give a wider range of products resulting from bidirectional benzyl radical addition.[35] Cumene (6h) did not give the one-to-one



[35]

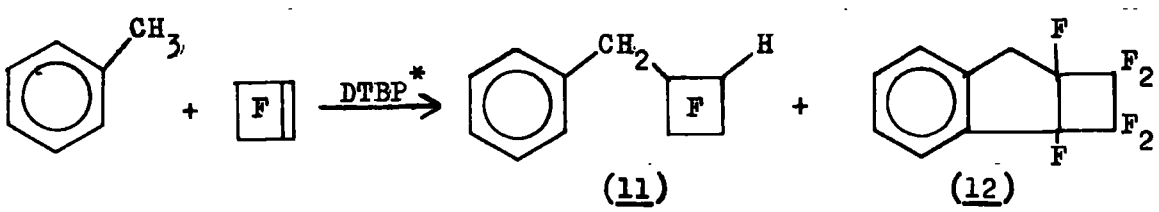
(6)

	R	R_1	R_2
a;	H	H	H
d;	H	H	p-CH_3
e;	H	H	p-Cl
g;	H	CH_3	H
i;	H	C_2H_5	H
h;	CH_3	CH_3	H

(10)

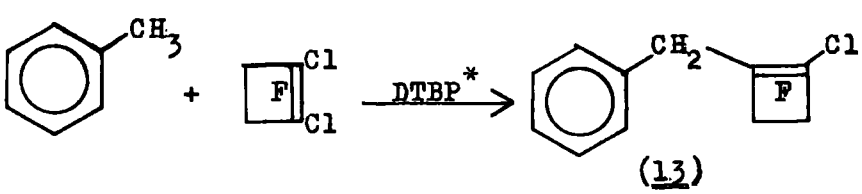
adducts, the major products being 1,2,2,2-tetrafluoroethyl benzene, 1,1-difluoro-2-methyl propene, a cyclobutane and the indanes (9h) and (10h).

1,1-dichloro-difluoroethene[37], 1,2-dichloro-difluoroethene[37], and chlorotrifluoroethene[38] have also been reacted with a variety of alkyl



(11) (12)

[39]



(13)

*DTBP = Di-tertiary butyl peroxide

benzenes to give one-to-one adducts, telomers and indanes. The only report to date of addition to fluorocycloalkenes describes the reaction of toluene with F-cyclobutene and with 1,2-dichloro-F-cyclobutene initiated by peroxide. Whereas the former gives both the one-to-one adduct (11) and the cycloadduct (12), the latter gives only the substitution product (13)[39]. Two stereoisomers of (11) were detected in the ratio 86:14 and the predominant isomer was assigned the trans-configuration.

(c) Alcohols

Radical addition of alcohols to fluoroalkenes involves formation of an α-hydroxyalkyl radical:

$$R_2CHOH \longrightarrow R_2\dot{C}OH + H\cdot$$

Joyce[40] first reported in a patent that the alcohols e.g., methanol, ethanol etc. added to F-ethene to form telomers thus

$$CH_3OH + CF_2{=}CF_2 \longrightarrow H(CF_2CF_2)_nCH_2OH \quad [40]$$
$$(n = 1\text{-}12)$$

Later Lazerte and Koshar[41] obtained one-to-one adducts in the addition of alcohols to F-propene, F-1-butene, and F-2-butene using benzoyl peroxide as initiator. Muramatsu and co-workers[42] found that, in alcohol additions to F-propene, the direction of attack was exclusively oriented to the difluoromethylene carbon: the products were of the form (14).

$$CF_3CF{=}CF_2 + RR'CHOH \xrightarrow{\gamma} CF_3CFHCF_2CRR'OH \quad [42]$$
$$(14)$$

RR'CHOH = CH_3OH; C_2H_5OH;
$n\text{-}C_3H_7OH$; $i\text{-}C_3H_7OH$.

This contrasts with the radical addition of e.g. thiols to F-propene[43] which yields adducts via attack at either carbon of the double bond. The latter observation illustrates the importance of polar effects and

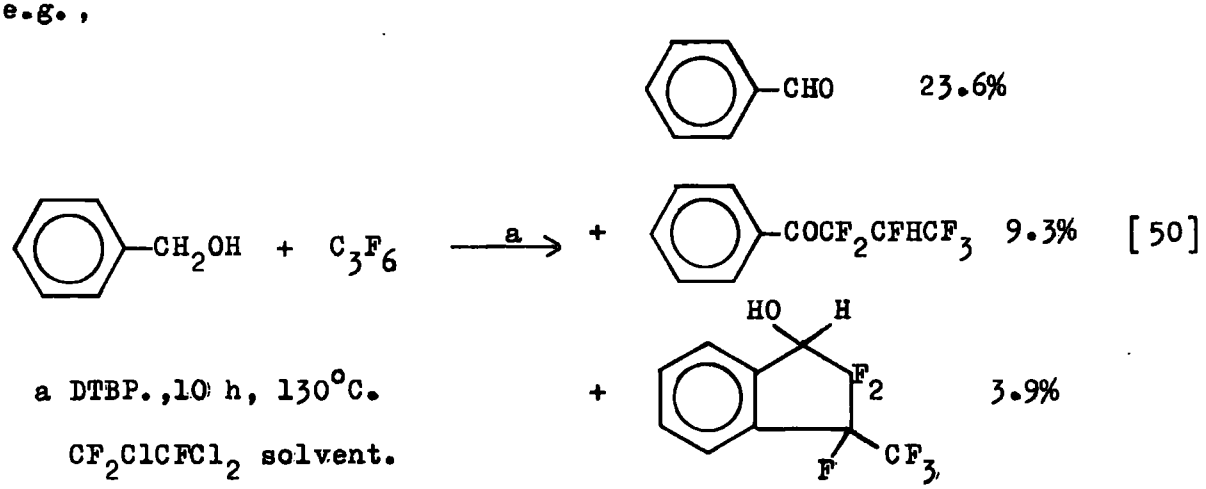
the specificity of attack is evidence of the nucleophilic character of the α-hydroxyalkyl radical. Thiyl radical additions will be discussed more fully in Section C.2(g).

Alcohols have also been added to chlorotrifluoroethene[44-47] using ultraviolet, peroxide or gamma-ray initiation to give the ono-to-one adducts and telomers via attack on the difluoromethylene end only. Likewise, addition to 1,2-dichloro-difluoroethene, trichlorofluoroethene, and 1,1-dichloro-difluoroethene gave good yields of the one-to-one adducts through reaction at the less sterically hindered end although the latter also formed telomers[48].

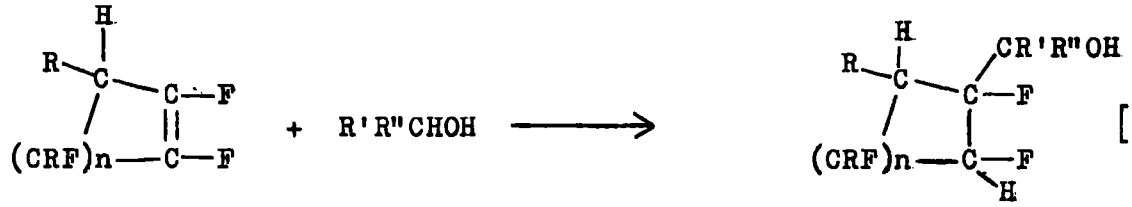
Three polyfluoroalcohols were identified when F-propene dimer, a mixture of (15) and (16), reacted with methanol in the presence of

$(CF_3)_2CFCF{=}CFCF_3$ (15) $(CF_3)_2C{=}CFC_2F_5$ (16)

benzoyl peroxide[49]. Aromatic alcohols, on the other hand, gave only oxidation and cyclization products in radical reactions with F-propene[50], e.g.,



An all-embracing patent[51] claims the invention of fluorinated cyclic alcohols by reacting fluorocycloalkenes with alcohols as shown on the top of the next page. Reports of additions of alcohols to specific F-cycloalkenes are less frequent than in acyclic systems. Courtieu and

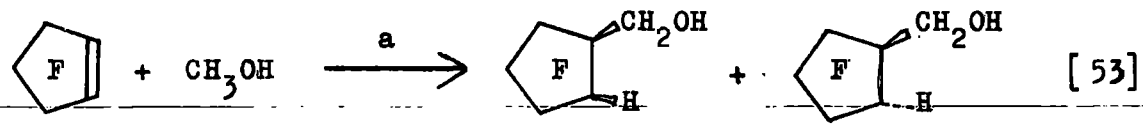


[51]

n = 1, 2, 3.

R = H, F, perfluoroalkyl ; R', R" = H or alkyl.

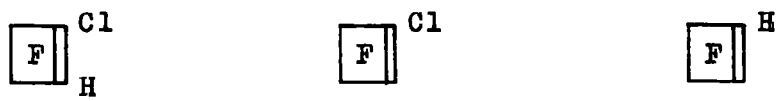
co-workers[52] mentioned the reaction of methanol with F-cyclohexene but gave no details and Stockel and Beachem[53] obtained a mixture of two isomers in the ratio 55:45 when they added methanol to F-cyclopentene. The products were the cis and trans one-to-one adducts (17) and (18) but



[53]

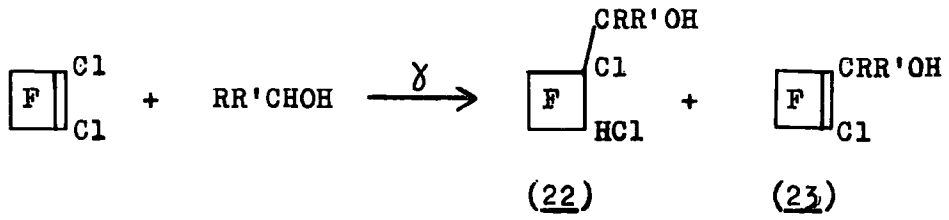
a benzoyl peroxide

they were not separated. F-cyclobutene gave excellent yields of the one-to-one adducts with a range of alcohols[54]. The stereochemistry of the products was assigned and in all cases the trans isomer was claimed to predominate although the trans:cis ratio declined as the length of the alcohol's alkyl chain increased. Gamma radiation initiated addition to the cyclobutenes (19 - 21) resulted[55] in attack of the α-hydroxyalkyl



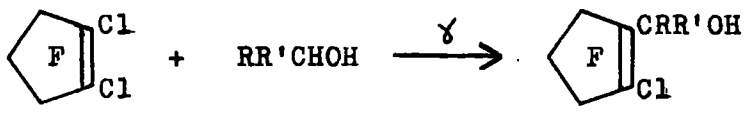
(19) (20) (21)

radical exclusively on the CH or CF end of the unsymmetrical double bond in (19) and (20) respectively but reaction took place at both ends in (21), the ratio of attack being dependent on the nature of the alcohol used. The compound 1,2-dichloro-F-cyclobutene also gave the corresponding one-to-one adducts (22) and the dehydrochlorinated adduct (23). Only the latter type of adduct (24) was obtained in the reaction of alcohols with 1,2-dichloro-F-cyclopentene[56].



(22) (23)

[56]

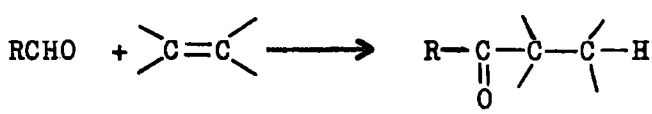


ROH = CH_3OH, C_2H_5OH, n-C_3H_7OH, i-C_3H_7OH.

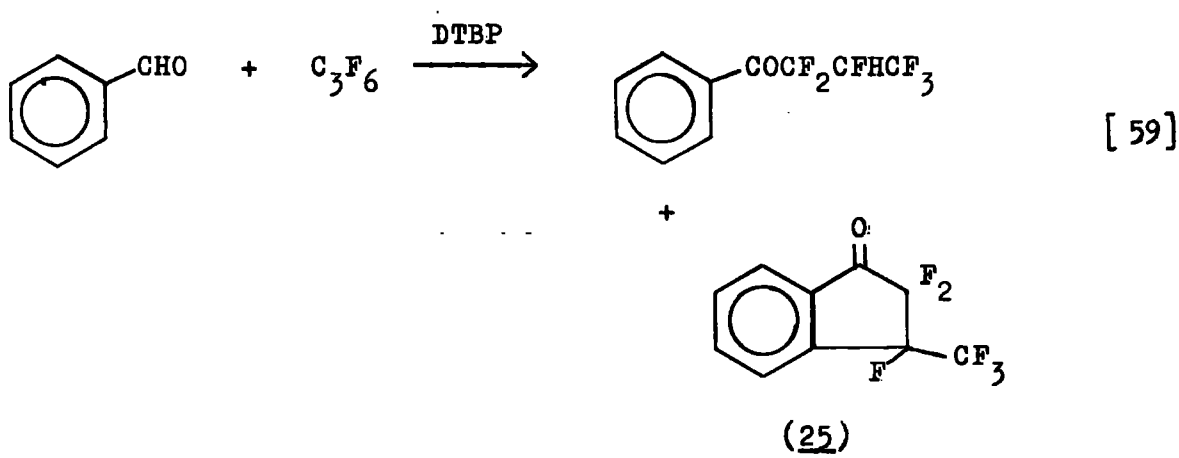
(24)

(d) Aldehydes

Abstraction of the hydrogen atom bearing the functional group in an aldehyde gives an acyl radical which adds to the alkene to yield a ketone. Fluorinated ketones have been obtained by peroxide-[41,49,57]



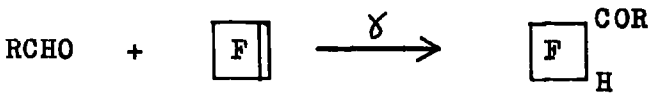
and gamma radiation- initiated[46,58] addition of aldehydes to fluoroalkenes. Benzaldehyde reacts with F-propene to give not only the one-to-one adduct but also the indanone (25)[59].



[59]

(25)

F-cyclobutene reacted readily with aldehydes[54], the yield of the one-to-one adduct increasing size of R. As in the corresponding alcohol additions[54], two stereoisomers of (26) were produced and once

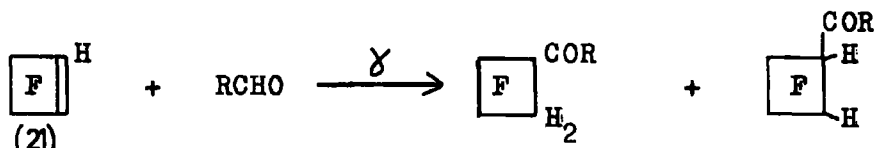


$$RCHO + \boxed{F}\!\!\| \xrightarrow{\gamma} \boxed{F}\!\!\begin{matrix}COR\\H\end{matrix} \qquad [54]$$

R = CH_3, C_2H_5, C_3H_7.

(26)

again the trans isomer was more abundant in all cases. The cyclobutene (21) experienced addition at both ends of the double bond[60] although the acyl radical preferred attack at the CF end giving a 2:1 ratio of (27) and (28).



$$\boxed{F}\!\!\begin{matrix}H\\(21)\end{matrix} + RCHO \xrightarrow{\gamma} \boxed{F}\!\!\begin{matrix}COR\\H_2\end{matrix} + \boxed{F}\!\!\begin{matrix}COR\\H\\H\end{matrix} \qquad [60]$$

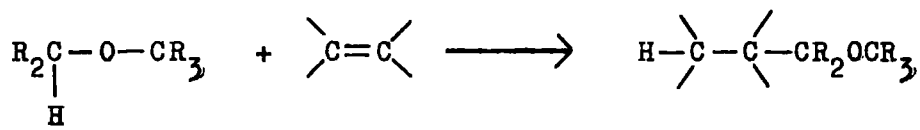
R = Me, Et, Pr, i-Pr.

(27) (28)

(e) Ethers and Esters

The addition reactions of ethers and esters are discussed together here since they both contain the alkoxy functional group.

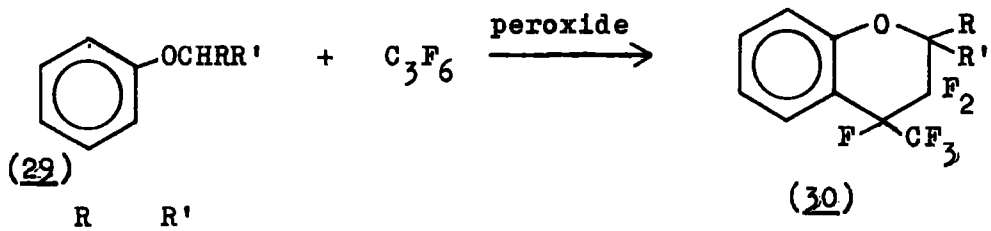
In all the literature reports of radical additions of ethers to fluoroalkenes, reaction has been found to occur at the carbon - hydrogen bond alpha to the oxygen, thus



$$R_2\underset{H}{C}-O-CR_3 + \diagdown C{=}C \diagup \longrightarrow H-\underset{\diagup}{\overset{\diagdown}{C}}-\underset{\diagup}{\overset{\diagdown}{C}}-CR_2OCR_3$$

Peroxide initiated addition of certain cyclic ethers to F-ethene to give one-to-one adducts and telomers was first described by Hanford[61]. Chlorofluoroalkenes react with diethyl ether[62,63], tetrahydrofuran (THF)[62,63], 1,4-dioxane[62] and dimethoxymethane[64] to give the one-to-one and two-to-one adducts. Abroskina[65] reported that both types of adducts were also obtained by reaction of THF with F-propene, F-2-methyl propene and with two perfluoro vinyl ethers although other workers[42,52] only found the one-to-one adduct with F-propene. F-propene was added to dimethyl ether under thermal[66] and photochemical[67] conditions. Gamma-

ray initiated additions of F-propene to 1,4-dioxane[42], diethyl ether[42], and other fluoroalkyl ethyl ethers[68] gave both the one-to-one and two-to-one adducts although when the fluoroalkyl ethyl ether contained a CF_2 group adjacent to the oxygen no two-to-one adduct was formed. The cycloadduct (30) was the only product identified when F-propene reacted with the phenyl alkyl ethers (29a-c)[69].



[69]

(29)

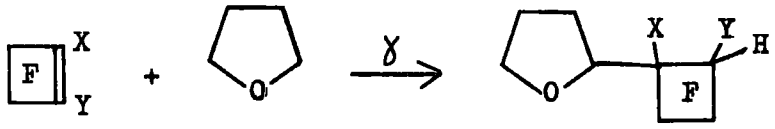
(30)

	R	R'
a;	H	H
b;	H	CH_3
c;	CH_3	CH_3

Ethers have been added to a variety of fluorocycloalkenes and these reactions are summarised in Table 8 overleaf. THF gives only the one-to-one adducts (31) with different fluorocyclobutenes[54,70-72] and with F-cyclohexene[52] but the product mixture is more complex with other systems. The one-to-one adduct (32) is the major product in the reaction of 1,4-dioxane with F-cyclobutene[54] and a two-to-one adduct of unspecified structure is also formed. However, 1,2-dichloro-F-cyclobutene with 1,4-dioxane[70] gives only a small amount of the one-to-one adduct (33), the dehydrochlorinated adduct (34) predominating. Only the latter type of compound, (35), is obtained in the addition of 1,4-dioxane to 1,2-dichloro-F-cyclopentene[70].

Diethyl ether, as with 1,4-dioxane, gives the one-to-one (36) and two-to-one (37) adducts with F-cyclobutene[54]. From 1,2-dichloro-F-cyclobutene not only are the analogous adducts (38) and (39) obtained but also their dehydrochlorinated analogues (40) and (41)[70]. However, 1,2-dichloro-F-cyclopentene reacts to give only a dehydrochlorinated one-to-one adduct (42)[70].

Table 8 Additions of Ethers to Fluorocycloalkenes



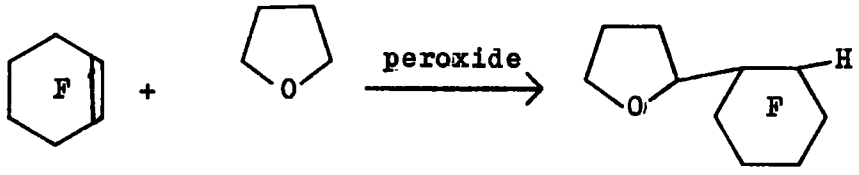
X=F, Y=F [54]

X=Cl, Y=Cl [70]

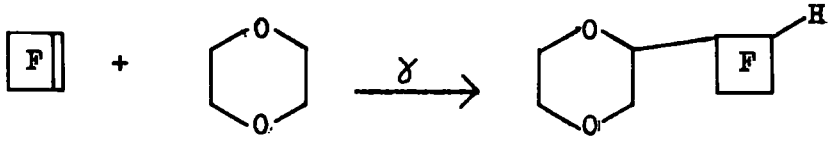
X=H, Y=Cl [71]

X=F, Y=Cl [72]

(31)

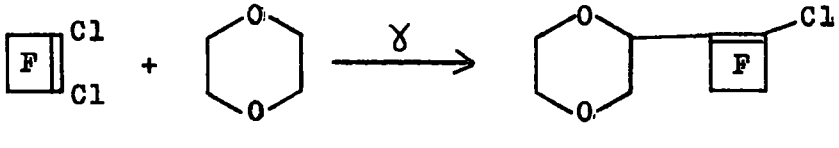


[52]



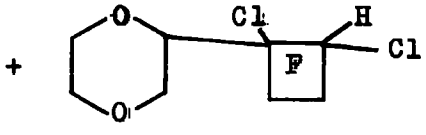
[54]

(32)

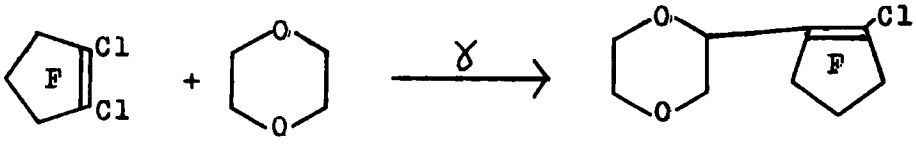


[70]

(34)



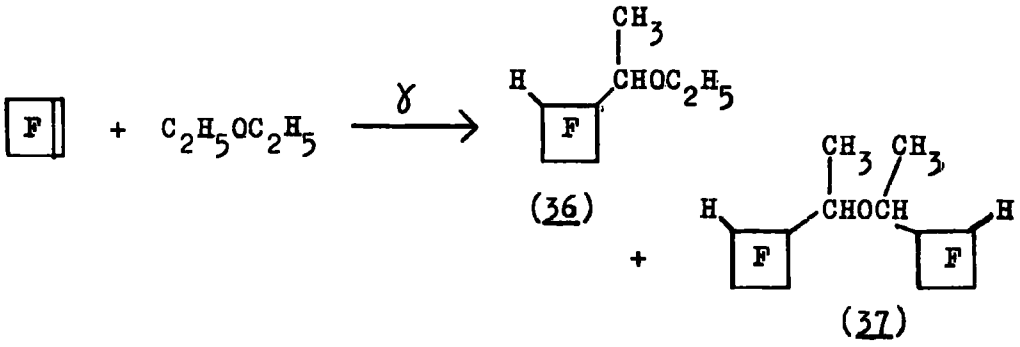
(33)



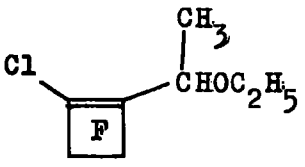
[70]

(35)

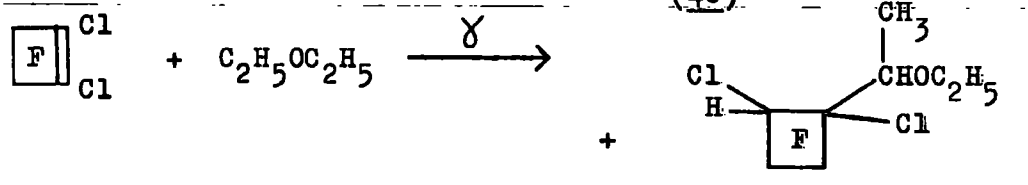
Table 8 continued....



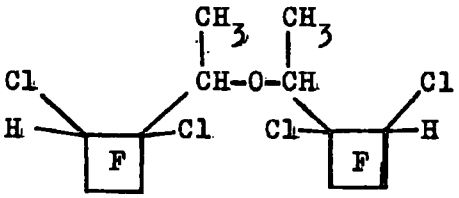
(36) + (37) [54]



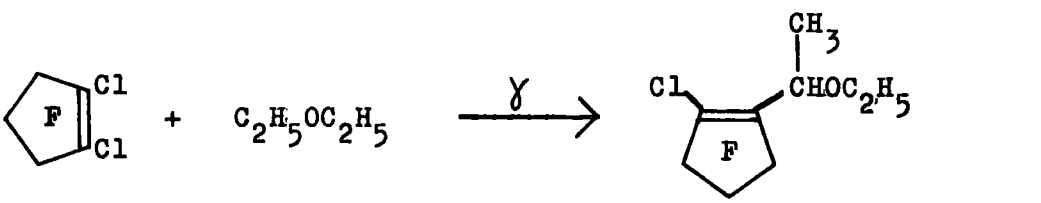
(40)



(38) + (39) [70]



(41)



(42) [70]

To date the only radical addition of esters to fluoroalkenes has been reported by Japanese workers[73]. Gamma-ray initiated addition of esters with the formula RCO_2R', where R, R' = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7 and n-C_4H_9, to F-propene have been reported to give the corresponding one-to-one adducts. These consisted of unspecified isomers carrying the fluoroalkyl side-chain at different positions. It was noted that the apparent reactivities of the carbon atoms in an ester molecule were: $CH > CH_2 > CH_3$ and that the atoms in the alkoxy group (R'O) were more reactive than those in the acyl group (RCO). Reactivity increased with distance along the carbon chain away from the carbonyl group. Diethyl carbonate also gave an adduct[73] but esters which contained an electronegative group e.g., $RCO_2C_2H_5$ (R = CH_2F, CHFCl etc.) either gave low yields of one-to-one adducts or failed to react altogether.

(f) Miscellaneous

Free-radical additions of several other functional molecules to fluoroalkenes which have been reported are mentioned in this section.

(i) Dimethylformamide

Reaction of dimethylformamide (DMF) with chlorotrifluoroethene under gamma-ray or acetone-sensitized ultraviolet initiation leads to two product types, (43) and (44)[72]. It was found that the ratio (43):(44) was around 1:4.5 for either mode of initiation.

$$HCON(CH_3)_2 + ClCF{=}CF_2 \xrightarrow[u.v.]{\gamma \text{ or}} (CH_3)_2\text{-N-}\underset{\underset{O}{\|}}{C}CF_2CFClH \quad (43) \qquad [72]$$

$$+ \quad CH_3\text{-N(CHO)-}CH_2(CF_2CFCl)_nH \qquad n = 1, 2. \quad (44)$$

(ii) Tertiary amines

Chlorotrifluoroethene gives one-to-one and two-to-one adducts with trimethylamine[74], triethylamine[74] and dimethylisopropylamine[75]. In each case homolytic cleavage of a carbon - hydrogen bond alpha to the nitrogen occurred as shown below.

$$ClCF{=}CF_2 + (RCH_2)_3N \xrightarrow[u.v.]{\gamma \text{ or}} \begin{matrix} (RCH_2)_2\text{-N-CHRCF}_2\text{CFClH} \\ + \\ \text{HCFClCF}_2\text{CHR-N-CHRCF}_2\text{CFClH} \\ | \\ CH_2R \end{matrix} \quad [74]$$

$$ClCF{=}CF_2 + Me_2CHNMe_2 \xrightarrow[u.v.]{\gamma \text{ or}} \begin{matrix} \text{HCFClCF}_2\text{CH}_2\text{N(Me)CHMe}_2 \\ + \quad \text{HCFClCF}_2\text{CMe}_2\text{NMe}_2 \\ + \quad \text{HCFClCF}_2\text{CMe}_2\text{N(Me)CH}_2\text{CF}_2\text{CFClH} \end{matrix} \quad [75]$$

2. Carbon - Heteroatom Bond Formation

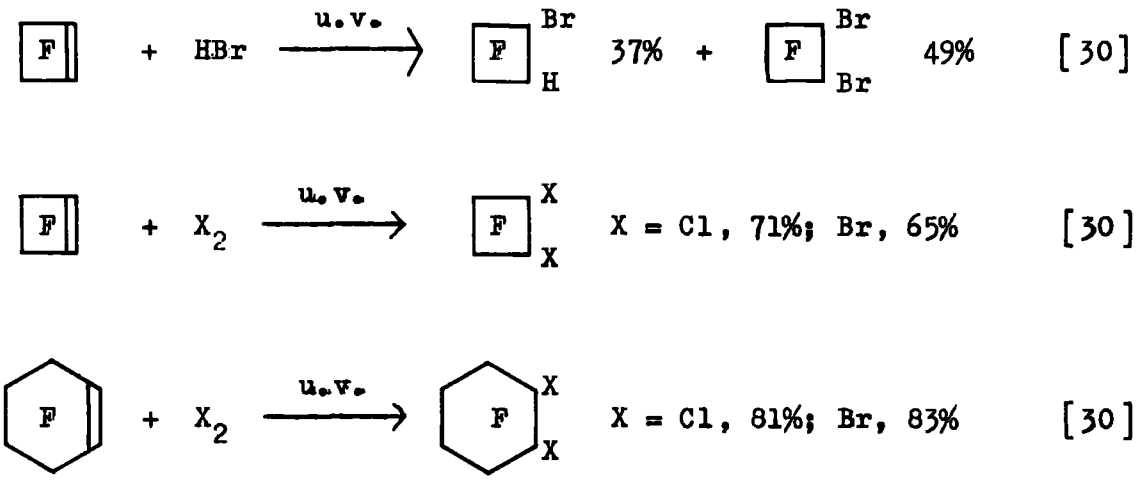
Heteroradicals add to form carbon - heteroatom bonds so that the reaction is very useful as a method of synthesizing organic compounds containing carbon-silicon, carbon-nitrogen, carbon-phosphorus, etc., bonds.

(a) Additions to Form Carbon - Halogen Bonds

Additions of hydrogen halides, especially hydrogen bromide, have been reviewed[8]. Ultraviolet irradiation of a mixture of F-cyclobutene and hydrogen bromide gave both the simple addition compound and 1,2-dibromo-F-cyclobutane but under the same condirions F-cyclohexene failed to react[30].

Chlorine and bromine added to both F-cycloalkenes[30]: the 1,2-dichloro-F-cyclobutane was estimated to be 80% trans by infra-red measurements[77].

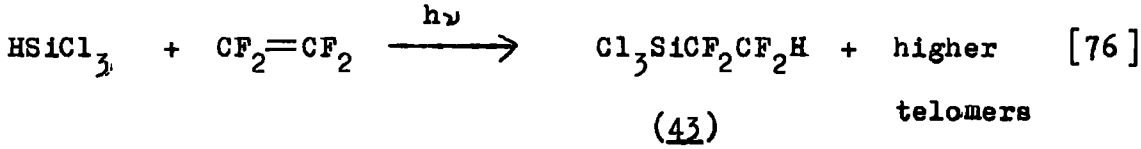
Halogens and hydrogen bromide have been added to a variety of other unsaturated perfluorinated cyclic compounds, under ultraviolet



irradiation generally[78-83]. All of these additions proceed readily.

(b) Additions to Form Carbon - Silicon Bonds

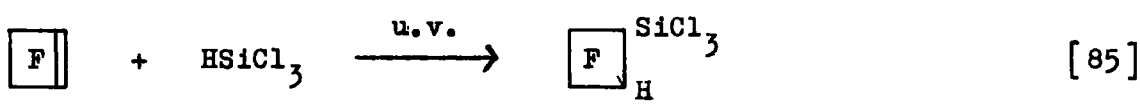
The synthesis of organosilicon compounds by radical addition can be accomplished with a silane having one or more hydrogen atoms attached to silicon. Thermal, chemical, and radiation initiation have all been used[8]. Telomer formation can be a complication with easily polymerizable alkenes but the yield of one-to-one adduct can be increased by increasing the amount of silane relative to alkene. For example, F-ethene can give at least 50% of the desired product (43) under the correct conditions[76].



(43)

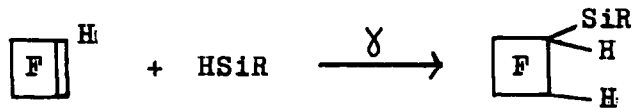
F-propene shows a lack of reactivity with trichlorosilane, giving only traces of adduct in the presence of ultraviolet or peroxide[84], which is surprising since it reacts readily with silane[85] and since F-2-butene gives a high yield on irradiation with trichlorosilane[85].

Photochemical reaction of trichlorosilane with F-cyclobutene[85] gave the adduct (44) which was found to be one isomer only, assigned

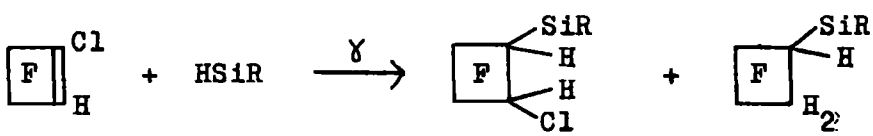


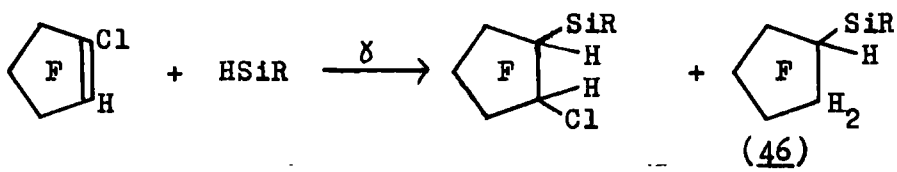
(44)

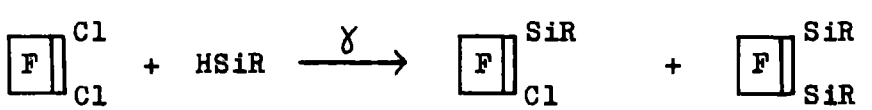
trans from comparison of its nuclear magnetic resonance spectra with those of a model compound (see Chapter III, Section A). Trimethylsilane also gives a single stereoisomer with both F-cyclobutene and with 1,2-dichloro-F-cyclobutene[86]. This isomer was originally assigned a cis structure but is regarded now as being the trans adduct[85]. 1-Hydro-F-cyclobutene reacts with trichlorosilane and dichloromethylsilane, the silyl radical adding at the CH end of the double bond only, to give the one-to-one adduct (shown below)[87].

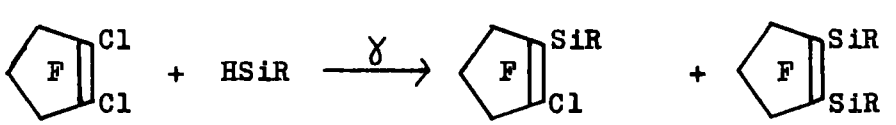


The cycloalkenes, 1-chloro-3,3,4,4-tetrafluorocyclobutene[87] and 1-chloro-3,3,4,4,5,5-hexafluorocyclopentene[87,88], give not only the one-to-one adducts but also reduction products (45) and (46) which are probably formed by H - Cl exchange reaction of the silane and the one-to-one adduct. 1,2-dichloro-F-cyclo-butene and -pentene, however, yield only dehydrochlorinated one-to-one and two-to-one adducts[88].









R = Cl_3, Cl_2Me, Cl_2Ph, $ClMe_2$, Et_3.

(c) Additions to Form Carbon - Germanium and Carbon - Tin Bonds

Germanium and tin hydrides add to alkenes in a similar manner to silanes. Reaction of both tin - hydrogen bonds occurred when a mixture of dimethyl stannane and F-ethene was irradiated[89] thus:

$$H_2SnMe_2 + CF_2{=}CF_2 \xrightarrow{u.v.} (HCF_2CF_2)HSnMe_2 + (HCF_2CF_2)_2SnMe_2 \quad [89]$$

Under the same conditions, trifluoro-, 1,1-difluoro-, and bromotrifluoroethene gave very unstable products which were inferred to be one-to-one adducts[89].

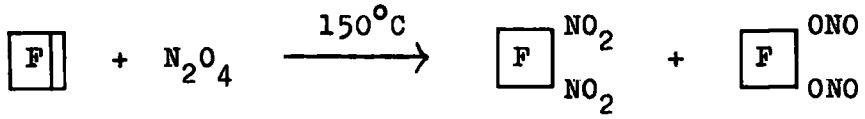
F-cyclobutene and 1,2-dichloro-F-cyclobutene reacted under thermal conditions with trimethyl and triethyl stannane and with trimethyl germane[86]. The products were reported to be single isomers in each case with the same stereochemistry and were assigned cis structures but a more recent reconsideration of the data led to the conclusion that they were in fact trans adducts[85].

(d) Additions to Form Carbon - Nitrogen Bonds

Dinitrogen tetroxide and nitryl chloride add to F-alkenes to give vicinal dinitroalkanes and chloronitroalkanes respectively[90] e.g.,

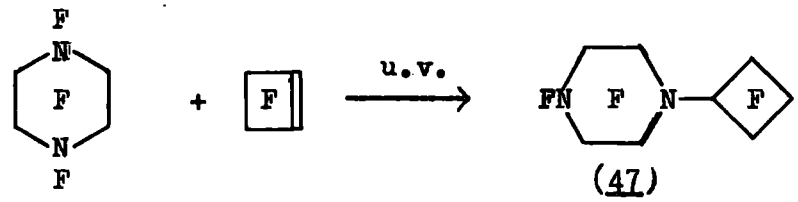
$$CF_2{=}CF_2 + N_2O_4 \longrightarrow O_2NCF_2CF_2NO_2 \quad 53\%$$
$$CF_2{=}CF_2 + NO_2Cl \longrightarrow CF_2ClCF_2NO_2 \quad 57\% \quad [90]$$

Radical addition of N_2O_4 to F-cyclobutene affords both a dinitro and a nitronitrite derivative[91]. The addition proceeds only in a narrow temperature range: below 130°C there is no reaction and above 160°C it is explosive.

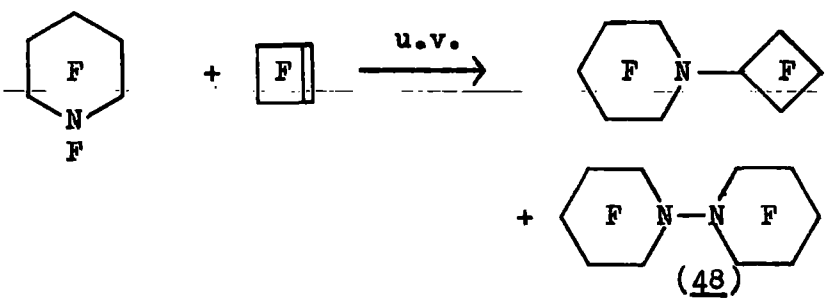


[91]

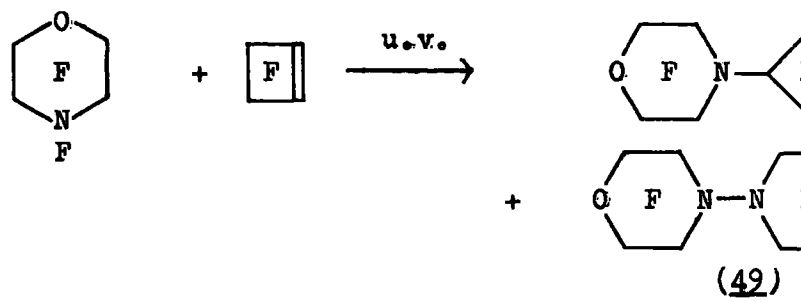
Several perfluorinated saturated heterocyclic compounds have been added to F-cyclobutene under ultraviolet irradiation to give the perfluoro-N-cyclobutyl adduct as the major product. Only the one-to-one adduct (47) is obtained from perfluoro-N,N'-difluoropiperazine[92] but perfluoro-N-fluoropiperidine[93] and F-morpholine[94] also give the dimers (48) and (49) respectively and F-bicyclobutyl (50).



[92]

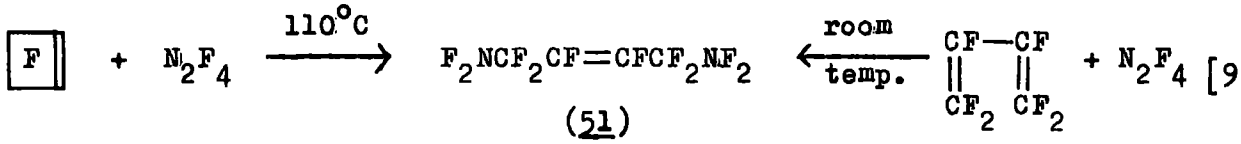


[93]



[94]

It has been reported[95] that the thermally induced reaction of tetrafluorohydrazine with F-cyclobutene gives the same product (51) as is obtained with F-butadiene.



[95]

The ring-opening is assumed to occur after addition of the difluoroamino radical has given an unstable perfluorocycloalkyl radical intermediate.

(e) Additions to Form Carbon - Phosphorus Bonds

Phosphorus compounds containing P - H bonds will add to alkenes by a free-radical route. Phosphines have been added to several fluoroalkenes. For example, ultraviolet[96] or thermally[97] initiated reaction of phosphine with F-etheme produces a mono- and di-adduct and the diphosphinoethane (52).

$$CF_2{=}CF_2 + PH_3 \longrightarrow CF_2HCF_2PH_2 + (CF_2HCF_2)_2PH + H_2PCF_2CF_2PH_2 \quad [96,97]$$

(52)

Chlorotrifluoroethene and 1,1-difluoroethene give one-to-one adducts by addition only at the CF_2 and CH_2 ends respectively and the latter alkene also forms a di-adduct with phosphine[96]. Secondary phosphines e.g. dimethyl phosphine and bis(trifluoromethyl)phosphine also react smoothly with F-ethene[98].

Dialkyl phosphites (53) have been studied more extensively: they add to fluoroalkenes to give dialkyl phosphonates (54). One-to-one

$$HPO(OR)_2 \quad (53) \quad + \quad \diagdown C{=}C \diagup \longrightarrow \quad H{-}C{-}C{-}PO(OR)_2 \quad (54)$$

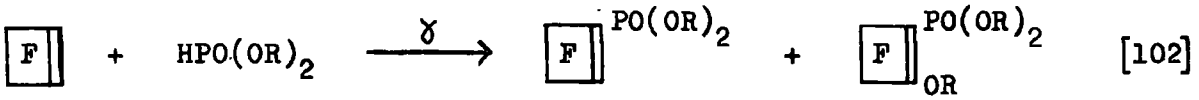
adducts of the type (54) were obtained in reactions with the fluoroalkenes listed in Table 9 overleaf. Addition to unsymmetrical alkenes was preferred at the less sterically crowded end of the double bond in each case.

Polyfluorocyclobutenes, however, give as the main products dehydrohalogenated one-to-one adducts rather than the expected simple addition compounds in reaction with dialkyl phosphites[102]. Thus reaction of a mixture of F-cyclobutene and dialkyl phosphite produced the phosphonates (55) and (56) and 1,2-dichloro-F-cyclobutene gave only a

Table 9 Dialkyl Phosphite Additions to Fluoroalkenes

Phosphite $HPO(OR)_2$	Alkene	Direction of Addition	Reference
R = Me, Et	$CF_2=CF_2$		99
Et	$ClCF=CF_2$	CF_2 end only	99
Me, Et, Pr	$Cl_2C=CF_2$	CF_2 end only; telomers	100
Me, Et, Pr	$CFCl=CFCl$		100
Me, Et, Pr	$CCl_2=CFCl$	CF end	100
Et	$CF_2=CH_2$	CH_2 end only	99
Et	$CF_3CF=CF_2$	4:1 CF_2/CF	99, 101
Et	$CF_3CH=CH_2$	CH_2 end	99

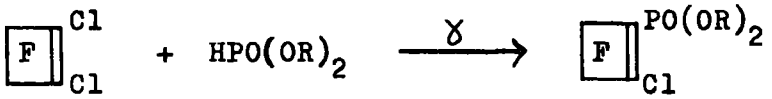
trace of (57). The cyclobutenes (19) and (21) gave (58) and the diphosphonate (59).



[102]

R = Me, Et, n-Pr.

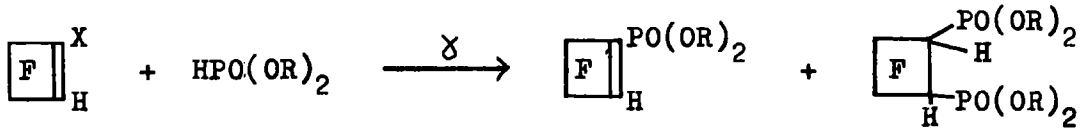
(55) (56)



[102]

R = Et.

(57)



[102]

X = Cl(19) R = Et.

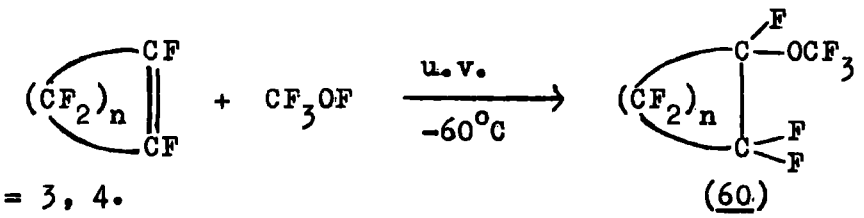
X = F (21)

(58) (59)

(f) Additions to Form Carbon - Oxygen Bonds

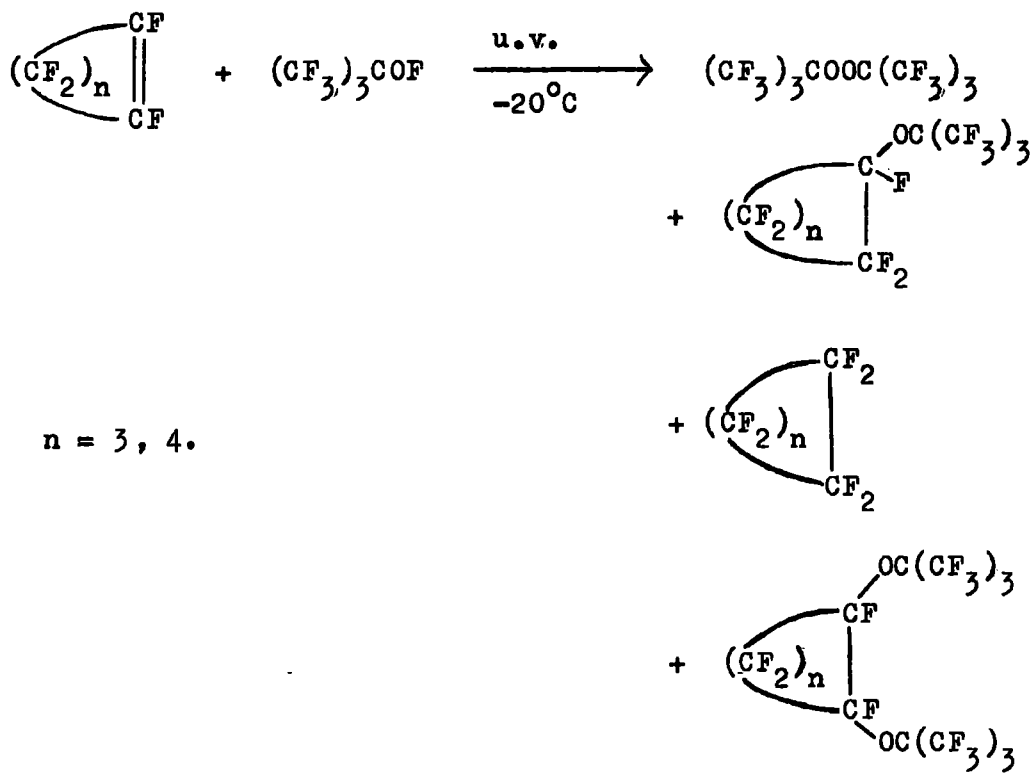
Relatively few oxygen-containing compounds have been added to

fluoroalkenes to give carbon - oxygen bonds. Photochemical reaction of trifluoromethyl hypofluorite (CF_3OF) with F-cyclo-pentene and -hexene[103] gave mainly the simple adducts (60) by initial O-F bond cleavage.



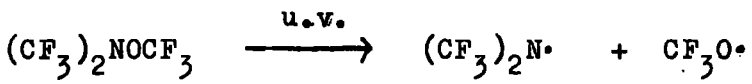
n = 3, 4. (60) [103]

F-cyclopentene also gave (60) in a thermally-induced reaction[104]. Perfluoro-t-butyl hypofluorite [$(CF_3)_3COF$] reacted somewhat differently[103]. The main product was found to be F-di-t-butyl peroxide. Also identified were the one-to-one adducts, the corresponding F-cycloalkanes, C_5F_{10} and C_6F_{12}, and a small amount of the vicinal-t-butoxycycloalkanes.

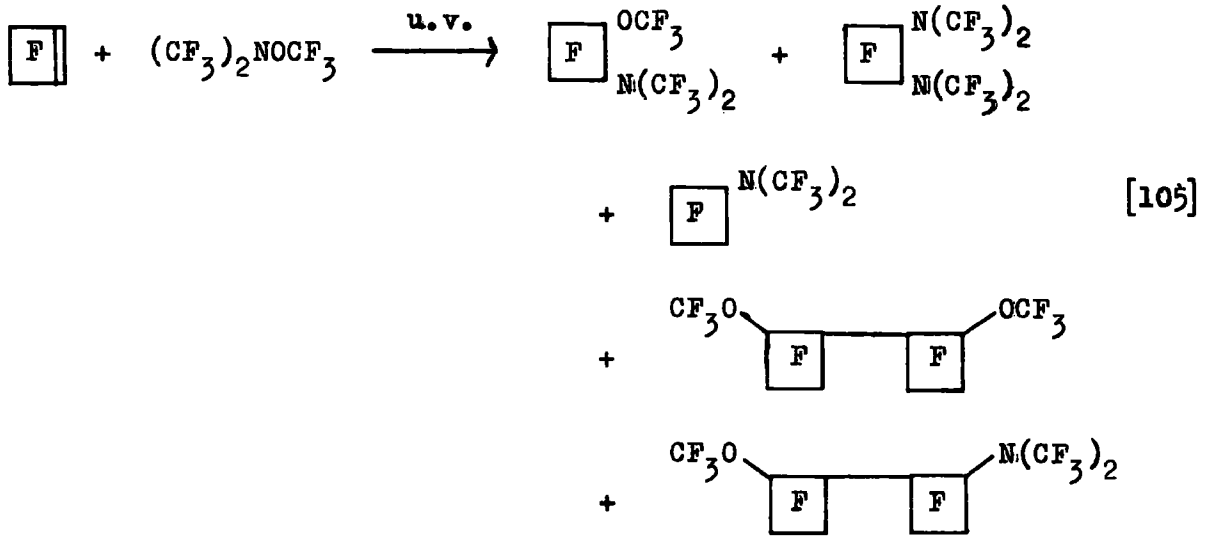


n = 3, 4. [103]

Tristrifluoromethylhydroxylamine, on photolysis, decomposes by fission of the relatively weak N-O bond to give $(CF_3)_2N\cdot$ and $CF_3O\cdot$ radicals.



Irradiation of a mixture of the hydroxylamine and F-cyclobutene[105] gave a range of adducts by addition of one or both of the above radicals, thus

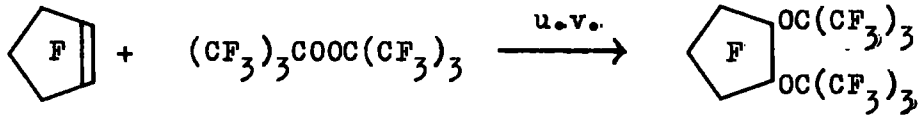


[105]

Reaction of fluoroperoxytrifluoromethane (CF_3OOF) with fluoroalkenes yields a mixture of peroxide and ether products[106], for example

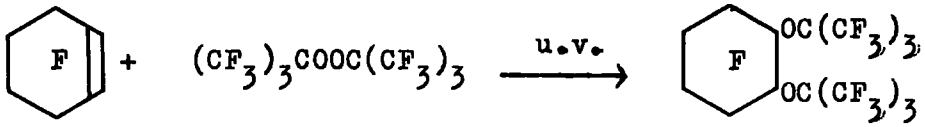
$$CFCl{=}CF_2 + CF_3OOF \longrightarrow CF_3OCF_2CF_2Cl + CF_3OCFClCF_3 + CF_3OOCFClCF_3 + CF_3OOCF_2CF_2Cl \quad [106]$$

F-cyclo-pentene and -hexene react readily with F-di-tertiary butyl peroxide to give the corresponding vicinal F-di-t-butoxycycloalkanes (61) and (62) and with bis(F-methyl) peroxide to give the compounds (63)[107].



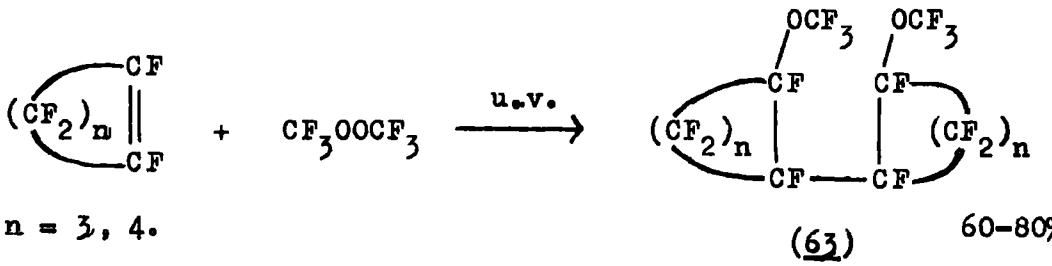
[107]

(61)



[107]

(62)



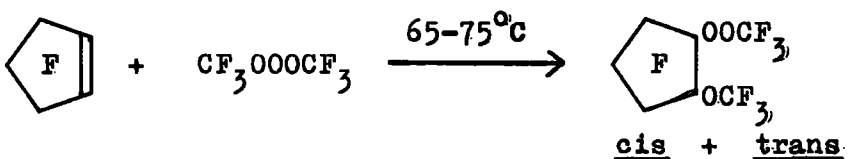
n = 3, 4. (63) 60-80% [107]

Two isomers of (61) in a 1:4 ratio were identified as cis and trans isomers respectively. The three isomers of (62) in a 1:4:2 ratio were tentatively assigned, by ^{19}F n.m.r., structures with the substituents in equatorial-equatorial, axial-equatorial, and axial-axial positions respectively.

Addition of bis(F-methyl)trioxide (CF_3OOOCF_3) to fluoroalkenes is believed to proceed by initial addition of a $CF_3O\cdot$ radical[108] and is bidirectional with unsymmetrical alkenes, for example

$$CF_3CF{=}CF_2 + CF_3OOOCF_3 \xrightarrow[3 \text{ hours}]{67^\circ C} CF_3OCF_2CF(CF_3)OOCF_3 \quad 70\%$$
$$+ \quad CF_3OCF(CF_3)CF_2OOCF_3 \quad 30\% \qquad [108]$$

Nearly equal amounts of cis and trans isomers (52:48) were formed from F-cyclopentene[108].



cis + trans [108]

(g) Additions to Form Carbon - Sulphur Bonds

Radiation (X-ray)-induced addition of hydrogen sulphide to fluoroethenes gives fluorinated ethanethiols as products[109]. Addition to unsymmetrical alkenes is bidirectional e.g.

$$CF_2{=}CFH + H_2S \xrightarrow{\text{X-rays}} HCF_2CFHSH + CFH_2CF_2SH \qquad [109]$$

Thiols, the most widely used source of thiyl radicals, can also add to both ends of unsymmetrical alkenes as illustrated overleaf[110,111].

$$RSH + CF_2{=}CFCF_3 \xrightarrow[\text{X-ray}]{\text{u.v. or}} \underset{(64)}{RSCF_2CFHCF_3} + \underset{(65)}{RSCF(CF_3)CF_2H} \quad [110]$$

R	(64)%	(65)%
CF_3	45	55
CF_3CH_2	70	30
CH_3	91	9

Preferential addition at the least substituted carbon of the double bond is expected but it can be seen from the results above[110] that polar effects are important in determining the orientation of addition. Thus, as the thiyl radical gains in electrophilic character, the amount of (65) increases. This is consistent with a polar influence.

Other sulphur-containing compounds viz. bisulphite ion[112,113], sulphonyl[114] and sulphenyl[115] halides, and sulphur chloride pentafluoride[116-119] have all undergone radical addition to fluoroalkenes and these reactions are summarised in Table 10 below.

Table 10 Miscellaneous Radical Additions with Carbon - Sulphur Bond Formation

$$CF_3CF{=}CF_2 + NaHSO_3 \xrightarrow{\text{peroxide}} CF_3CFHCF_2SO_2Na \quad 64\% \quad [113]$$

$$CF_2{=}CF_2 + ClSO_2F \xrightarrow{\text{peroxide}} Cl(CF_2CF_2)_nSO_2F \quad [114]$$

n, average = 4-5

$$CFCl{=}CF_2 + CF_3SCl \xrightarrow{\text{u.v.}} \underset{42\%}{CF_3SCFClCF_2Cl} + \underset{12\%}{CF_3SCF_2CFCl_2} \quad [115]$$

$$CFH{=}CF_2 + SF_5Cl \xrightarrow{\text{peroxide}} SF_5CFHCF_2Cl \quad 62\% \quad [116]$$

DISCUSSION

CHAPTER II

GAMMA RADIATION INITIATION

II.A ADVANTAGES

A high-energy radiation source for initiating free-radical reactions possesses a flexibility that is not available to chemical initiators. Although the latter have the advantages of ease of handling and modest equipment requirements, they have disadvantages in their temperature requirements and in the side reactions[7] they may undergo. Since addition reactions require a continual supply of radicals to start chains, a given initiator is chosen so that the desired reaction time corresponds to not more than a few half-lives of the initiator. Benzoyl peroxide, for example, is thus only useful in a narrow temperature range around 80°C where the half-life is of the order of four hours[2]. Other factors can restrict the use of a particular initiator. For example, azobisisobutyronitrile is ineffective as an initiator for alcohol additions[7], presumably because of the stability of the cyanoisopropyl initiator radical and primary and secondary alcohols induce the decomposition of acyl peroxides[120] which renders most of the peroxide ineffective as an initiator for the desired chain reaction.

High-energy radiation is temperature-independent, permitting the use of any desired combination of temperature and irradiation conditions and does not require the addition of extra chemical reagents to the reaction mixture. However, more elaborate equipment is necessary. A purpose-built facility housing a cobalt-60 gamma radiation source is available to these laboratories. When such a source is available, it can be used routinely as a free-radical initiator but with the scope for manipulating the reaction conditions at will.

II.B ENERGETICS OF COBALT-60

Gamma-rays are electromagnetic radiation of nuclear origin with

short wavelength in the region 3×10^{-9} to 3×10^{-11} cm. It is more convenient to describe the radiation in terms of energy since it is the energy absorbed that is of interest. The relationship between wavelength and energy is given by

$$E = \frac{hc}{\lambda}$$

where h is Planck's constant, c the speed of light and λ is the wavelength. In terms of energy, the wavelength range mentioned above becomes approximately 40 keV to 4 MeV (10^6 to 10^9 J per einstein).

One of the most popular gamma radiation sources, and the one employed in these laboratories, is cobalt-60 which has a half-life of 5.26 years and emits beta- and gamma-rays according to the equation

$$_{27}Co^{60} \longrightarrow {}_{28}Ni^{60}\ (\text{stable}) + \beta^- + \gamma$$

The housing for the radioactive source serves to filter out the beta-rays emitted. The gamma-rays emitted by cobalt-60 are of two discrete energies giving equal numbers of gamma-photons of energy 1.332 MeV and 1.173 MeV.

II.C INTERACTION OF GAMMA-RADIATION WITH MATTER

Unlike alpha- and beta-particles which lose their energy gradually through a number of small energy transfers, gamma-rays tend to lose the greater part of their energy through a single interaction. The result is that, whereas monoenergetic alpha-particles and electrons are slowed down by thin absorbers, in the same situation a part of the incident gamma-rays are completely absorbed but the remainder continue with their original energy. Thus gamma-rays do not have a definite range in matter, an absorber serving to reduce the intensity of the gamma radiation passing through it.

There are three processes causing absorption. These are the photoelectric effect, the Compton effect, and pair production. In each

energetic electrons are released within the absorbing medium as photons interact. Their relative importance depends on the energy of the photon and the atomic number of the stopping material. A detailed account of the various processes can be found elsewhere[121-123]. In general, the photoelectric effect is favoured for low photon energies i.e., below about 1 MeV and becomes more favourable the lower the energy. The Compton effect is important from roughly 1-3 MeV, while at higher energies pair-production becomes more likely.

1. The Compton Effect

The Compton effect is most predominant for photon energies around 1 MeV and is the chief mode of energy absorption when using a cobalt-60 source which emits gamma-rays at discrete energies of 1.332 and 1.173 MeV in equal numbers. In this process a photon interacts with an electron that may be loosely bound or free so that the electron is accelerated and the photon deflected with reduced energy (Figure 1).

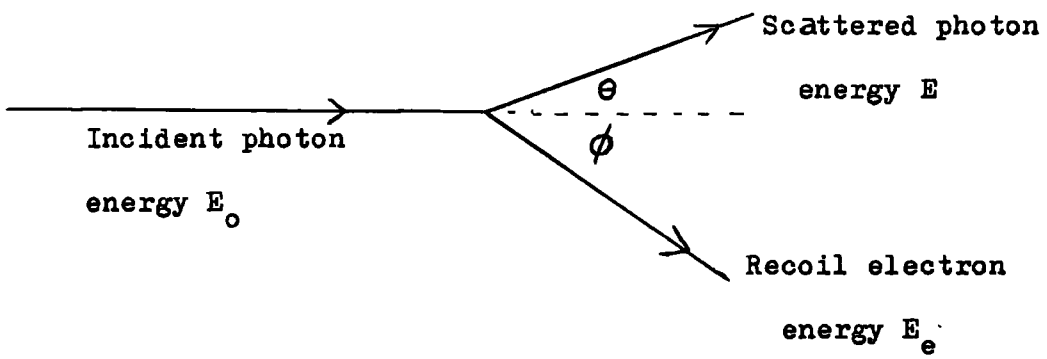


Figure 1

The greater the angle of deflection, the greater the energy loss of the photon.

2. The Photoelectric Effect

In the photoelectric effect the photon loses all its energy and disappears in the interaction. An inner electron, for example, an electron in the K-shell of an atom is ejected with all the photon energy

except that used to "pry the electron loose".

3. Pair-Production

When pair-production occurs, the photon disappears in the single event and a pair, an electron and a positron, is created. Although the process occurs within an atom, it occurs near the nucleus and does not involve the extranuclear electrons. For the process to occur, the photon must have an energy of at least 1.02 MeV, the energy equivalent of the rest mass of two electrons. Any energy which the photon has in excess of the minimum appears as kinetic energy of the pair.

II.D SECONDARY ELECTRON EFFECTS

Electrons released by the photoelectric effect, pair-production, and the Compton effect are called secondary electrons. They lose energy chiefly by inelastic collisions, i.e., through Coulomb interactions with electrons of the stopping material. Interaction in this way gives rise to a trail of excited and ionized atoms and molecules.

II.E REACTIONS OF IONS AND EXCITED MOLECULES

The ions and excited molecules, formed by the absorption of ionizing radiation in matter, bring about chemical change by breaking down and/or reacting with the substrate. A full description of the breakdown patterns and reactions of these entities is available[121] and an abbreviated version is given here.

Ions are neutralised by reaction with an electron or a negative ion to give a neutral but highly excited molecule.

$$A^+ + e^- \longrightarrow A^{**}$$

$$A^+ + A^- \longrightarrow A^* + A$$

This molecule usually dissociates to give either molecular products or free-radicals, one of which is excited.

$$A^* \text{ (or } A^{**}) \longrightarrow M^* + N$$

$$A^* \text{ (or } A^{**}) \longrightarrow R\cdot^* + S$$

Excited molecules break down to give, most commonly, free-radicals or, sometimes, molecular products.

$$A^* \longrightarrow R\cdot + S\cdot$$

$$A^* \longrightarrow M + N$$

Gamma radiation, therefore, does not itself induce homolytic bond fission. The cobalt-60 is generally encapsulated inside a steel tube and the secondary electrons are generated by interaction of the radiation with the dense metal casing. Radical formation is caused by the interaction of the secondary electrons with the organic substrate being irradiated through the processes described above.

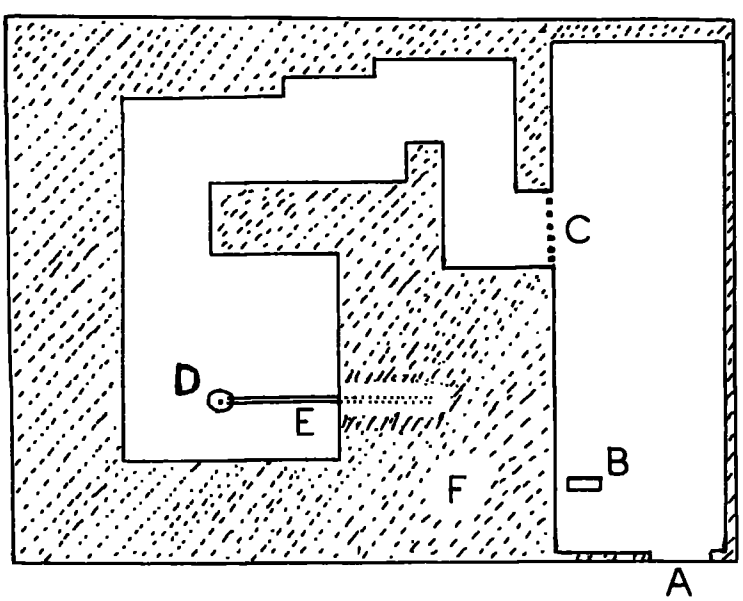
In radiation chemistry free-radical reactions tend to dominate and thus high-energy radiation is a convenient method of producing radicals for addition reactions.

II.F SOURCE FACILITY AND SAMPLE DISTRIBUTION

1. The Source

The radiation source is located in a secure dedicated building situated at a distance from the nearest regularly inhabited buildings.

Figure 2 The Irradiation Facility



KEY:

A Door

B Winding mechanism control

C Gate

D Irradiating site

E Course of steel tube

F Concrete housing

SCALE 1:100

It consists (Figure 2) of an outer room for the winding mechanism, a central lead-within-concrete block for shielding and containing the cobalt-60 when not in use ("at rest" position) and an irradiation chamber into which the source is wound on a steel hawser inside a steel tube. The building is thermostatically maintained at a constant 18°C throughout the year.

2. Safety Features

Several items combine to ensure that no risk is involved in using the source. Entry to the facility is restricted. Once entry is obtained, a locked gate (marked C in Figure 2) prevents access to the irradiation chamber. The gate is unlocked by a key which is only released when the winding mechanism has taken the source to the "rest" position. A series of alarms warn of the passage of the source hawser from the chamber to the "rest" position and vice versa. A hand-held gamma radiation detector is used before each entry to the chamber area as a final check to ensure the source has not come apart from its hawser and been left in the chamber. Each visit to the facility is recorded in a notebook provided for that purpose.

3. Sample Distribution

When the source is in the irradiation chamber it is positioned near the bottom of the steel tube (Figure 3A). A steel Carius tube

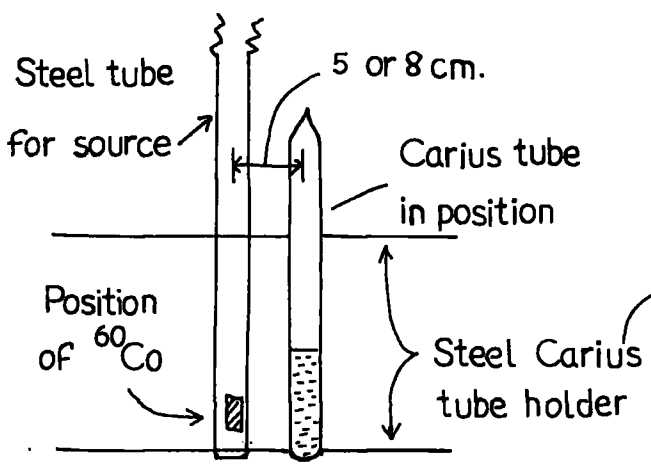


Figure 3A Vertical View

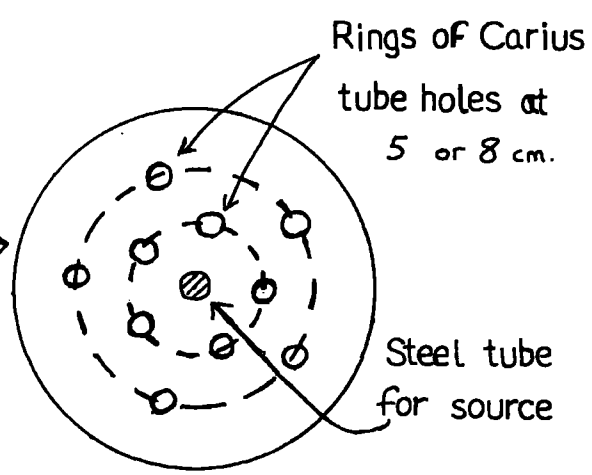


Figure 3B Horizontal View

holder (figures 3A and 3B) was manufactured and connected to the central steel tube so that the sample to be irradiated was in line with the cobalt-60. In all, up to ten Carius tube samples can thus be irradiated at once at distances of 5 and 8cm from the centre of the source steel tube to the centre of the carius tube holes (see Figure 3B). A removable heater is available for carrying out irradiations at above room temperature. It consists of an insulated heating coil wrapped around a central steel cylinder and is connected to a rheostat calibrated to provide temperatures up to 160°C. It fits between the top and bottom plates of the Carius tube holder and a steel jacket fits over the top of the tube in case of explosion occurring.

II.G DOSIMETRY

Studies involving the use of high-energy radiation require a knowledge of the amount of energy transferred to the absorbing material (usually called the dose). The unit of measure used is the rad and a dose - measured in rads - is usually called an absorbed dose.

1. Dosimeters[124,125]

The radiation dose rate was determined by two methods using lithium fluoride and Fricke dosimeters.

(a) Lithium Fluoride Dosimeter

(i) Rationale

Lithium fluoride is an example of a thermoluminescent dosimeter[126-128]. Irradiation induces defects in the material (trapped electrons and positive holes) and these defects recombine with the production of fluorescence when the irradiated solid is heated to 195°C. The absorbed dose is related to the number of fluorescence photons emitted on heating and are measured at ca. 400 nm. However the dosimeter is limited by the range over which it gives accurate results. Reproducibility is best for an absorbed dose range of 10^{-3} to 10^{5} rad[126].

(ii) Results

Lithium fluoride (in inert polytetrafluoroethene support) micro-rod dosemeters were supplied by the National Radiological Protection Board (N.R.P.B.)** for irradiation and returned to the Board for measurement of the doses absorbed. A formula (see Chapter VII, Section A.2) was obtained relating dose rate to the distance of the sample from the source. From the formula it was calculated that samples at the 5cm. positions (Figure 3B) received a dose rate of 24,360 rads/hour and at the 8cm. positions the dose rate was 8,760 rads/hour.

(b) Fricke Dosimeter[122,125]

The reaction involved in the Fricke dosimeter is the oxidation of an acid solution of ferrous sulphate to the ferric salt, in the presence of oxygen and under the influence of radiation. A sample of solution is irradiated for a measured length of time at the desired distance from the source. An ultraviolet spectrophotometer measures the amount of ferric ion formed. The absorbance at the wavelength at which ferric ion shows maximum absorption (about 304 nm.) is used. From the readings obtained it was calculated that samples at the 5cm. positions (Figure 3B) received a dose rate of 18,435 rads/hour and at the 8cm. positions the dose rate was 8,365 rads/hour.

Dosimetry by the Fricke method took place seven months after the lithium fluoride measurements. Since cobalt-60 loses 1.1% of its activity per month, the measurements at 8 cm. by the two methods are consistent while those at 5 cm. differ by about 20%. Since a quantitative measure of the dose rate is not a critical factor in the irradiations

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carried out for this thesis but only serves as a guide to an approximate absorbed dose, the dose rates obtained by the lithium fluoride method have been used throughout without correction for loss of activity by the source.

2. Absorbed Dose and Irradiation Time

A total dose absorbed of about 1 x 10^7 rad was taken as a guide for a typical sample irradiation for the purposes of comparison of results. To achieve this dose, samples were irradiated for about three weeks at the 5 cm. positions and up to six weeks at the 8 cm. positions or any combination necessary to give the desired total absorbed dose.

CHAPTER III

STEREOCHEMISTRY OF ADDITIONS TO PERFLUOROCYCLOALKENES

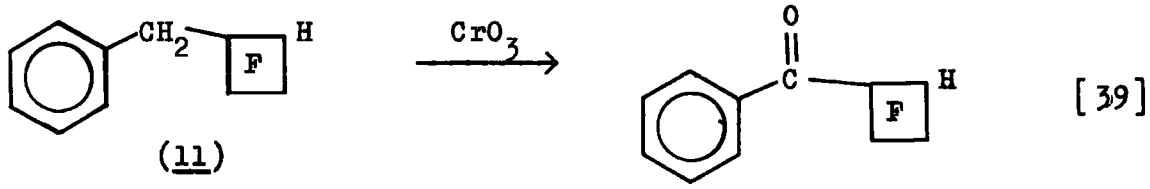
The use of gamma radiation presents a particularly easy way of initiating free-radical additions and has been used extensively by many workers[129]. In this chapter, systematic radical additions of functional hydrocarbons to the F-cycloalkenes are discussed.

III.A RESULTS

Free-radical additions to the F-cycloalkenes described by other workers are reported in Chapter I. Stereochemistry was assigned in several instances[52,54,39,85] but the conclusions reached, although reasonable, cannot be considered to be entirely unambiguous since, as will become clear, the structures of the compounds themselves were not absolutely established.

In the addition of ethanol and acetaldehyde to F-cyclobutene, assignment to the cis and trans forms was made by relating structures to vinyl derivatives which, themselves, were assigned dy dipole-moment measurements[54].

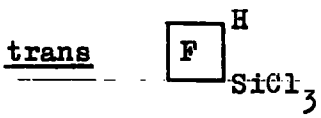
The geometric isomers of (11), formed by reaction of F-cyclobutene



(11) (66) [39]

and toluene, were assigned on the basis of the internal chemical shift values between two non-equivalent fluorine atoms of CF_2 groups[39]. Muramatsu reported[39] that the CF_2 signals for the predominant isomer of (11) were an AB multiplet and a broad singlet and for the other isomer the CF_2 signals were two AB multiplets. Now it is claimed that fluorine chemical shifts in fluorocyclobutanes can be predicted by considering

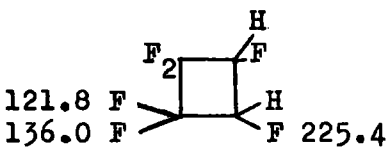
the electric-field effect of the neighbouring substituents[130]. Muramatsu therefore argued that since, in the cis-isomer, the electric-field effect of the substituents is additive on the same geminal fluorine nucleus, whereas in the trans-isomer this effect is partially compensated for, the cis-isomer should show a greater non-equivalence than does the trans-isomer. Thus the predominant isomer was assigned a trans structure. The stereochemistry of the oxidation product (66) was assigned on a similar basis and by comparison of its coupling constants and chemical shifts with those given by Haszeldine and co-workers[85] for the one-to-one adduct (44).

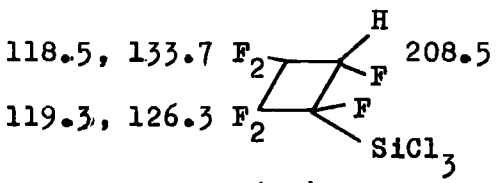


trans [85]

(44)

Addition of trichlorosilane to F-cyclobutene had been found to be stereospecific[85]. The product of catalytic hydrogenation of F-cyclobutene, cis-dihydro-F-cyclobutane[131], (chemical shifts in p.p.m. relative to $CFCl_3$ shown) was used as a model of known stereochemistry in assigning





[85]

(44)

a structure to (44). Two AB multiplets for the CF_2 groups in (44) were observed and were assigned as shown above. In each case the lower field absorption was assigned to the fluorine cis to the substituent. Haszeldine argued that since the shift of the CFH fluorine in (44) was considerably lower than in the model compound it suggested strongly that the fluorine in the CFH group of (44) had an adjacent cis-$SiCl_3$ group rather than a cis-fluorine and thus the adduct (44) had a trans configuration.

Reactions with methanol, cyclohexanol, acetaldehyde, or dimethyl ether using gamma-ray initiation at room temperature, were carried out by sealing the F-cycloalkene with excess of the reagent in a Carius tube, after careful degassing of the mixtures. For comparison, analogous reactions (except cyclohexanol) initiated by benzoyl peroxide were also carried out.

As a class, ethers (other than dimethyl ether) have been added successfully to a variety of fluoro-alkenes and -cycloalkenes (see Chapter I, Section C.1(e)). It is quite remarkable that free-radical reactions of dimethyl ether appear to be confined to patent claims in the literature[67,68] since this method provides a direct and simple route to partly fluorinated ethers of the type $R_fCH_2OCH_3$ which are otherwise difficult to prepare. One may conclude that the main consideration has been the difficulty in handling the ether (b.p. -24°C).

Yields of adducts are shown in Table 11 and no telomers were

Table 11 Additions to F-Cycloalkenes

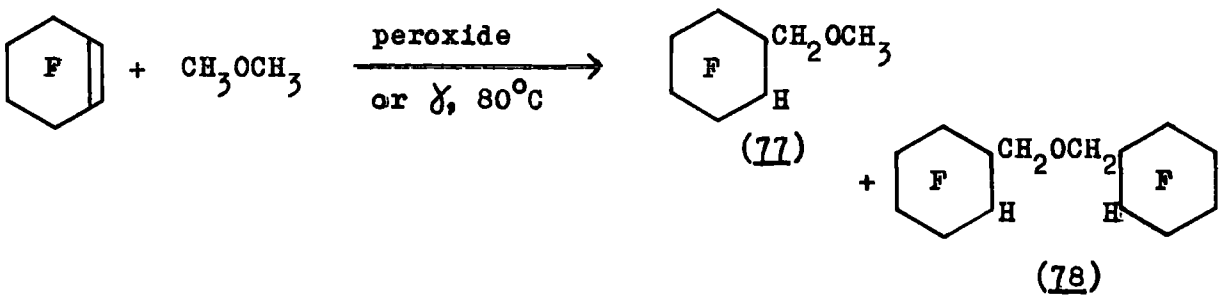
Cycloalkene		Methanol		Cyclohexanol		Acetaldehyde		Dimethyl Ether	
		% Yield	Trans/Cis	% Yield	Trans/Cis	% Yield	Trans/Cis	% Yield[c]	Trans/Cis
	(γ)[a]	85	8.7 (67)	25	3.3 (69)	67	3.4 (72)	74	8.0 (75)
	(P)	57	5.0			88	2.6	51	8.0
	(γ)	68	1.0 (17)	16	0.5 (70)	81	0.8 (73)	58	2.0 (76)
	(P)[b]	64	1.4			49	0.6	51	1.8
	(γ)	79	0.7 (68)	12	1.0 (71)	87	all-cis (74)	78	0.7 (77)
	(P)	67	0.4			89	0.05	74	0.9

a Induced by gamma-rays at room temperature.

b Induced by benzoyl peroxide at ca. 85°C.

c Yield of one-to-one adduct only.

were produced under these conditions although two-to-one adducts, e.g., (78) were formed in peroxide-initiated or high temperature irradiation (see Chapter V.B) reactions. In most cases mixtures of geometric



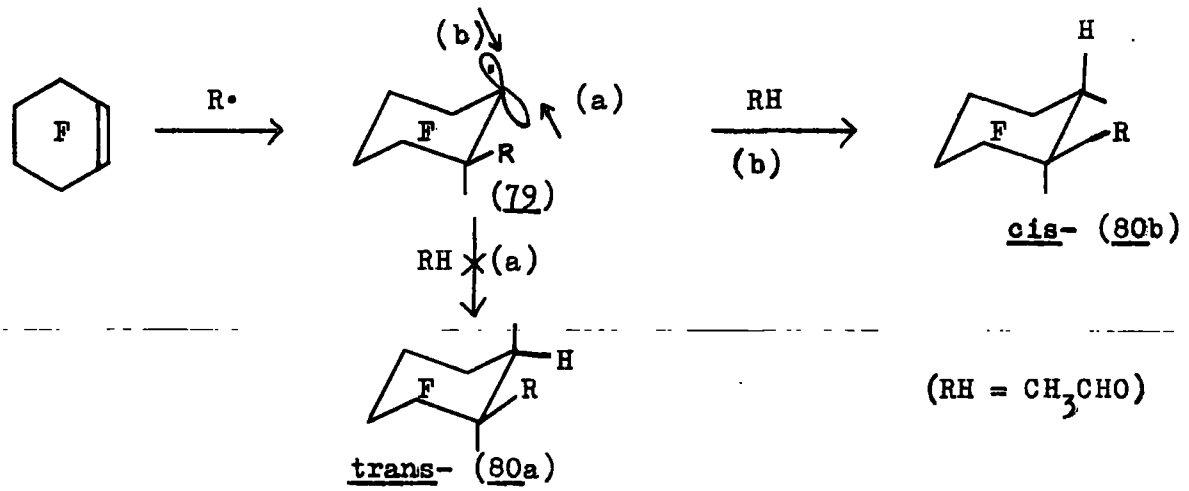
isomers were obtained and the observed ratios are indicated. Isomers of the various methanol and cyclohexanol adducts were difficult to separate; only the F-cyclobutene systems (67) and (69) could be separated by preparative-scale g.l.c. and indeed the F-cyclohexene systems (68) and (71) could only be partly resolved by analytical-scale g.l.c. In fact, isomers of (77) were unresolvable on any of the g.l.c. columns available. In contrast, isomers of the acetaldehyde adducts were readily separated by fractional distillation.

A series of separate experiments established that the isomers are not equilibrated under the conditions of preparation i.e. the product mixtures arise from kinetic control. Samples of some of the geometric isomers in excess of the functional hydrocarbon were irradiated. In every case the F-19 n.m.r. spectrum was unchanged as a result of the irradiation.

In Table 11, there is a pronounced trend, from F-cyclo-butene to -hexene, for the proportion of the cis isomer to increase and furthermore this effect is more pronounced with dimethyl ether in comparison with corresponding alcohol additions and is greatest with acetaldehyde additions. Indeed, it is remarkable that, in the gamma-ray initiated addition of acetaldehyde to F-cyclohexene, only the cis isomer of (74) is detectable. A clear cut explanation for this

stereospecific addition cannot be propounded at this stage but a possible basis for this observation can be considered.

The e.s.r. spectra of cyclohexyl radicals are consistent with rapidly interconverting chair conformers with a planar radical centre[132]. Therefore it might be anticipated that radical addition to a cyclohexene system would, in the first instance, produce an intermediate radical (79).



Approach of RH to the intermediate radical from the direction (a) or (b) could then be affected by steric effects. In the absence of any consideration of the steric effects of RH a product with a hydrogen atom in the axial position (80b) is, no doubt, preferable to the isomer (80a) with the fluorine atom in the axial position. However, there is probably a subtle competition between this effect of axial fluorine and and the preference of RH to approach (79) via (a) than (b) which would vary with the steric requirements of RH.

III.B ASSIGNMENT OF STEREOCHEMISTRY TO THE ADDUCTS

1. Analysis of F-19 N.M.R. Spectrum of (74) (In Collaboration with J.W. Emsley*).

Analysis of the ^{19}F n.m.r. data on polyfluorinated cyclic systems

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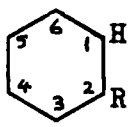
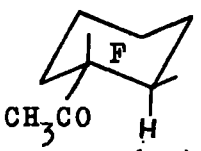
* J.W. Emsley, Department of Chemistry, The University, Southampton, SO9 5NH.

is complex but fluorinated cyclohexanes are probably the most extensively studied of the series[133-135]. Even so, adducts of the general formula (81) cannot yet be completely analysed because of the complexity that arises from the presence of large long-range spin coupling.



(81)



(74)

However, in the case of (81, R = CH_3CO), which is a single geometric isomer viz. compound (74), it is possible to effect sufficient analysis of the data to be confident that the structure is the cis-isomer, with $COCH_3$ equatorial and H axial. For simplicity, (74) is represented as an undistorted cyclohexane although, as will be argued later, this is unlikely to be the case. In the ^{19}F n.m.r. spectrum of (74) there are twelve resolved complex bands in the low field CF_2 region, a broad unresolved band from CFR at higher field, and a complex band from CFH at highest field. The bands associated with the CF_2 groups are shown in Table 12 (signals numbered with increasing field) and internuclear

Table 12 ^{19}F n.m.r. Data for the Adduct (74)

Peak[a]	δ_A[b] (p.p.m.)	δ_B (p.p.m.)	J_{AB} (Hz)
1,2a,7,8	120	134	280 ± 5
3,5,9,10	124	140	285 ± 5
2b,4,11,12	123	145	295 ± 5
6	128	128	not measurable

a $CFCOCH_3$ δ 193 p.p.m. ; CFH δ 231 p.p.m.

b Shifts relative to $CFCl_3$ calculated from values obtained from C_6F_6 as internal standard, according to the relationship $\delta_{CFCl_3} = \delta_{C_6F_6} + 163$. The spectrum was recorded in a 10% v/v solution in CCl_4.

double resonance (INDOR) experiments assigned the bands as arising from overlapping AB quartets, with a geminal coupling, $^2J_{FF}$, in the region of 280 Hz. Saturating the solution with the lanthanide shift reagent, $Yb(fod)_3$, showed that the AB quartet comprising peaks 1,2a,7,8 arise from the CF_2 at the 3-position (i.e. closest to CH_3CO), since these peaks are the most affected.

The spectrum of (74) did not change appreciably over a temperature range -100 to +100°C, indicating that the compound is essentially in a fixed conformation, in contrast to polyfluorocyclohexanes[133-135]. The CH_3CO group can therefore be assumed to be in an equatorial position. Consequently, in order to determine the structure of (74), it must be established whether the fluorine atom at the 1-position is in an axial or equatorial position. On the basis of a relationship between ^{19}F shielding and internal electric fields, Emsley[136] has suggested that the axial fluorine of a CF_2 group in polyfluorocyclohexane derivatives resonates at the lower field value, a point amply illustrated in the work of Thomas and co-workers[133,134] who examined the ^{19}F n.m.r. spectra of various polyfluorocyclohexanes. It may be assumed, therefore, that when δ_{AB} is significant then the lower field component arises from axial fluorine. In order to distinguish the position of the 1-F, the chemical shifts for this fluorine both in the axial and equatorial

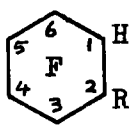
Table 13 Substituent Chemical Shifts in (81)

Substituent		Shift of F (p.p.m.)					
		1a	1e	2a	2e	3a	3e
1 R (= CF_3)	equatorial	+24		-4	-11	-2	-2
1 H	axial		+72	+4	-14	-3	+1
	equatorial	+48		-3	-11	-3	-3

position were calculated. It is probable that a substituent group R (where R = CH_2OH, c-$C_6H_{10}OH$, CH_3CO, CH_2OCH_3) will affect the neighbouring CF_2 group in a way similar to that of CF_3 and, therefore, substituent shift parameters were derived from 4H-F-methylcyclohexane[134] and are shown in Table 13. The shift parameters can then be used in calculating values for systems like (81).

The signals for CF_2 at positions 4-, 5-, and 6- are assigned, in Table 14, to give the best fit with the odserved signals but the signals due to 3a- and 3e-F, assigned by the lanthanide shift experiment, are

Table 14 Calculated and Observed ^{19}F Chemical Shifts for (81)

		Calculated		Observed
		H-equatorial	H-axial	
 (81, R = CH_3CO)	3a	117	117	120
	3e	128	132	134
	4a	119	122	124
	4e	137	140	139
	5a	121	121	121
	5e	139	143	145
	6a	119	126	128
	6e	129	126	128
	1	207	224	231
	2a	184	191	193

also very close to the calculated values. More important, there is a very clear distinction between the two possibilities for 1-F and 2-F, the experimental and calculated values for 1-H in the axial position being in very good agreement. While this work was in progress, Julien and co-workers[52] reported and examined the ^{19}F n.m.r. spectrum of (74)

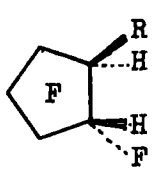
and the conclusions reached here are in accord.

2. Observed Chemical Shifts of Derivatives

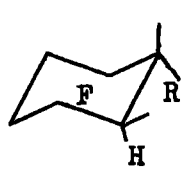
^{19}F chemical shifts are contained in Table 15 for the CFH and CFR positions for various derivatives. For the cyclohexane adducts, there is a very good correlation between these observed and the calculated values contained in Table 14, which adds further weight to the process. However, what is surprising is that there is a remarkable similarity between corresponding chemical shifts for the whole series of adducts and it is this method that is advanced as a simple way of assigning these geometric isomers. One can have confidence in the cyclohexene series because of the partial analysis of ^{19}F n.m.r. data, already described and the structures of the adducts (72) of acetaldehyde to F-cyclobutene have been assigned[54] on the basis of dipole-moment measurements. Since two extremes of the series can be accepted with confidence, it seems reasonable to accept the method also, for the cyclopentane derivatives.

3. Conclusions

It is quite surprising , perhaps, that the chemical shifts for CFH and CFR, contained in Table 15, are so close for the three types of system. The stereochemical relationship of groups in e.g. a cis derivative (83) of cyclopentane would normally be quite different from



(83)



(84)

the relationship of these groups in a corresponding cyclohexane (84). Nevertheless it is quite likely that, in the highly fluorinated derivatives corresponding to (83) and (84), considerable distortion takes place to minimise the eclipsing of C-F bonds in derivatives of (83) and to

Table 15 ^{19}F N.M.R. Data for CFR and CFH Positions in the Adducts

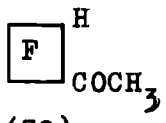
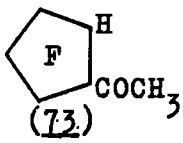
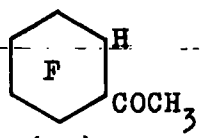
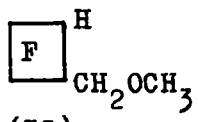
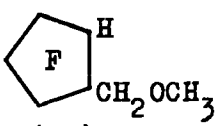
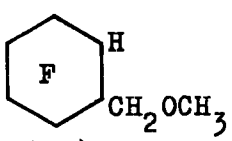
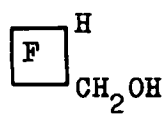
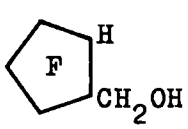
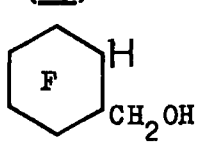
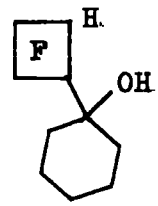
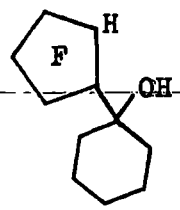
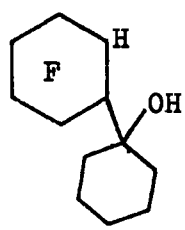
Adduct	Trans				Cis			
	B.p. (°C)	G.l.c.[a]	^{19}F δ[b]		B.p. (°C)	G.l.c.[a]	^{19}F δ[b]	
			CFR	CFH			CFR	CFH
 (72)	116	2	173	215	100	1	197	223
 (73)	128	2	174	216	112	1	191	228
 (74)	143	2	176	215	128	1	193	231
 (75)	106	1	181	220	124	2	198	222
 (76)	121	1	181	212	127	2	193	227
 (77)	c	d	187	211	c	d	194	234
 (67)	128	1	183	220	141	2	199	225
 (17)	139	1	181	214	c	2	196	226
 (68)	c	1	189	210	c	2	195	232

Table 15 continued....

Adduct	Trans				Cis			
	B.p. (°C)	G.l.c.[a]	^{19}F [b]		B.p. (°C)	G.l.c.[a]	^{19}F [b]	
			CFR	CFH			CFR	CFH
 (69)	196	1	169	214	m.p.54	2	195	221
 (70)	c	1	177	208	c	2	190	219
 (71)	c	1	187	208	c	2	195	226

a Order of elution from column Z.

b P.p.m., measured from $CFCl_3$ as external reference, positive shifts to high field.

c Pure sample of the isomer could not be obtained.

d Unresolved on all available g.l.c. columns.

minimise 1,3-interactions in (84). The resultant of these distortions is likely to be a much closer angular relationship of groups in the cyclohexane derivatives in comparison with corresponding cyclopentane or cyclobutane derivatives than is normally the case.

Boiling points and order of g.l.c. retention times (Table 15) for

alcohol and dimethyl ether adducts are in the expected order with cis isomers having higher boiling points and longer retention times. The acetaldehyde adducts also give a consistent series but in this case, the trans isomers give the higher boiling points and longer retention times. Clearly, these physical properties are a useful guide in relating stereochemistry within a series but are not useful between different series.

III.C RESOLUTION OF ENANTIOMERS

Corroborative evidence for the correlation of geometric isomer structure and ^{19}F n.m.r. chemical shifts would, of course, be desirable. Agreement between the results obtained from an X-ray structure analysis of one of the geometric isomers and the structure predicted by the ^{19}F n.m.r. method developed above would be indisputable confirmation.

However, the alcohols, ketones, and ethers prepared (Table 15) are generally liquids at room temperature; only the trans isomer of (74) and the cyclohexanol mixtures of isomers are low melting point solids and thus would not remain as integral crystals while an X-ray study was in progress.

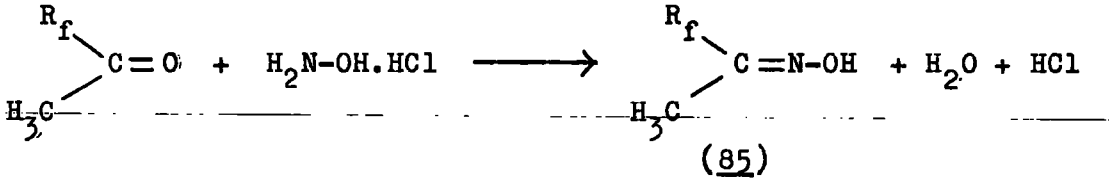
1. Preparation of a Solid Derivative

Ethers are comparatively unreactive as far as functional compounds are concerned[137]. The ether linkage is quite stable toward bases, oxidizing agents, and reducing agents; acid cleavage takes place only under vigo rous conditions to yield alkyl halides which are unlikely to be stable solid compounds.

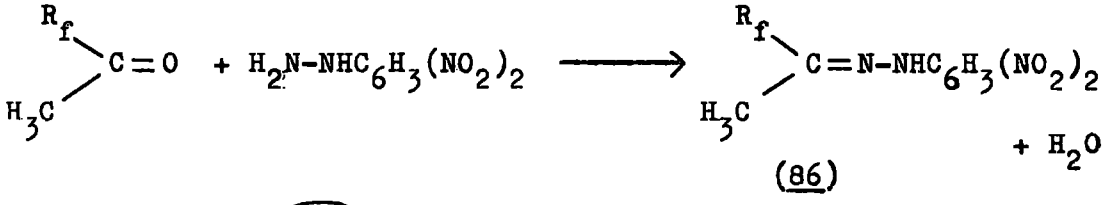
Conversion of alcohols is, in theory, more attractive but difficulty arises from the necessity for a reasonable quantity of a single geometric isomer: the alcohol isomers ars difficult to separate even using preparative-scale g.l.c.

The isomeric methyl ketones, easily separable by fractional

distillation, contain the carbonyl group which is convenient for chemical conversion. Nucleophilic addition of ammonia derivatives to carbonyl compounds has long been used as a convenient method for giving solid products as a means of identification of the initial aldehyde or ketone. Thus, as will be seen in Chapter VI, the polyfluorocycloalkyl methyl ketones were systematically reacted with hydroxylamine hydrochloride and 2,4-dinitrophenylhydrazine to give the corresponding oximes (85) and 2,4-dinitrophenylhydrozones (86) respectively. The oximes (85), although in general crystalline solids, defeated the object



(85)



(86)

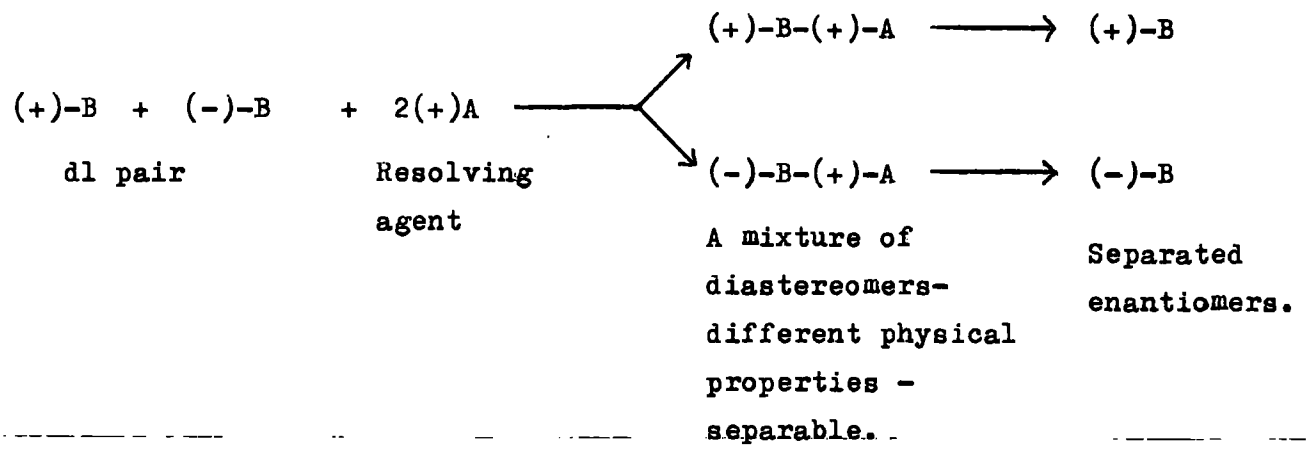
R_f = $(CF_2)_n$ CFH / CF- n = 2,3,4. cis or trans

of the exercise by exhibiting a tendency to sublime readily. The derivatives (86) were stable, high melting point crystalline solids. However, the starting material (74) consists of a pair of enantiomers. In order to obtain interpretable X-ray data, a single enantiomer must be available.

2. Optical Resolution

The most generally applicable way to effect the separation of a racemic modification (a dl pair) is to allow it to react with a dissymmetric reagent (a resolving agent). This will convert the two enantiomers into two diastereomers which can then be separated by

conventional techniques by virtue of their different physical properties. The separated diastereomers can be decomposed by appropriate chemical reagents to liberate the individual enantiomers. The general sequence is illustrated by the following equation:



(a) Formation of Diastereomers

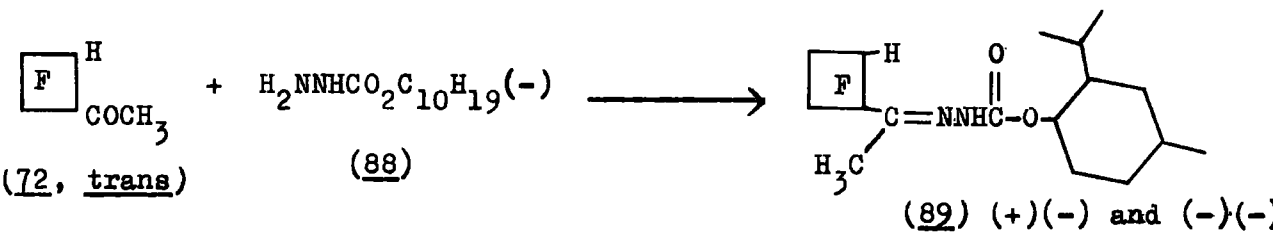
(i) The use of (-)-menthydrazide (88)

The resolution of racemic carbonyl compounds is usually attempted using optically active hydrazine derivatives. In attempting to resolve 1-bromo-1-chloro-1-fluoroacetone, Hargreaves and Modarai[138] found that the well known carbonyl resolving agents 5-(α-phenylethyl) semioxamazide[139] and tartramic acid hydrazide[140] did not react with the halogeno-ketone under all conditions tried. In contrast, the ketone reacted smoothly with (-)-menthyl N-aminocarbamate "(-)-menthydrazide" (88)[141]. This reagent (88) was thus prepared[141] and used in an attempt to resolve a dl pair of one of the geometric isomers of the methyl ketones (72), (73) or (74) since it would be reasonable to expect these compounds (general form R_fCOCH_3) to behave in a similar manner to 1-bromo-1-chloro-1-fluoroacetone (form R_xCOCH_3).

As the ^{19}F n.m.r. data on (74,cis) has been investigated most completely, this geometric isomer was chosen for attempted resolution. However, this compound did not give the expected solid derivative with

(-)-menthydrazide even under quite vigorous reaction conditions. This lack of reaction can be attributed to the steric effect of the cyclohexyl ring.

In contrast, (72,trans) reacted smoothly with (88) under relatively mild conditions to give a good yield of the corresponding diastereomeric (-)-menthydrazones (89) as a white powder.



(ii) Attempted diastereomer separation

- Fractional crystallisation

A range of techniques were tried in an attempt to separate the menthydrazones (89). Fractional crystallisation has been used successfully by other workers[138,141]. However, after three recrystallisations from aqueous alcohol no change in the specific rotation resulted ($[\alpha]_D^{20}$ = -52.7°). A similar observation was noted after two recrystallisations from toluene. Cyclohexane, carbon tetrachloride, and benzene did not affect the rotation value. It was found that, for all the solvents mentioned above, a crystalline material could not be obtained: only an amorphous powder was recovered in each case

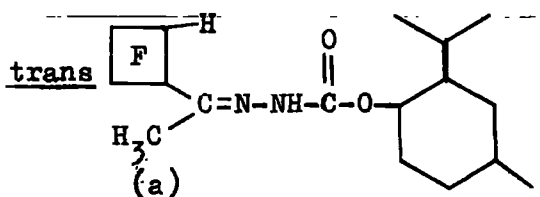
- T.l.c. and h.p.l.c.

Long (15 cm.) thin layer chromatography plates were used in an attempt to observe at least partial separation of the diastereomers. Various solvents selected from the eluotropic series and solvent systems were employed. Generally one spot only was observed under both long (366 nm.) and short (254 nm.) wavelength ultraviolet light although the spot shape changed slightly in some cases on changing the wavelength. Addition of ammonia to the solvent systems caused some decomposition.

Analytical-scale high pressure liquid chromatography (h.p.l.c.), a technique developed for the analysis of solid samples in the same way as g.l.c. is used for liquid and gas samples, was unable to detect more than a single component. Use of two different column packings and a variety of solvent systems failed to give observable partial resolution.

(iii) Effect of chemical shift reagents

As a possible alternative to g.l.c. or h.p.l.c. for following the effect of successive recrystallisations on the diastereomer resolution, the use of chemical shift reagents was investigated. In principle, if a mixture of compounds (89) is present, addition of a chemical shift



(89)

reagent should affect the n.m.r. signals of each diastereomer slightly differently. Thus the ^{1}H n.m.r. singlet due to the methyl group [marked (a) above] should appear as a doublet - one part due to each compound. As resolution is achieved, one part of the doublet signal is reduced in intensity. It was found that the reagents Eud_3 (for downfield shifts away from TMS) and Prd_3 (for upfield shifts towards TMS) did not produce the desired splitting.

(b) Alternative Means of Resolution

If an optically active amine bisulphite were allowed to react with a racemic ketone, it is apparent that the product would be a mixture of four stereoisomers since a new asymmetric carbon holding the hydroxyl group would be introduced. Whether or not all four isomers are formed

$$\underset{\text{dl}}{R_fCOCH_3} + \underset{\text{d or l}}{RNH_3SO_3H} \longrightarrow \underset{\text{dl dl}}{R_fCHOHSO_3H_3NR}\ \underset{\text{d or l}}{}$$

is of minor significance since the success in resolution will depend on the ease of isolation of a single optically pure product.

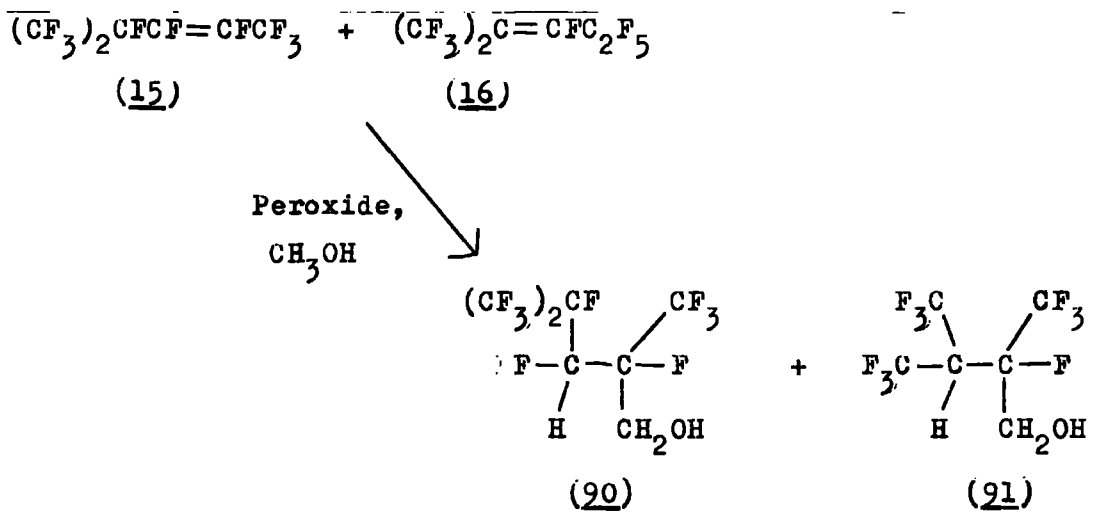
The amine hydrogen sulphite, prepared from (-)-1-phenyl ethylamine[142], however, gave only a white paste with (74,cis) which was not investigated further.

CHAPTER IV

ADDITIONS TO OTHER UNSATURATED FLUOROCARBONS

The free-radical chemistry of non-terminal F-alkenes and in particular tetra-F-alkylated ethenes has, in general, not been investigated.

Previously reported radical additions to non-terminal F-alkenes, other than polyfluorocycloalkenes, have been largely restricted to reactions with halogens and hydrogen halides[78-83], although Ishikawa and co-workers[49] have described the addition of methanol and acetaldehyde to F-propene dimer. The dimer, a mixture of (15) and (16), reacted in



[49]

the presence of benzoyl peroxide. With methanol, three polyfluoroalcohols were formed, giving (91) and the erythro and threo forms of (90) in the ratio 1:2:2 and with acetaldehyde, three polyfluoroketones were produced.

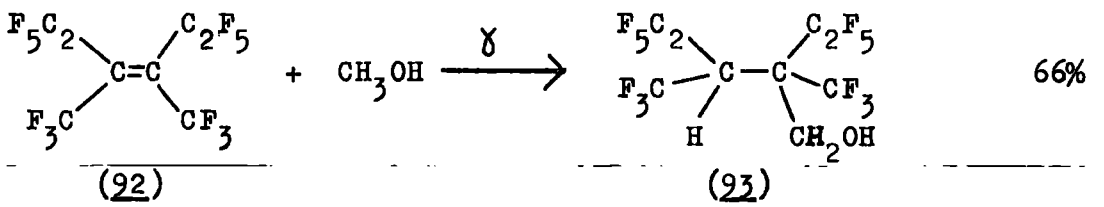
In this chapter, free-radical reactions of several readily available tetra-F-alkyl ethenes and the acetylene, F-2-butyne, are discussed. Additions of the functional hydrocarbons to F-2,3-dimethyl buta-1,3-diene are also described.

IV.A ALCOHOLS

1. Methanol

(a) F-3,4-dimethyl hex-3-ene (92)

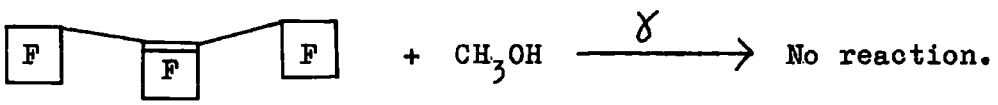
It is well known that (92), the tetramer of F-ethene, is unreactive towards neutral methanol even under vigorous conditions[143,144]. Thus, nucleophilic attack will not occur unless there is base present[144]. Under gamma-ray initiation, (92) reacted readily with methanol to give the corresponding one-to-one adduct (93) in good yield.



(92) (93)

(b) F-1,2-bis(cyclobutyl)cyclobutene[145-147]

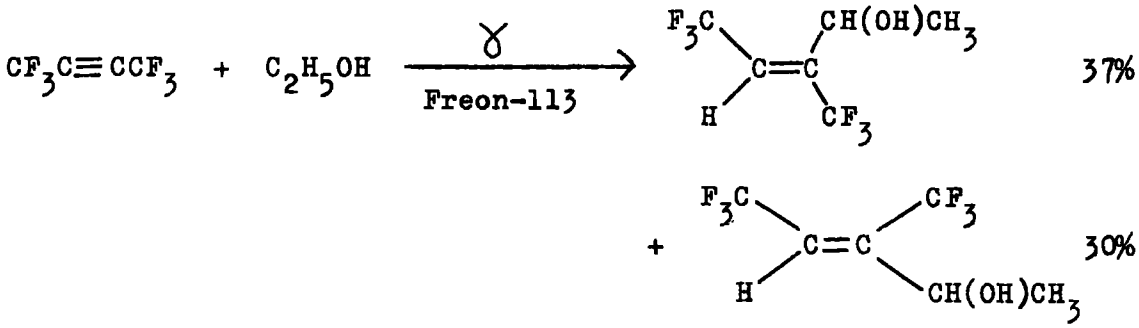
The trimer, obtained by pyridine-induced oligomerisation of F-cyclobutene, failed to react significantly with methanol. Although the



reactants are immiscible, the same is true for (92) plus methanol; the latter reacts readily and so it is unclear whether a solvent effect is the cause of the lack of reaction. The F-cyclobutyl substituents are perhaps causing steric hindrance.

(c) F-2-butyne

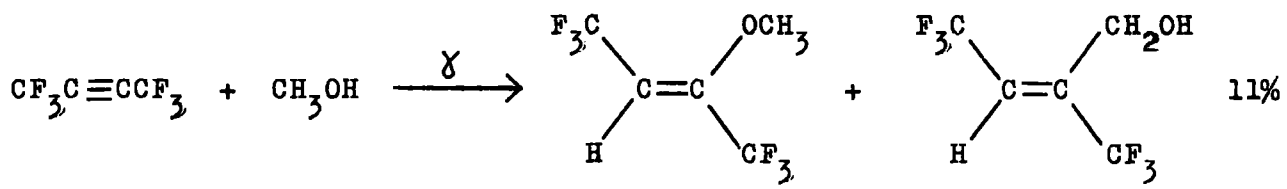
Radical additions to fluorinated acetylenes are known[148] but are confined to reactions of compounds with a relatively weak bond viz., the halogens, hydrogen bromide, polyhaloalkyl iodides and hydrogen sulphide. To date only one report of a radical addition of a functional hydrocarbon to F-2-butyne has appeared in the literature[149]. In a patent claim, Muramatsu[149] described the radiation-induced addition of



[149]

ethanol to F-2-butyne. Using Freon-113 (1,1,2-trichloro-trifluoroethane) as a solvent, a good yield of the cis and trans one-to-one adducts (shown above) was obtained.

A low yield of the one-to-one adduct (95) was obtained in the reaction of F-2-butyne and methanol; the main product was (94) which results from nucleophilic addition of the alcohol. No solvent was used.



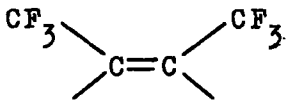
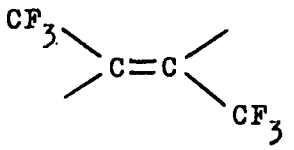
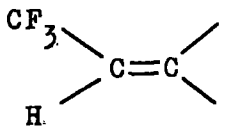
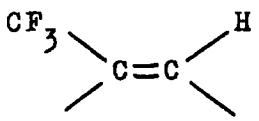
(94) (95)

(i) Structural assignments

Compound (94) is a known compound[150] and was identified by comparison of its infra-red and n.m.r. with authentic spectra[150]. The assignment of a trans structure to (95) was made on the basis of well-established n.m.r. coupling constants[150-152]. The ranges of various CF_3 coupling constants are shown in Table 16 overleaf.

The ^{19}F n.m.r. signals due to (95) are sharp multiplets and the largest coupling measured was J = 8Hz, arising from geminal H-CF_3 coupling. By inspection of Table 16, this immediately rules out the possibility of two cis CF_3 groups and the only alternative is the structure assigned (95).

Table 16 Characteristic CF_3 Coupling Constants[150-152]

	J = 11 - 13 Hz
	J = 1 - 2 Hz
	J = 7 - 9 Hz
	J = 0 - 2 Hz

(d) F-2,3-dimethyl buta-1,3-diene[143,153]

It was found that nucleophilic addition and substitution were preferred over radical reaction[143].

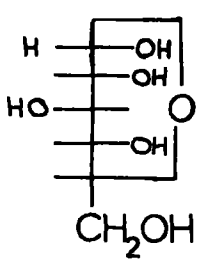
2. Other Alcohols

(a) Ethanol and Cyclohexanol

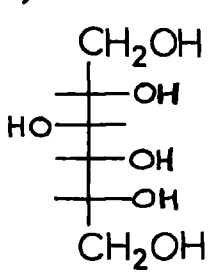
Attempted radical additions of these alcohols to F-ethene tetramer (92) were unsuccessful. This was probably due to the steric interaction of the bulky hydroxyalkyl radicals with the F-alkyl substituents on the alkene.

(b) Glucose and Sorbitol

Both the monosaccharides, glucose, and its reduction product sorbitol,



D-(+)-glucose



Sorbitol

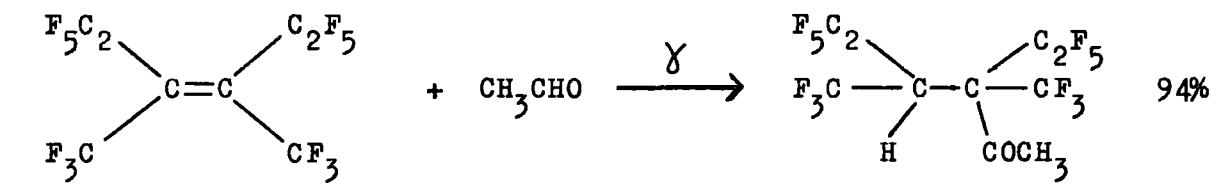
can be considered to be alcohols of the form RCH_2OH. As such they might be expected to react in a similar manner to other primary alcohols with an F-alkene, under free-radical conditions, to give fluorine-containing sugar molecules which would have novel and potentially useful properties.

However, a simple mixture of solid glucose and F-propene did not react. Further, solutions of each sugar in dimethyl sulphoxide did not react with F-propene, even on heating.

IV.B ACETALDEHYDE

1. F-3,4-dimethyl hex-3-ene(92)

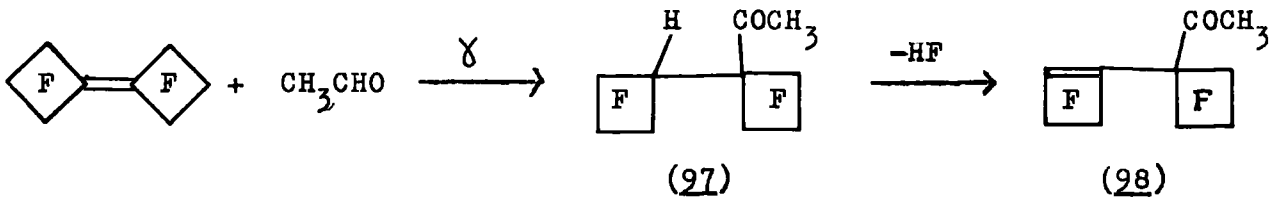
Under gamma-ray initiation, acetaldehyde reacted readily with (92) to give the one-to-one adduct (96) in excellent yield. Compound (96) undergoes a fascinating cyclisation in the presence of base (see Chapter VI).



(92) (96)

2. F-bicyclobutylidene[145-147]

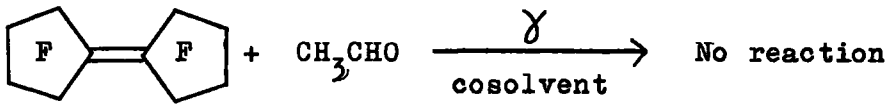
The symmetrical dimer reacted rapidly with acetaldehyde to give the corresponding one-to-one adduct (97) which was only observed before opening the reaction vessel (a Pyrex n.m.r. tube). The compound (97) was not isolated: it eliminated hydrogen fluoride in the process of being separated by preparative-scale g.l.c., (98) being recovered and identified spectroscopically.



(97) (98)

3. F-bicyclopentylidene[154]

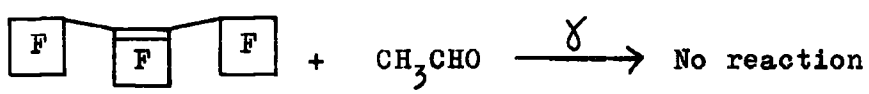
In contrast to the facility of the previous reaction, this symmetrical dimer failed to react with acetaldehyde. Addition of a cosolvent did not change the situation. The reactivity of



F-bicyclobutylidene has been attributed to the relief of ring-strain resulting from removal of the double bond[145]. No such ring-strain exists in F-bicyclopentylidene and thus the driving force for reaction is absent.

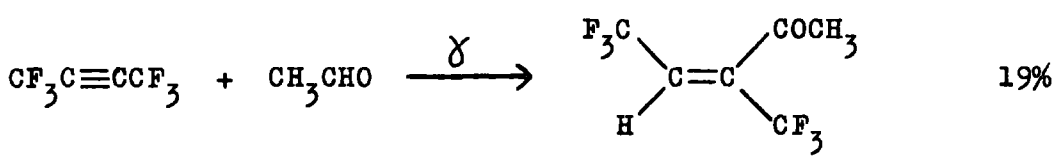
4. F-1,2-bis(cyclobutyl)cyclobutene

There was no reaction between the trimer and acetaldehyde. It is likely that the F-cyclobutyl substituents are causing steric hindrance to the approach of the acyl radical.



5. F-2-butyne

In the absence of competing nucleophilic reactions, only radical addition can occur between acetaldehyde and F-2-butyne. A modest yield of product was obtained and identified as the one-to-one adduct (99)

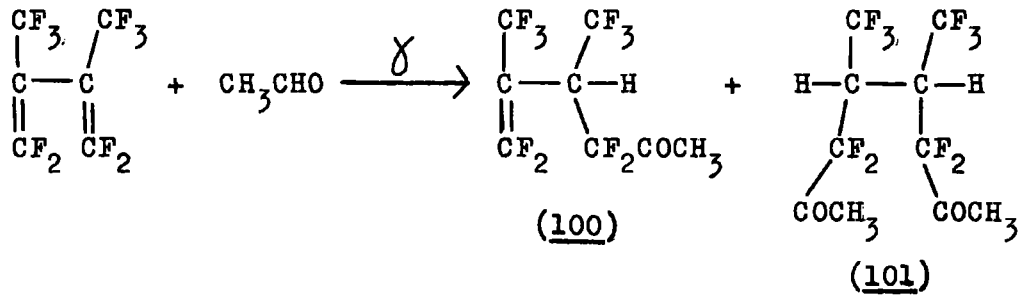


(99)

with the CF_3 groups trans to each other. The trans assignment was made, as in Section A.1(c), on the basis of the relative magnitudes of n.m.r. coupling constants (Table 16). For compound (99), the largest coupling measured was J = 7.5 Hz, corresponding to the geminal H-CF_3 coupling, which rules out a structure with cis CF_3 groups.

6. F-2,3-dimethyl buta-1,3-diene

The diene reacted readily with acetaldehyde to give equal amounts of the products (100) and (101) arising from addition across one and both double bonds respectively. There was no evidence for an adduct arising from 1,4 addition to the diene.



(100)

(101)

Successful radical addition to the diene is, perhaps, unexpected since other workers have found that attempted radical bromination of the diene did not occur[143,155].

IV.C DIMETHYL ETHER

The reactions of dimethyl ether with a range of fluoroalkenes are summarised in Table 17.

It is noteworthy that when tetra-F-alkylated ethenes were used they tended to give the two-to-one adduct rather than the one-to-one adducts. In fact, compounds (109) and (110) were the only products when using F-ethene tetramer (92) and F-bicyclopentylidene respectively.

Muramatsu and co-workers[68] determined that formation of the two-to-one adduct involved an intramolecular hydrogen atom transfer rather than successive addition of two molecules of fluoroalkene. They found that, in the addition of F-propene to diethyl ether, the ratio of the two-to-one to the one-to-one adduct was independent of irradiation time, being almost constant if the alkene/ether ratio was kept constant. Further, the adduct ratio was found to increase with increasing the alkene/ether ratio.

Table 17 Radical Additions of Fluoroalkenes to Dimethyl Ether

$$CF_2{=}CF_2 + CH_3OCH_3 \xrightarrow{\gamma} H(CF_2CF_2)_nCH_2OCH_3 \quad (102) \quad n = 1,2,3. \quad + \text{higher telomers}$$

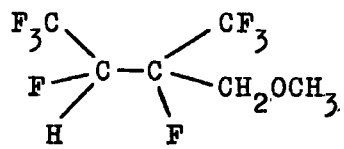
$$CFCl{=}CF_2 + CH_3OCH_3 \xrightarrow{\gamma} H(CFClCF_2)_nCH_2OCH_3 \quad + \text{higher telomers}$$

(103) n = 1

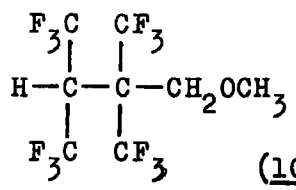
(104) n = 2

$$CF_3CF{=}CF_2 + CH_3OCH_3 \xrightarrow[\text{Peroxide}]{\gamma \text{ OR}} CF_3CFHCF_2CH_2OCH_3 \quad (105) \quad 59 - 68\% \quad [66,67]$$

$$CF_3CF{=}CFCF_3 + CH_3OCH_3 \xrightarrow{\gamma} \quad (106) \quad 30\%$$

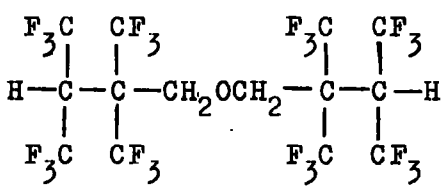


$$\text{(CF}_3\text{)}_2\text{C=C(CF}_3\text{)}_2 + CH_3OCH_3 \xrightarrow{\gamma}$$



(107)

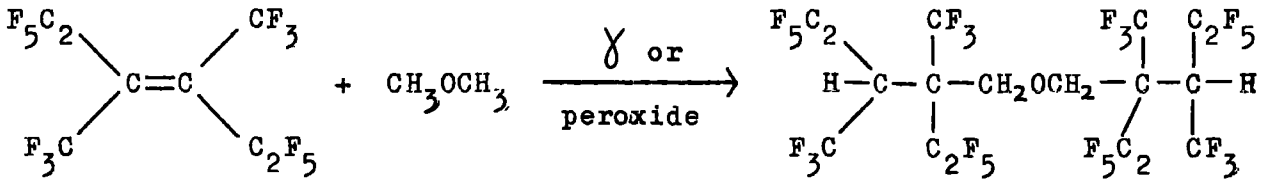
+



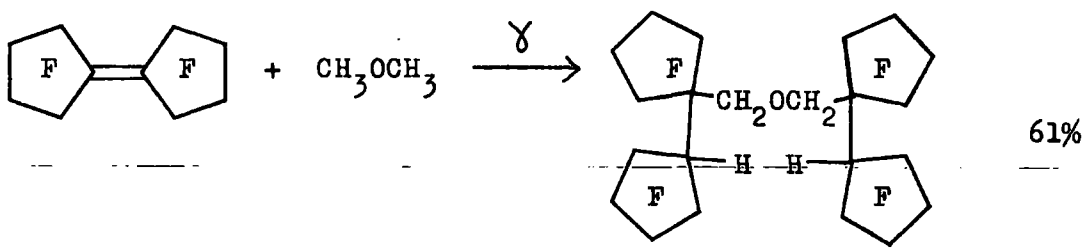
(108)

Continued....

Table 17 Continued....

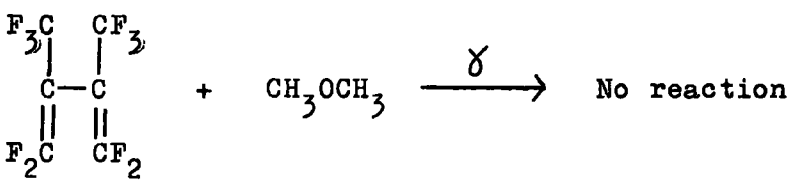


(92) (109) 21-28%

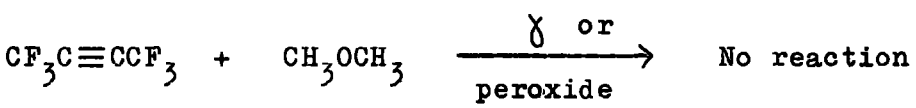


61%

(110)



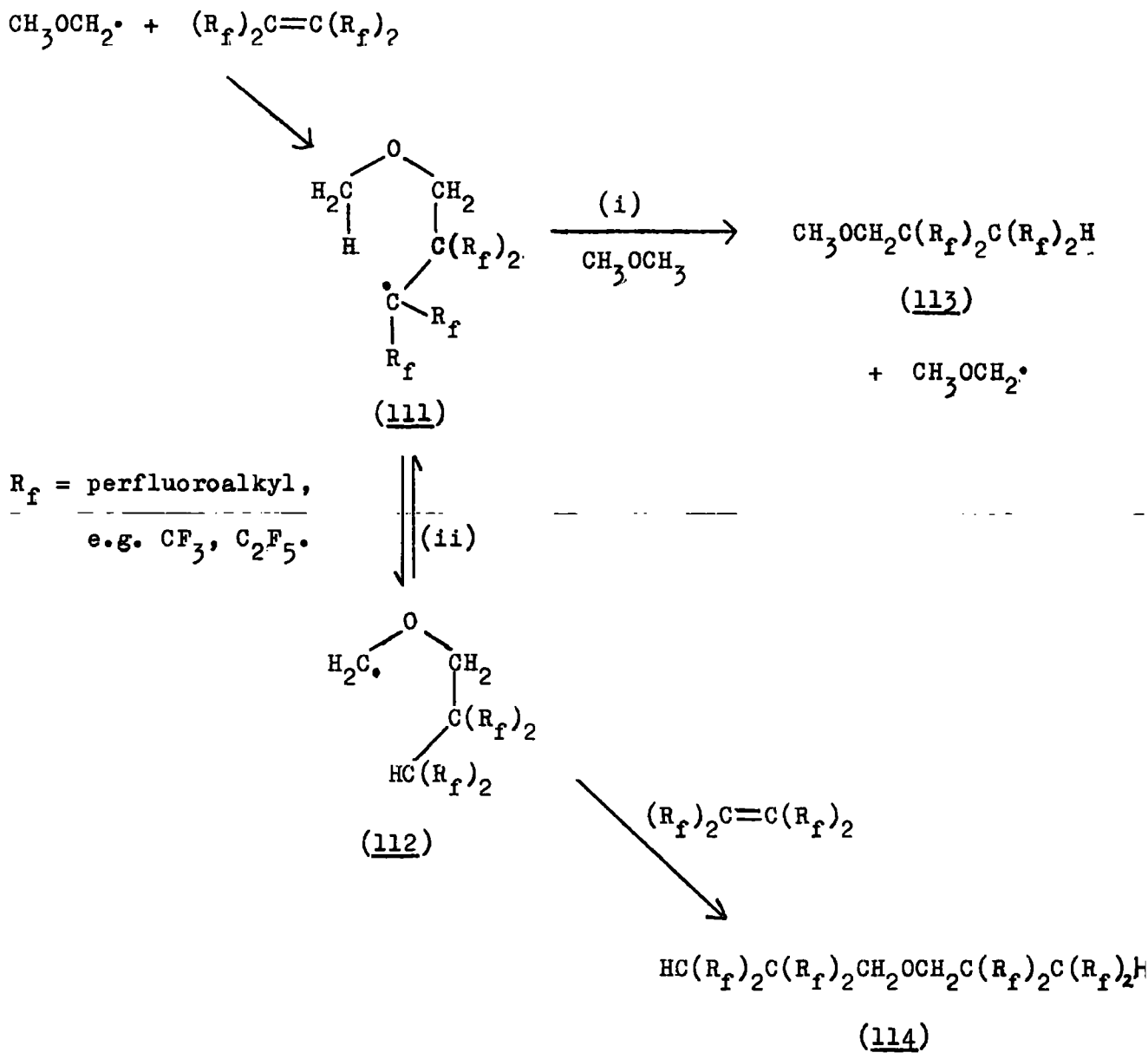
No reaction



No reaction

A process similar to that described by Muramatsu[68] is shown in Scheme 1 overleaf to account for the two-to-one adduct (114). For one-to-one addition, the intermediate radical (111) abstracts a hydrogen atom from dimethyl ether to give the product (113). For rearrangement to occur, radical (111) must be in equilibrium with radical (112) which then adds to a second molecule of alkene to give the two-to-one adduct

Scheme 1

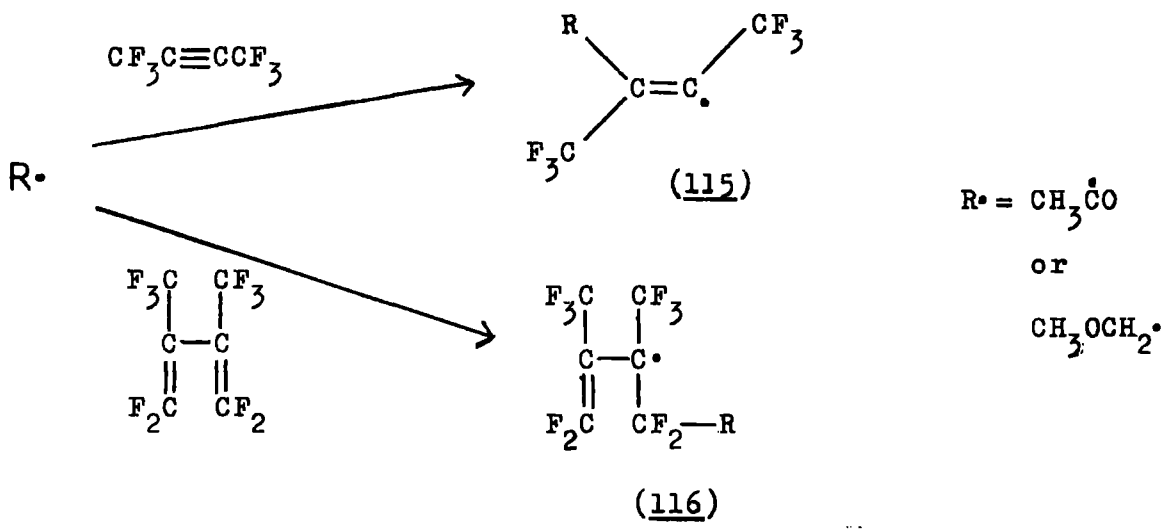


(114). Normally reaction proceeds via path (i) but it is clear that the presence of two perfluoroalkyl groups in (111) stabilise the radical sufficiently for it to rearrange via path (ii). At the moment it is unclear which factors control the balance between paths (i) and (ii).

As expected with easily telomerised alkenes[156], a range of telomers was obtained from radiation-induced addition to both F-ethene and

chlorotrifluoroethene. The low telomers (102) were identified by their mass spectrum fragmentation patterns whereas (103) and (104) were isolated and characterised. Addition of dimethyl ether to F-propene gave (105) which has been reported previously in the patent literature[66,67]. Of the tetra-F-alkyl ethenes, only F-2,3-dimethyl but-2-ene[143,157] gave both the one-to-one (107) and two-to-one (108) adducts. These products were formed in equimolar proportions.

It is uncertain why F-2-butyne and the diene did not give adducts. Certainly from the results displayed in Table 17, it is obvious that the first step in the radical chain addition reaction is occurring viz., dimethyl ether forms radicals quite readily. Now acetaldehyde has been shown to give adducts with both these fluorocarbons, so addition of the radical to the fluorocarbon can be considered to be taking place to give (115) and (116). Thus, it is likely that there is some subtle



difference between the intermediate radicals (115) and (116) which, for the case of R = CH_3CO, allows chain propagation to proceed, but for the case of R = CH_3OCH_2, inhibits chain propagation. At the present time, the nature of the difference is unclear but could be a polar effect.

1. Structural Assignments

Satisfactory elemental analysis was obtained for the one-to-one

adducts which were isolated (other than (107)), as well as for the two-to-one adducts. The methyl ethers had characteristic ^{1}H n.m.r. spectra, with a sharp singlet due to the methoxy protons at around 3.5-3.8 p.p.m. Of course, the methylene and tertiary protons were further shifted downfield, to around 4.0 and 5.3 p.p.m. respectively.

It can be seen from inspection of the structures of the two-to-one adducts (Table 17) that their ^{1}H n.m.r. spectra would be expected to be substantially different from that of the one-to-one adducts. Indeed, one observes, in all of them, a single signal at around 4.5 p.p.m. due to the methylene group. In compound (108), the tertiary proton signal can be shifted from underneath this resonance by using a dilute solution of the compound but for (109) and (110) this does not work. Further, the ^{19}F n.m.r. spectra of the two-to-one adducts are all relatively simple, due to the symmetry of the molecules and a minimum of signals is observed.

CHAPTER V

INVESTIGATION OF SUBSTITUENT EFFECTS ON CARBON-HYDROGEN BOND REACTIVITY - A PRELIMINARY STUDY

In Chapters III and IV of this thesis the addition of some alcohols, acetaldehyde, and dimethyl ether to unsaturated fluorocarbons were described. It is clear that these functional hydrocarbons react readily under free-radical conditions. Thus it can be concluded that the substituent functional group in these molecules activates the carbon-hydrogen bond. Further, the derived α-hydroxyalkyl, acyl and methoxymethyl radicals (shown below) are then able to add readily to

$\cdot CH_2OH$ $\cdot COCH_3$ $\cdot CH_2OCH_3$

fluoroalkenes and initiate a rapid chain addition reaction.

In this chapter, the effect of a substituent 'X' on the reactivity of the nearest carbon-hydrogen bond in the functional molecule is examined.

V.A THE EFFECT OF SUBSTITUENTS 'X' ON THE REACTIVITY OF THE METHYLENE GROUP IN COMPOUNDS OF THE TYPE $X-CH_2OCH_3$

It is well established that a secondary C-H bond is broken more easily than a primary C-H bond[158] - the greater number of substituents weaken the secondary bond and also serve to stabilise the resultant radical. In recent years the concept of the stabilisation of radicals by simultaneous conjugation with electron donor and acceptor groups has been developed by several authors[159-162]. Terms like "push-pull substitution"[159,160] and "merostabilisation"[161] have been superceded by "capto-dative substitution"[162] to describe this effect. Essentially the stabilisation of radicals (117) (shown over) from otherwise easily

(117)

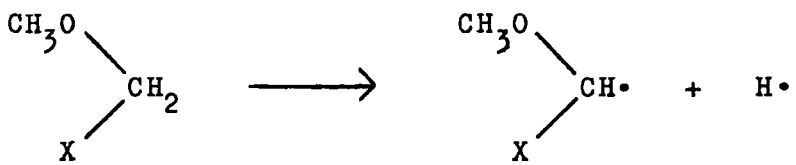
M = Donor, e.g. $-SCH_3$

N = Acceptor, e.g. -CN

polymerised alkenes is explained by the effect of the donor and the acceptor substituents and (117) proceeds to dimerise or combine with R• rather than polymerise.

This theory can be tested further by considering compounds of the type $X-CH_2OCH_3$ and the products resulting from reaction of them with an F-alkene. Already a donor group (CH_3O) is present and product type should depend on the nature of X. Reactions of compounds $X-CH_2OCH_3$ are summarized in Table 18 and the substituents X are classified in Table 19 into activating and deactivating groups according to whether or not reaction occurred at the CH_2 site.

It is clear from the results that the substituent X affects the



(117')

reactivity of radical (117') but it is also apparent that when X is an acceptor type group e.g., phenyl, polyfluorocyclohexyl, there is deactivation since only starting materials are recovered.

Thus, formation of radical (117') is reversible and recombination with H• occurs in preference to dimerisation. Further, inhibition of reaction of (117') with the F-alkene can be explained by considering that the electron-withdrawing substituent is causing the radical to become more electrophilic: addition of an electrophilic radical to an

Table 18 Radical Additions to $X-CH_2OCH_3$

X = H

$$CH_3OCH_3 + C_3F_6 \xrightarrow[\text{or Peroxide}^d]{\gamma\text{, R.T.}^c} CF_3CFHCF_2CH_2OCH_3 \quad (105) \quad 59\text{-}68\%^a$$

X = CH_3O

$$CH_3OCH_2OCH_3 + C_3F_6 \xrightarrow{\gamma\text{, R.T.}} {}^*R_fCH_2OCH_2OCH_3 \quad (118) \quad 66\%^b$$

$$+ \; R_fCH_2OCHR_fOCH_3 \quad (119) \quad 18\%$$

$$+ \; R_fCH_2OCH_2OCH_2R_f \quad (120) \quad 16\%$$

$^*R_f = CF_3CFHCF_2-$

X = CH_3OCH_2

$$CH_3OCH_2CH_2OCH_3 + C_3F_6 \xrightarrow{\gamma\text{, R.T.}} CH_3OCHR_f^*CH_2OCH_3 \quad (121) \quad 53\%^a$$

$$+ \; R_fCH_2OCH_2CH_2OCH_3 \quad (122) \quad 47\%$$

$$+ \; R_fCH_2OCHR_fCH_2OCH_3 \quad (123)$$

$$+ \; R_fCH_2OCH_2CHR_fOCH_3 \quad (124)$$

} minor components

$^*R_f = CF_3CFHCF_2-$

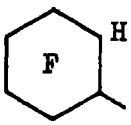
X = $HOCH_2$

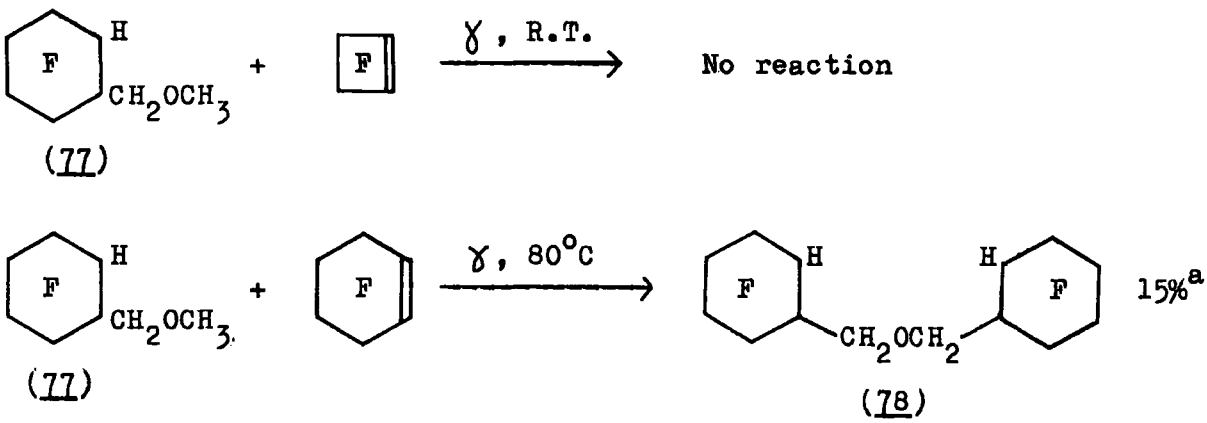
$$HOCH_2CH_2OCH_3 + C_3F_6 \xrightarrow{\gamma\text{, R.T.}} HOCHR_f^*CH_2OCH_3 \quad (125) \quad 34\%^b$$

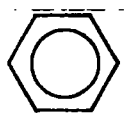
$$+ \; HOCH_2CHR_fOCH_3 \quad (126) \quad 33\%$$

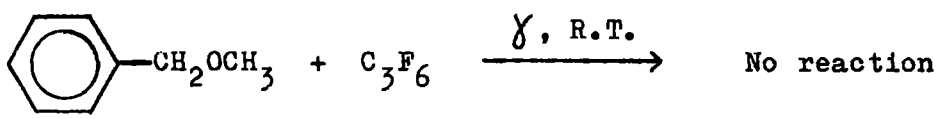
$$+ \; HOCH_2CH_2OCH_2R_f \quad (127) \quad 34\%$$

Table 18 Continued....

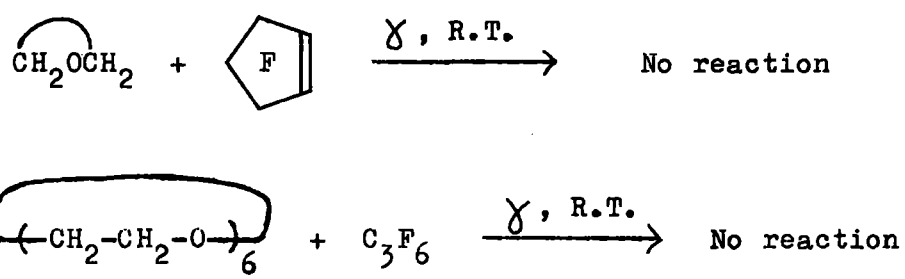
X = 



X = 



X = Ring



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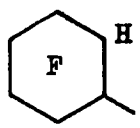
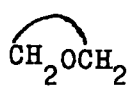
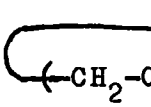
a Percentage yields of each component baesd on masses of recovered products.

b Percentage yields based on g.l.c. peak area measurements.

c Gamma-ray initiation at room temperature.

d Benzoyl peroxide initiation at ca. 80°C.

Table 19 Activating and Deactivating Groups X in Compounds of the Type $X-CH_2OCH_3$

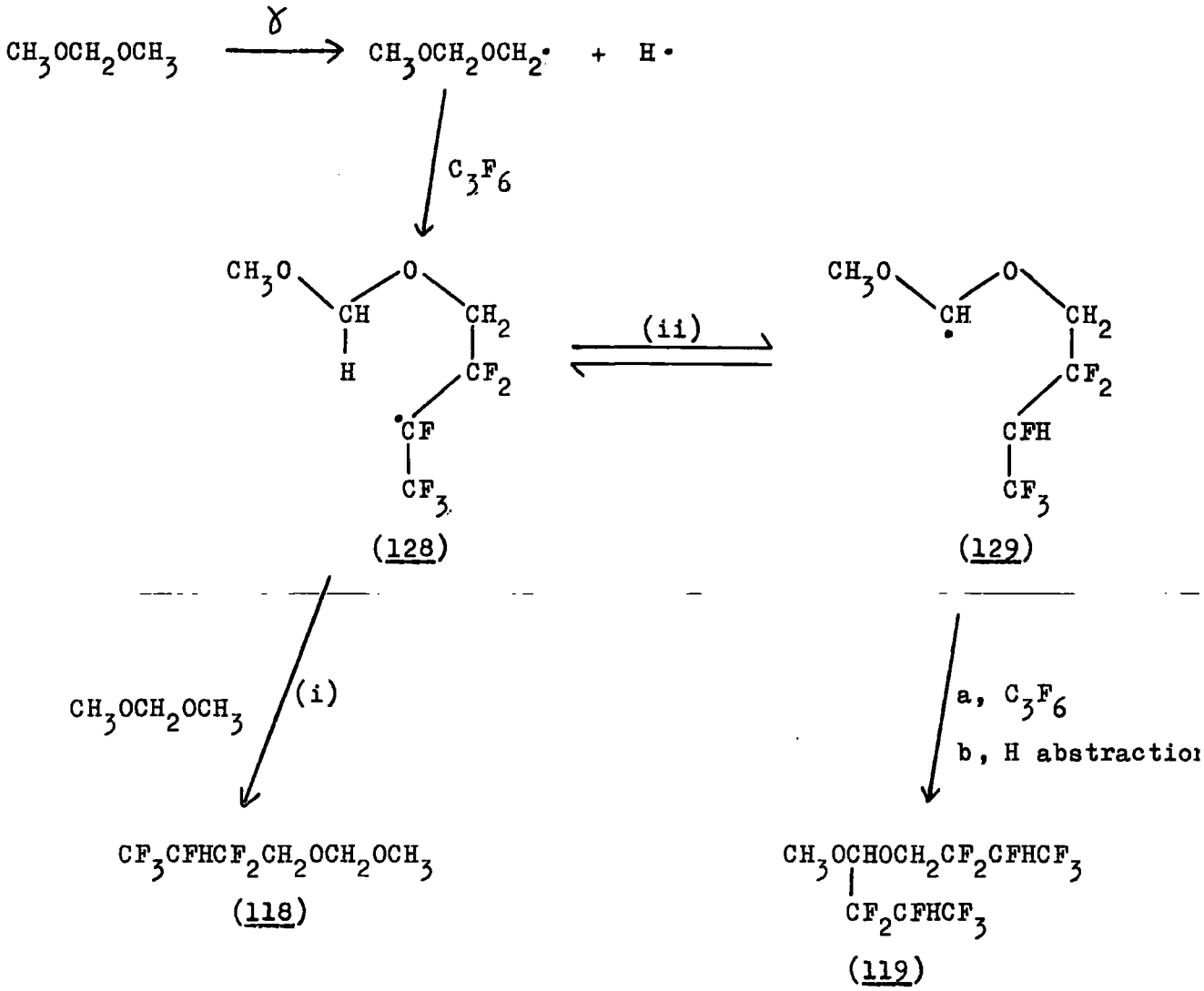
Activating	Deactivating
X = H	X = CH_3O
CH_3OCH_2	
$HOCH_2$	
	
	

electron-deficient double bond is not a favourable process.

When the substituent X is H, CH_3OCH_2, or $HOCH_2$, the carbon-hydrogen bond in the methylene group is activated and the radical adds readily to F-propene. However, for X = CH_3O, deactivation occurs. Formation of the two-to-one adduct (119) may appear, at first sight, to indicate that the methylene C-H bond is being activated but it is much more probable that (119) is produced via an intramolecular 1,5 hydrogen transfer (Scheme 2). From the relative proportions of the one-to-one (118) and two-to-one (119) adducts formed, it is clear that the radical (128) prefers to abstract a hydrogen atom from the starting material (path (i)) but is stable enough for rearrangement to (129) to occur (path (ii)) to give (119).

Hence, although the concept of stabilisation of radicals by "capto-dative" substitution works well for some systems, it does not account for the reactions described here.

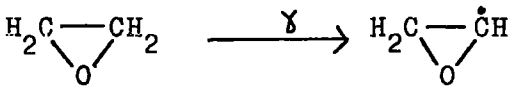
Scheme 2



It is unclear at the moment whether the substituent X is affecting the initiation or the propagation step in the radical chain reaction. Further investigation is necessary to establish which step is being affected. For example, deuterium exchange experiments may indicate whether or not bond fission to give radical (117') was occurring and thus provide information on the effect of X on the initiation stage.

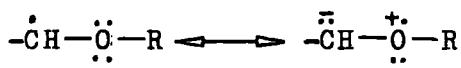
The failure of the cyclic ethers to react is unexpected. Other cyclic ethers, e.g. tetrahydrofuran, 1,4-dioxan, have been shown to react readily with fluoroalkenes (see Chapter I.C.1(e)) so there is

little doubt that the C-H bond alpha to the oxygen should be easily broken. In the case of ethylene oxide, however, formation of radical



(130)

(130) may be an unfavourable process. Stabilization of a radical derived from an ether can involve resonance forms as shown below:



The polar effect of the charge separation would then cause the C-O bond to shorten. In ethylene oxide it is unlikely that resonance stabilization via the hybrid shown above can occur since the ring, already strained, would be unable to contract further.

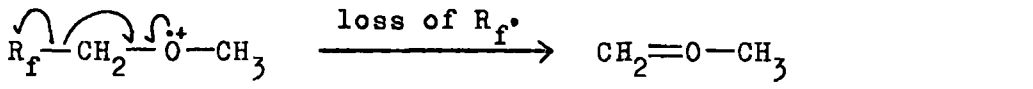
The unreactivity of the crown-ether is, most likely, a physical effect. This is supported by the formation of (78) when the irradiation was carried out at increased temperature. Indeed, it is conceivable that several of the reactions described which did not proceed at room temperature would go at higher temperatures. The activation energy for the addition step would then be reduced sufficiently for the chain addition reaction to take place.

1. Structural Assignments

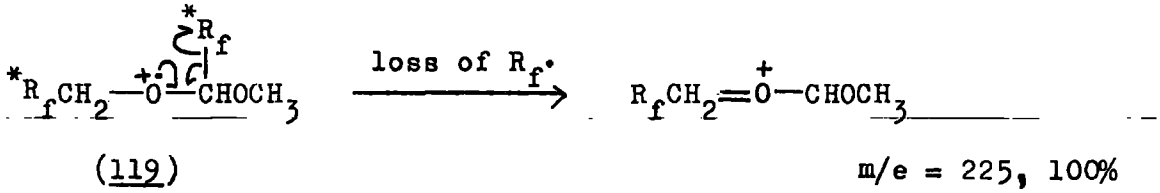
Identification of the one-to-one adducts followed from their n.m.r. spectra. Satisfactory elementary analysis was obtained for all the one-to-one adducts (except (127)) in Table 18, for (78), and for the two-to-one adduct mixture of (119) and (120).

Compounds (119) and (120) were characterised as a mixture and assigned the structures shown (Table 18) from an examination of their mass spectral fragmentation patterns. It is well known that for ethers α-cleavage (cleavage of a bond β to oxygen) is a common process,

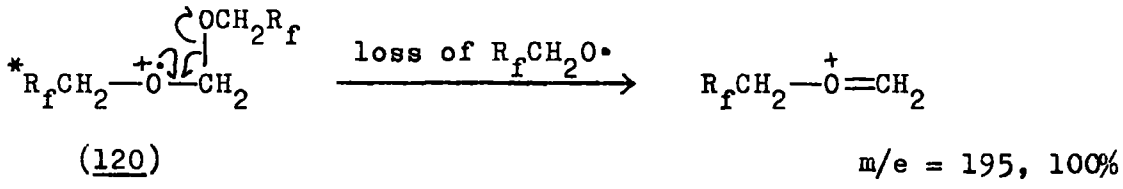
favouring the loss of a more highly substituted fragment[163]. Thus, for compounds of the type $R_fCH_2OCH_3$, fission occurs as follows:



This type of fission usually accounts for the base peak: a point that is amply demonstrated in Appendix III in the mass spectra of ethers of the type $R_fCH_2OCH_3$. It follows, therefore, that compounds (119) and (120) should fragment as shown below:



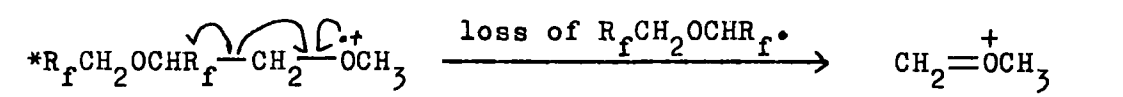
(119)



(120)

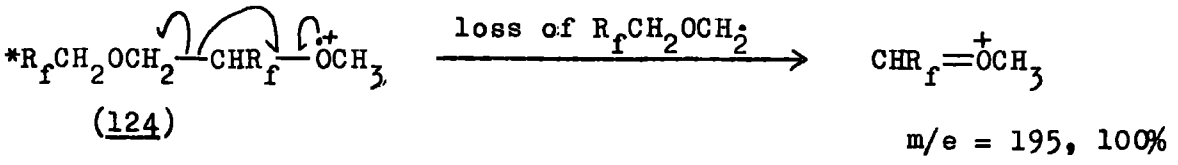
*R_f = CF_3CFHCF_2-

The base peaks observed for (119) and (120) are indeed found to be 225 and 195 respectively (see mass spectra 36 and 37 respectively). Likewise, the two-to-one adducts (123) and (124) formed in the reaction of F-propene with 1,2-methoxyethane, although not isolated, can be similarly assigned the structures shown in Table 18 by comparing how they fragment differently to give their respective base peaks (see mass spectra 40 and 41 respectively). Thus:



(123)

*R_f = CF_3CFHCF_2-



(124)

m/e = 195, 100%

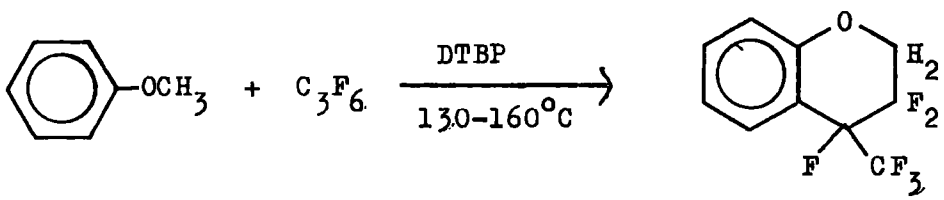
* $R_f = CF_3CFHCF_2-$

The base peaks of (123) and (124) are observed at 45 and 195 respectively.

V.B THE EFFECT OF SUBSTITUENTS 'X' IN COMPOUNDS OF THE TYPE X-OCH_3-

Although substituted methyl ethers are the main group of compounds considered, methyl esters were also investigated. Some of the ether reactions were described in Section A (Table 18) where the effect of substituents on the methylene C-H bond reactivity was studied. For convenience, these reactions are shown again in Table 20 to compare the effect of substituents X on the reactivity of the methoxy C-H bond.

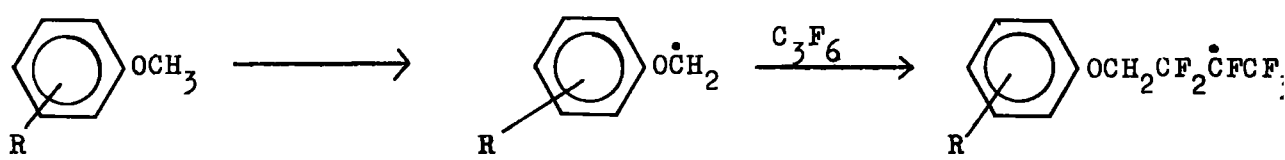
In general the substituent X activates the methoxy group but it is notable that an aromatic or substituted aromatic nucleus deactivates the group even when not directly attached e.g., methyl benzoate, benzyl methyl ether. Since it is known that F-propene can be added to anisole under free-radical conditions to give the chroman (30)[69], it is clear



[69]

(30)

that the intermediate radical (135A) can be formed. Using the cobalt-60



R = H, CH_3O (135A) (135B)

Table 20 Radical Additions to X-OCH_3

X = CH_3-

$$CH_3OCH_3 + C_3F_6 \xrightarrow[\text{or Peroxide}^e]{\gamma\ ,\ \text{R.T.}^d} CF_3CFHCF_2CH_2OCH_3 \quad (105) \quad 59\text{-}68\%^a$$

X = CH_3OCH_2-

$$CH_3OCH_2OCH_3 + C_3F_6 \xrightarrow{\gamma\ ,\ \text{R.T.}} {}^*R_fCH_2OCH_2OCH_3 \quad (118) \quad 66\%^b$$

$$+\ R_fCH_2CHR_fOCH_3 \quad (119) \quad 18\%$$

$$+\ R_fCH_2OCH_2OCH_2R_f \quad (120) \quad 16\%$$

N.B. ${}^*R_f$ = CF_3CFHCF_2- throughout

X = $CH_3OCH_2CH_2$-

$$CH_3OCH_2CH_2OCH_3 + C_3F_6 \xrightarrow{\gamma,\ \text{R.T.}} CH_3OCHR_fCH_2OCH_3 \quad (121) \quad 53\%^a$$

$$+\ R_fCH_2OCH_2CH_2OCH_3 \quad (122) \quad 47\%$$

$$+\ R_fCH_2OCHR_fCH_2OCH_3 \quad (123)$$

$$+\ R_fCH_2OCH_2CHR_fOCH_3 \quad (124)$$

} minor components

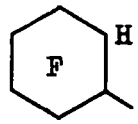
X = $HOCH_2CH_2$-

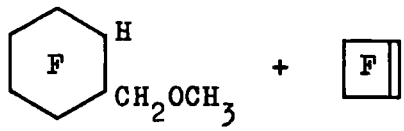
$$HOCH_2CH_2OCH_3 + C_3F_6 \xrightarrow{\gamma,\ \text{R.T.}} HOCHR_fCH_2OCH_3 \quad (125) \quad 34\%^b$$

$$+\ HOCH_2CHR_fOCH_3 \quad (126) \quad 33\%$$

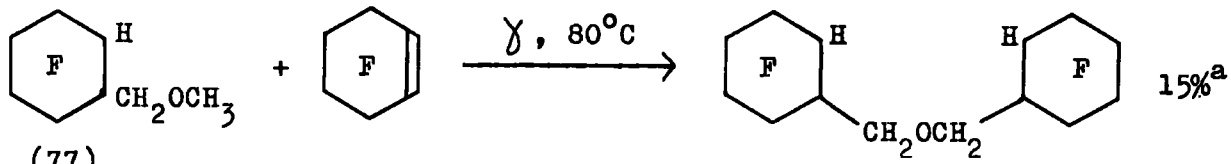
$$+\ HOCH_2CH_2OCH_2R_f \quad (127) \quad 34\%$$

Table 20 Continued....

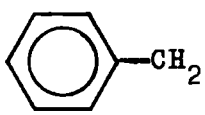
X = 

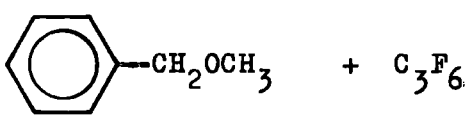


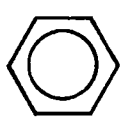
(77)

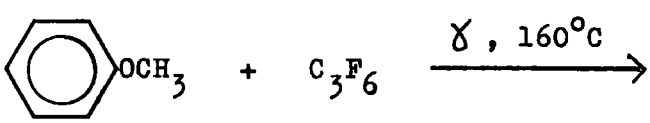


(77) (78) 15%[a]

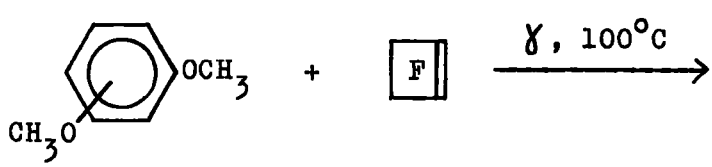
X = 



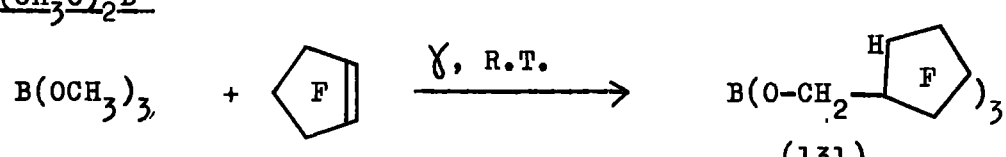
X = 



X = m- or p-$MeOC_6H_4$-



X = $(CH_3O)_2B$



(131) 49%[a,c]

Table 20 Continued....

X = $(CH_3O)_2PO$

$$(CH_3O)_3PO + C_3F_6 \xrightarrow[\text{Peroxide}]{\gamma \text{ or}} CF_3CFHCF_2CH_2O(CH_3O)_2PO$$

(132) γ, 13%[a] at R.T.
γ, 50% at 100°C.
Peroxide, 3%.

X = $Si(CH_3)_3$-

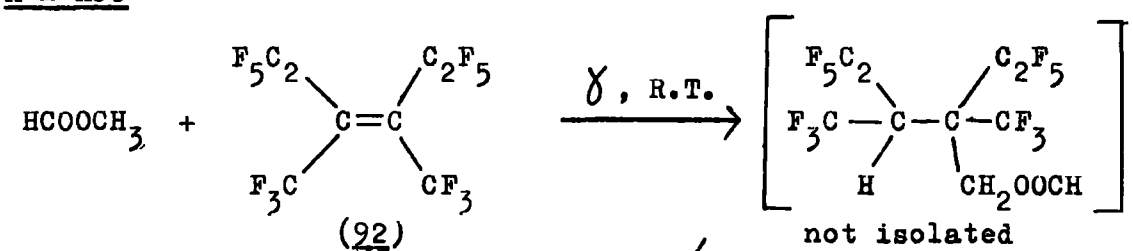
$$CH_3OSi(CH_3)_3 + C_3F_6 \xrightarrow{\gamma,\ \text{R.T.}} CF_3CFHCF_2CH_2OSi(CH_3)_3 \quad 62\%^b$$

(133)

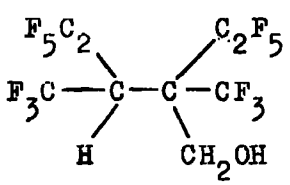
X = PhCO

$$PhCOOCH_3 + \boxed{F} \xrightarrow{\gamma,\ \text{R.T.}} \text{No reaction}$$

X = HCO



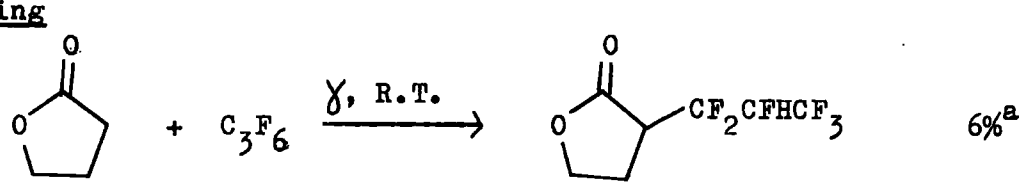
(92) not isolated



30%[a]

(93)

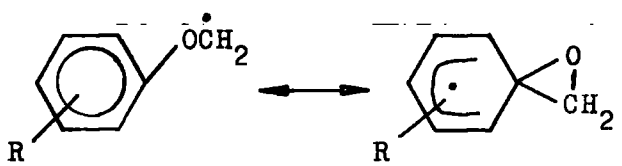
X = Ring



(134)

a Percentage yields of the component based on masses of recovered products.
b Percentage yield based on g.l.c. peak area measurements.
c No F-cyclopentene recovered - completely consumed.
d Gamma-ray initiation at room temperature.
e Benzoyl peroxide initiation at ca. 80°C.

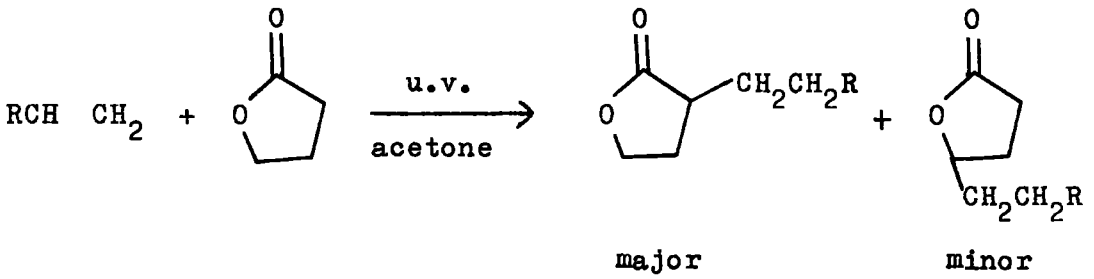
source, a steady, high intensity supply of radical initiator is available so that formation of (135A) (page 86), especially at elevated temperature, should not be a problem. Muramatsu[69] attributed the lack of one-to-one adduct formation to the incapacity of the radical (135B) to abstract a hydrogen atom from the anisole substrate. Since not even a cyclised product was obtained, it is evident that the addition step to give (135B) did not occur (or at least the equilibrium with (135A) lies well to the left) and so radical (135A) must be stabilised. Stabilisation can be accounted for by delocalisation of the unpaired electron into the ring via a bridged intermediate, thus



R = H, CH_3O

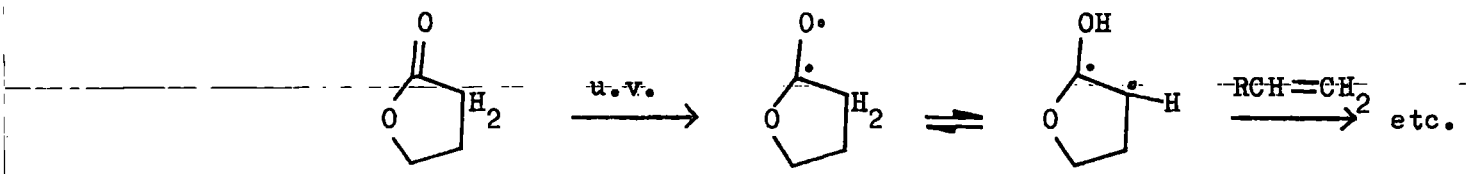
It is interesting that, whatever the electronic properties of a heteroatom adjacent to the methoxy group happen to be, activation occurs. Electron-rich phosphorus and silicon and electron-deficient boron all activate the methoxy C-H bond. The very low yield of the fluorinated phosphate ester (132) in the peroxide-initiated reaction and the much higher yield in the high temperature radiation-initiated reaction suggest that, in this instance, the chain length of the radical reaction is very short.

The reactions of the esters, methyl formate and γ-butyrolactone, present a stark contrast. In the former, reaction was found to be exclusively at the methoxy C-H bond. One would thus expect addition to the lactone to occur at the C-H bond adjacent to the oxygen but this is not the case. Another worker[164] has also found that, in the ultraviolet initiated addition of hydrocarbon alkenes, reaction is preferred at the C-H bond adjacent to the carbonyl group. It is uncertain whether this



[164]

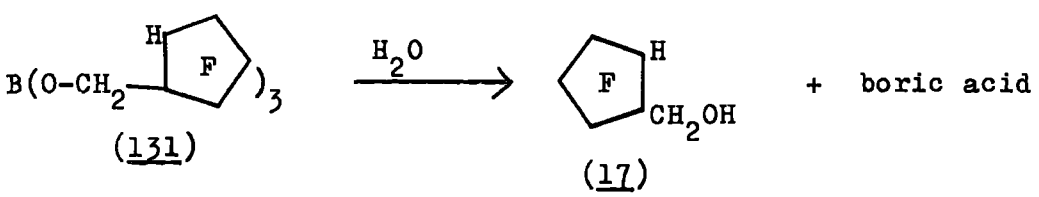
addition reaction (shown above) is as simple as it perhaps appears. It is quite possible that photolysis first activates the carbonyl group and then transfer of an adjacent hydrogen atom follows before the chain reaction begins, thus



1. Structural Assignments

Structures of many of the products were discussed in Section A.1. For convenience, only those reaction products not mentioned previously will be considered here.

The identity of the fluorinated borate ester (131) was further confirmed by a quantitative hydrolysis experiment. As usual with borate esters, hydrolysis immediately gives the corresponding alcohol and boric acid. Thus, (131) gave the alcohol (17) which has been characterised previously (Chapter III).



(131) (17)

The structure of the lactone (134) followed simply from comparison of its ^{1}H n.m.r. spectrum with that of the hydrocarbon starting material: the signal due to the CH_2 group next to the oxygen (at 4.55 p.p.m.) was

Table 21 Radical Additions to X-CH_2OH and X-CHO

A. X-CH_2OH

X = CH_3OCH_2-

$$CH_3OCH_2CH_2OH + C_3F_6 \xrightarrow{\gamma,\ R.T.^{c}} CH_3OCH_2CHR_f^{*}OH \quad 34\%^{a}$$

(125)

$^{*}R_f$ = CF_3CFHCF_2-

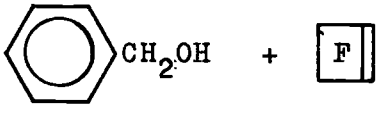
$$+\ CH_3OCHR_fCH_2OH \quad 33\%$$

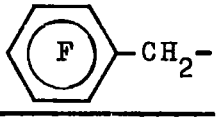
(126)

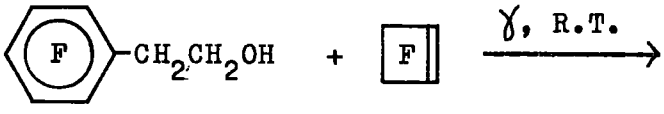
$$+\ R_fCH_2OCH_2CH_2OH \quad 34\%$$

(127)

X = 



X = 



B. X-CHO

X = CH_3-

$$CH_3CHO + C_3F_6 \xrightarrow[\text{Peroxide}^{d}]{\gamma,\ R.T.\ \text{or}} CF_3CFHCF_2COCH_3 \quad 60\%^{b}$$

(136)

X = 

a Percentage yields based on g.l.c. peak area measurements.

b Percentage yield based on the mass of the product recovered.

c Gamma-ray initiation at room temperature.

d Benzoyl peroxide initiation at 80°C.

unchanged and the complex multiplet around 2.60 p.p.m. (from the CH_2 groups attached to another carbon) was much simplified.

V.C THE EFFECT OF SUBSTITUENTS 'X' IN COMPOUNDS OF THE TYPE X-CH_2OH AND X-CHO

The investigation of the effect of X on carbon-hydrogen bond reactivity in compounds of the types X-CH_2OH and X-CHO is at a very early stage, The reactions carried out are summarized in Table 21. The initial conclusion that can be drawn from the few results available is that when X is an aromatic nucleus it deactivates the C-H bond in both types of compounds. There is not enough data available to expand further a discussion of the effect of X in these types of compounds at this stage.

V.D SUMMARY

In this preliminary study, a variety of F-alkenes and -cycloalkenes have been used in the addition reactions. Although there is no reason to suspect that changing the F-alkene would dramatically alter the course of the reactions, for direct comparison of all the results it would be preferable to use a standard F-alkene for all the reactions, viz., F-propene. At the time of writing this thesis, such reactions are known to be in progress.

Many more reactions, especially at elevated temperatures, need to be carried out before a clear and coherent picture will emerge as to the precise properties of the substituents 'X' which are affecting the reactivity of the adjacent C-H bond of functional hydrocarbons in free-radical reactions.

CHAPTER VI

SOME REACTIONS OF FUNCTIONAL FLUOROCARBON DERIVATIVES

Although radical additions of functional hydrocarbons to fluoroalkenes have been carried out by many workers (see Chapter I), there are relatively few instances where the chemistry of the partly fluorinated products has been investigated. In this chapter the reactions of the fluorine-containing alcohols, methyl ketones, and methyl ethers whose formation has been described in previous chapters, are discussed with particular reference to the influence of the polyfluoro-alkyl and -cycloalkyl substituents adjacent to the functional group.

VI.A METHYL KETONES

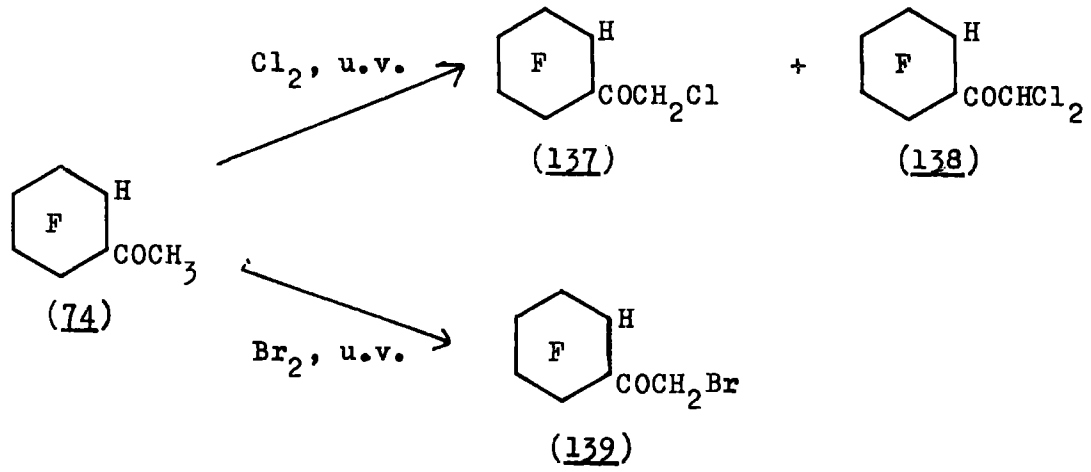
The polyfluorinated group adjacent to the acyl group can influence both the carbonyl and the methyl moieties as a result of its electron-withdrawing inductive effect. This leads to a decrease in electron density at the carbonyl, enhancing the electrophilicity of the carbonyl carbon atom and also tends to make the hydrogen atoms of the methyl acidic. Competing with inductive effects are steric effects. Polyfluoro-alkyl and -cycloalkyl groups have considerably larger effective diameters than their hydrocarbon analogues and the main steric factors are hindrance of the approaching molecule and shielding. Inductive and steric effects can be seen to be operating in the reactions of the partly fluorinated methyl ketones described below.

1. Halogenation

(a) Chlorine and Bromine

Radical halogenation proceeds normally. Photochemical chlorination of compound (74) gave both the mono- and di-chloromethyl ketones, (137) and (138) respectively as a result of the reactivity of the chlorine

atoms. The less reactive bromine gave only the mono-bromo product (139).



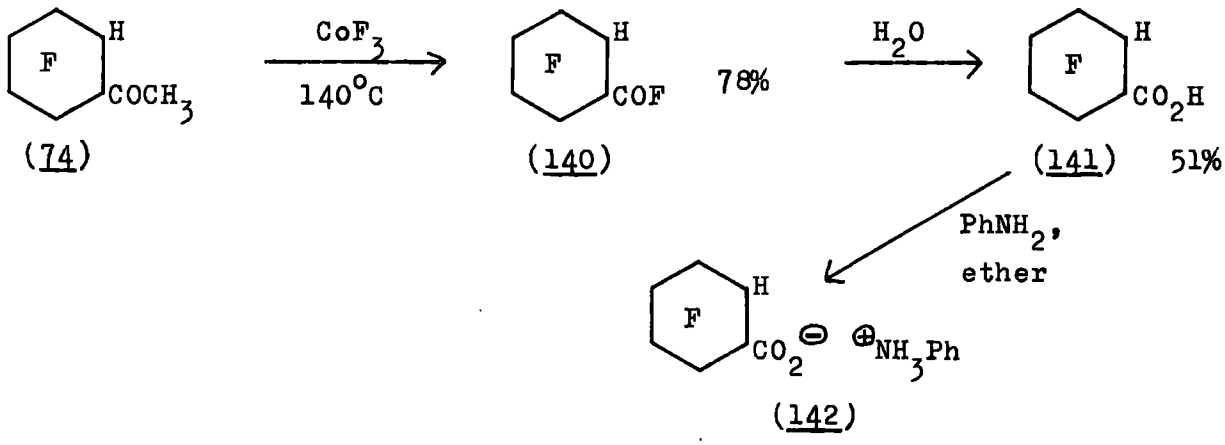
(b) Cobalt Trifluoride Fluorination

Although little of certainty can be said about the mechanism of cobalt trifluoride fluorination, it is believed[165] that initially one electron oxidation of the compound occurs, thus

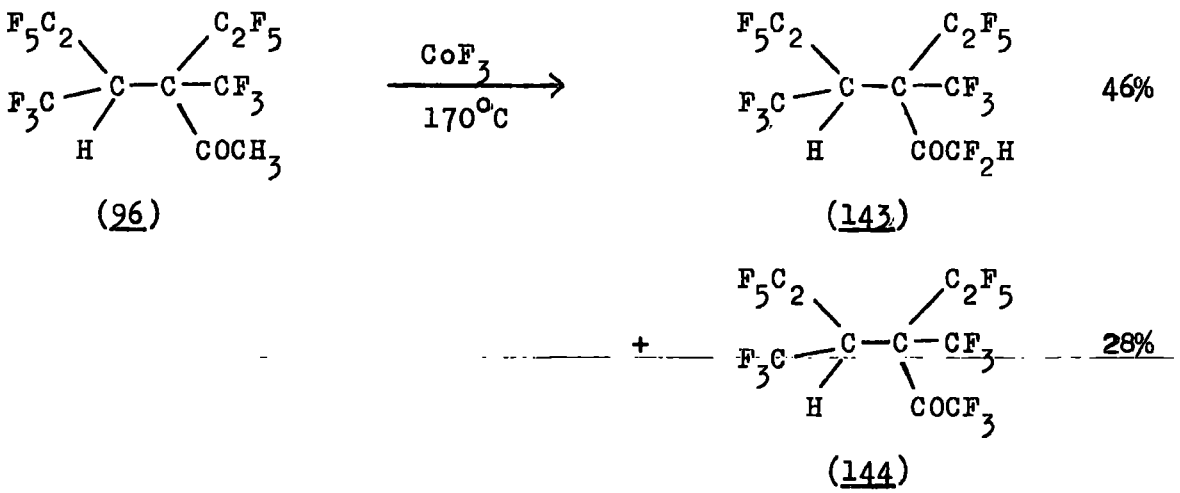
$$X \xrightarrow[-e]{Co^{3+}} [X]^{+\cdot}$$

Beyond this stage, the course of the reaction is uncertain. The presence of fluoroalkyl substituents in X reduce the ability of the compound to be oxidized as shown above.

Thus it is not surprising that attempted fluorination of hydrocarbon ketones leads to decarbonylation during the reaction[166-168] since the radical cation is formed quite readily. However, partly fluorinated methyl ketones are found to be more stable under the same reaction conditions. Compound (74) is quantitatively converted to the corresponding acid fluoride (140) which was identified by the



characteristic[151] very low field ^{19}F n.m.r. chemical shift (-23.5 p.p.m. relative to $CFCl_3$) of the fluorine atom attached to the carbonyl. As expected, the acid fluoride (140) hydrolysed readily to the parent carboxylic acid (141) which was further characterised as the anilinium salt (142). Compound (96) is even more stable: no carbon-carbon bond

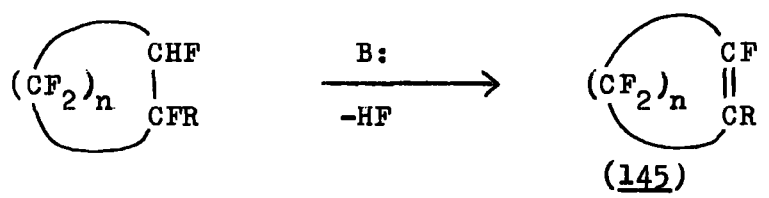


(96) (143) (144)

fission occurred and good yields of the corresponding difluoromethyl and trifluoromethyl ketones, (143) and (144) respectively, were obtained. When the one-to-one adduct (136) from F-propene and acetaldehyde was fluorinated, a mixture of unidentified gases was produced. Evidently bond fission occurred on both sides of the carbonyl group, resulting in the production of fluoroalkanes. It is tempting to conclude that the steric effect of the greater number of fluoroalkyl substituents adjacent to the acyl group in (96) is contributing to the stability of the ketone during the fluorination reaction.

2. Reaction with Base

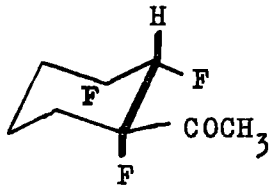
Dehydrofluorination of the polyfluorocycloalkyl derivatives is a potential route to the unsaturated compounds (145) which would be otherwise difficult to produce.



(145)

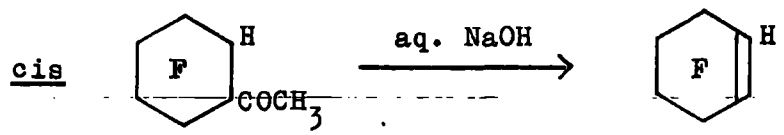
n = 2,3,4
R = $COCH_3$, CH_2OH, CH_2OCH_3.

For example, compound (74, cis) would appear to have a suitable



(146)

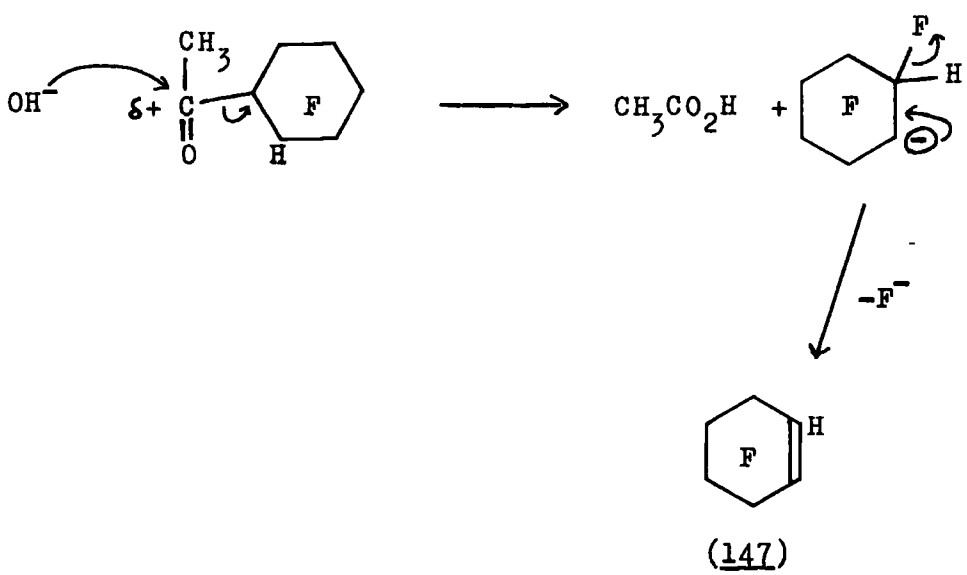
configuration (shown above, (146)) for 1,2 anti elimination of hydrogen fluoride. However, it was found that the product obtained in the reaction of (74) with aqueous sodium hydroxide solution was (147) which is a



(74) (147)

known compound[169,170]. It appears that dehydrofluorination was accompanied by haloform cleavage although it is possible that a displacement, rather than an addition reaction, takes place followed by loss of fluoride ion (Scheme 3)[171].

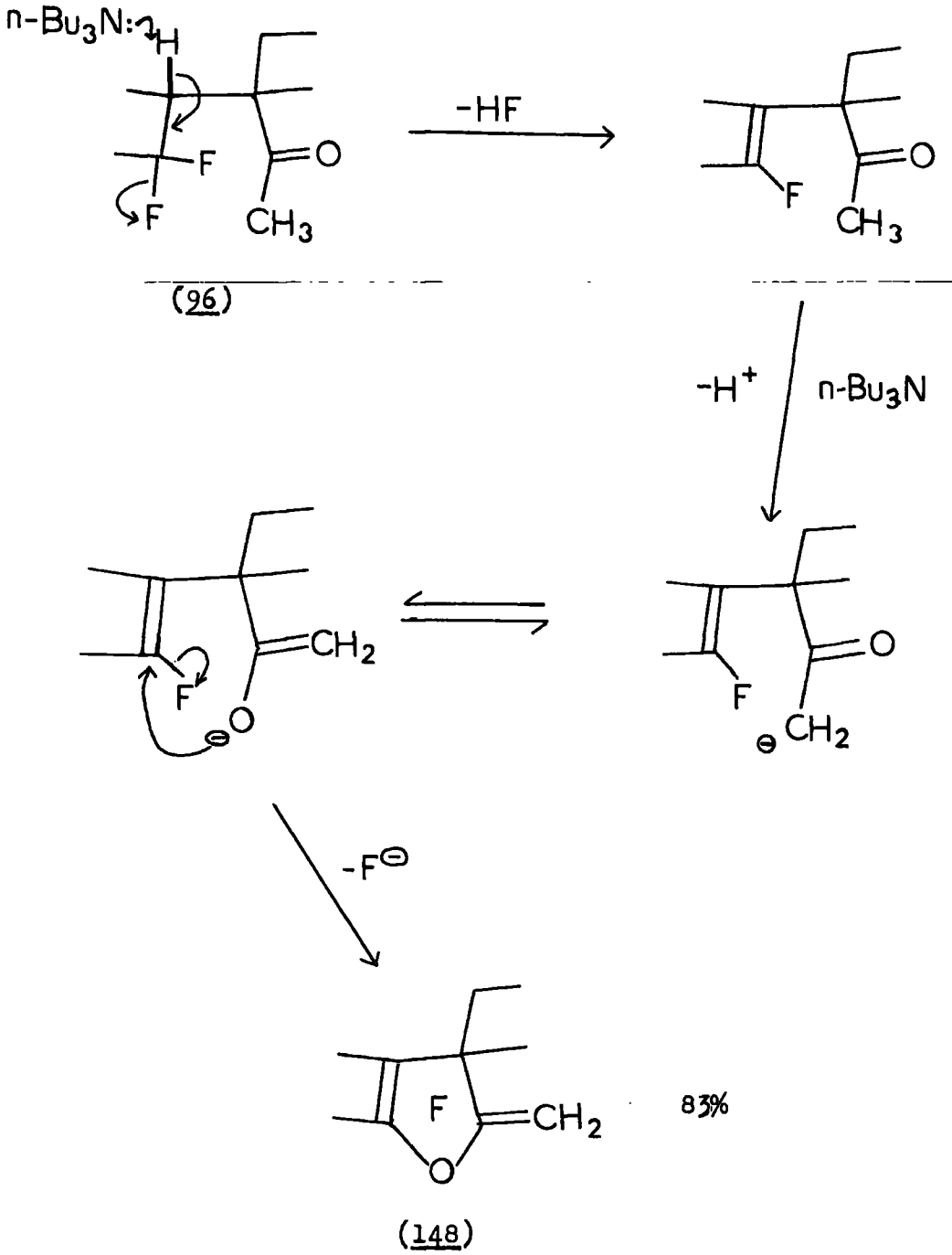
Scheme 3



(147)

When compound (96) was reacted with tri-n-butylamine, a fascinating cyclisation took place with a nett loss of two molecules of hydrogen fluoride to give (148). The mechanism proposed to account for the formation of (148) is illustrated in Scheme 4. The influence of the

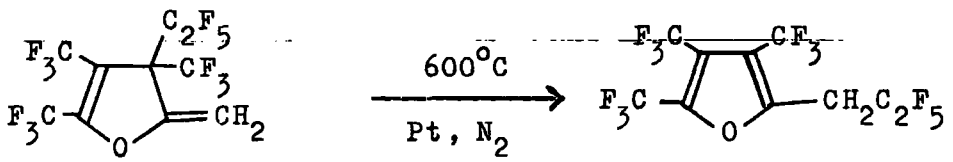
Scheme 4



N.B. All unmarked bonds are to fluorine.

fluoroalkyl groups adjacent to the acyl group is readily seen in the second stage of the reaction (Scheme 4) : the hydrogen atoms of the methyl group are sufficiently acidic for removal of one by the base to occur. Base-promoted enolate ion formation ensues and attack on the vinylic fluorine takes place via this enol form rather than the keto form.

To establish the proposed mechanism, a sample of (148) was pyrolysed by passing it in a flow of nitrogen through a platinum lined and packed tube at 600°C. There was quantitative conversion to a single product which was identified as the furan (149). Formation of (149) involves a 1,3 migration of the pentafluoroethyl group. Another worker[172]



(148) (149)

has found that (149) can be photochemically dehydrohalogenated to the corresponding acetylene.

(a) Structural Assignments

Compounds (148) and (149) gave satisfactory elemental analysis and weak parent peaks at 404 in their mass spectra. Their structures followed from their n.m.r. and infra-red spectra. The ^{19}F n.m.r. chemical shifts of fluorine nuclei in different environments (Table 22) and the data for some known fluorinated furans and dihydrofurans (Table 23) were used for comparison.

Thus, for compound (148), it was readily established that it contained two CF_3 groups attached to a double bond and C_2F_5 and CF_3 groups attached to a saturated carbon. A sharp singlet in the ^1H n.m.r. spectrum of (148) at 5.32 p.p.m. corresponds to hydrogen attached to a double bond. The infra-red spectrum confirmed the presence of two double bonds.

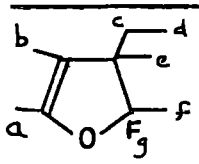
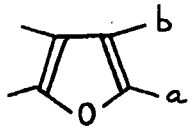
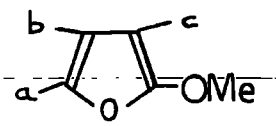
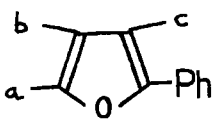
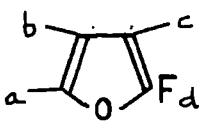
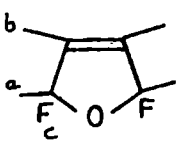
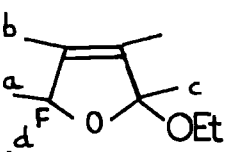
Table 22 ^{19}F N.M.R. Spectral Characteristics of Perfluorocarbons[151,176]

Structural Type	Approximate Shift Region (p.p.m. w.r.t. $CFCl_3$)
$CF_3-C<$	60 - 70
$CF_3-C(-)=C<$	60 - 70
$\underline{CF_3}-CF<$	70 - 80
CF_3-CF_2-	80 - 90
$>C=CF_2$	60 - 80
$>C=CF-$	90 - 120
$-CF_2-$	100 - 150
$-CF<$, $-CFH-$	>160

All unmarked substituents are carbon.

The structure of (149) followed from the remarkably close resemblance of the ^{19}F n.m.r. signals due to the olefinic CF_3 groups to those of other substituted tris(trifluoromethyl) furans whose chemical shift data are shown in Table 23. The substituent propyl group was assigned from the coupling found between the adjacent CH_2 and CF_2 groups.

Table 23 Selected Spectral Data on Fluorinated Furans and Dihydrofurans

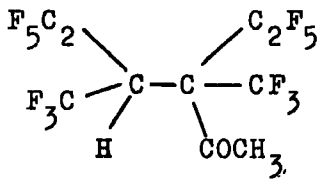
Compound*	Signal	Chemical Shift	Multiplicity** J values in Hz.	$\nu_{C=C}$	Reference
	a	68.3	M		
	b	58.3	M		
	c	105.4	M		
	d	80.6	M	1695	[172,173]
	e	71.1	M		
	f	79.4	D, J_{fg}=35		
	g	117.0	M		
	a	65.6		1640	[143,174, 175]
	b	60.0			
	a	63.3	Q, J=8.5		
	b	59.6	St	1610,1650	[143]
	c	58.7	Q, J=7		
	a	61.5	Q, J=8.7		
	b	58.5	St	1580,1620	[143]
	c	57.2	Q, J=8		
	a	64.5	D of Q, J=8.3		
	b	60.2	M	1610,1635, 1680	[143]
	c	60.5	Q, J=6.8 of D		
	d	103.7	Q of Q		
	a	63	M		
	b	85	M	not observed	[143,174]
	c	112, 123	M		
	a, c	81	M		
	b	62	M	1700	[143,174]
	d	106, 113	M		

* All positions, other than those marked, are to fluorine.

** D, doublet; Q, quartet; St, septet; M, multiplet.

3. Reduction

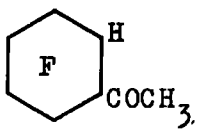
The effect of the fluorine-containing substituent on the carbonyl reactivity in reduction experiments appears to be mainly steric in nature. Thus, attempted chemical reduction of compound (96) with sodium borohydride was unsuccessful: approach of borohydride ion was hindered.



(96)

$\xrightarrow{NaBH_4}$ No reaction

A similar reaction occurred when (74) was irradiated by ultraviolet light in propan-2-ol solution. Photochemical reduction of fluorine-



(74)

$\xrightarrow[(CH_3)_2CHOH]{u.v.}$ No reaction

containing ketones have been reported, e.g. hexafluoroacetone[177], but the steric requirement is somewhat less in the latter.

Bimolecular reduction also gave a negative result. In a control experiment, acetone readily dissolved the mercuric chloride used in the reaction and pinacol was produced as expected. The fluorinated methyl ketone used, (72), did not dissolve the chloride and this is perhaps the main factor causing lack of reaction.

(72)

$\xrightarrow[\text{toluene}]{Mg + HgCl_2}$ No reaction

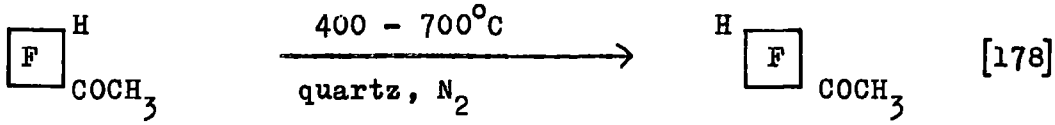
4. Pyrolysis

Because the partly fluorinated methyl ketones are mainly compounds

containing carbon-fluorine bonds, it is reasonable to expect that the high C-F bond strength would exert its influence when these compounds are subjected to conditions where a C-H bond would be unstable. This is indeed the case when the polyfluorocycloalkyl methyl ketones were pyrolysed.

(a) Compound (72)

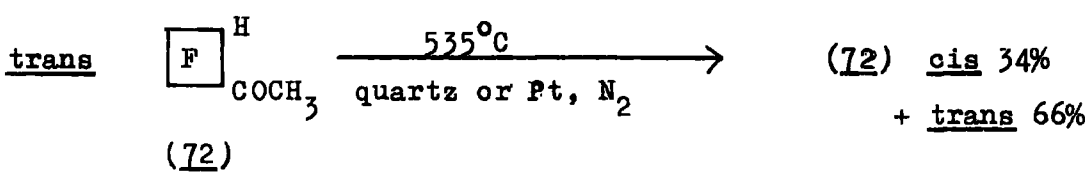
In a patent, Japanese workers claimed the thermal rearrangement of (72) to the corresponding 3-hydro compounds (150)[178]. This claim has



[178]

(72) isomers (150) isomers

been confirmed. It has further been shown that the rearrangement only occurs efficiently when the isomer mixture of (72) is used. Thus, when the trans isomer was pyrolysed at 535°C, only isomerisation was observed to give both isomers in the ratio indicated below but no rearrangement

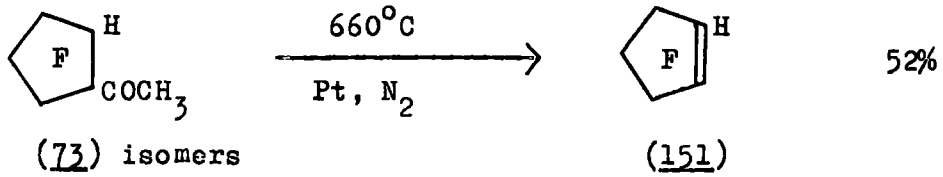


(72)

was detected. At 575°C, pyrolysis of the cis isomer caused mostly isomerisation but also a little rearrangement. The isomer mixture, as obtained from the radical addition reaction, when pyrolysed at, e.g. 625°C, went almost completely to (150) with very little starting material unchanged. At higher temperature (690°C) breakdown of the molecules gave a very low recovery of material.

(b) Compound (73)

Unlike (72) above, when the isomer mixture of (73) was pyrolysed the molecule fragmented losing acetyl fluoride overall to give (151) which is a known compound[179]. Only the cyclopentene (151) was formed

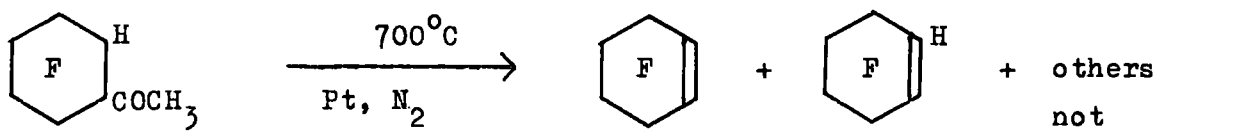


(73) isomers (151)

in this reaction; at 630°C there was a low conversion but apart from (151) only starting material was detected by g.l.c. and at 660°C there was a much higher conversion with only a small quantity of (73) remaining.

(c) Compound (74, cis)

Pyrolysis of (74) required very vigourous conditions to obtain a high conversion of starting material. A complex mixture of volatile products was recovered. It was only possible to separate and identify two components. These were F-cyclohexene and 1-hydro-F-cyclohexene (147). Both were identified by their n.m.r. spectra.



(74) (147)

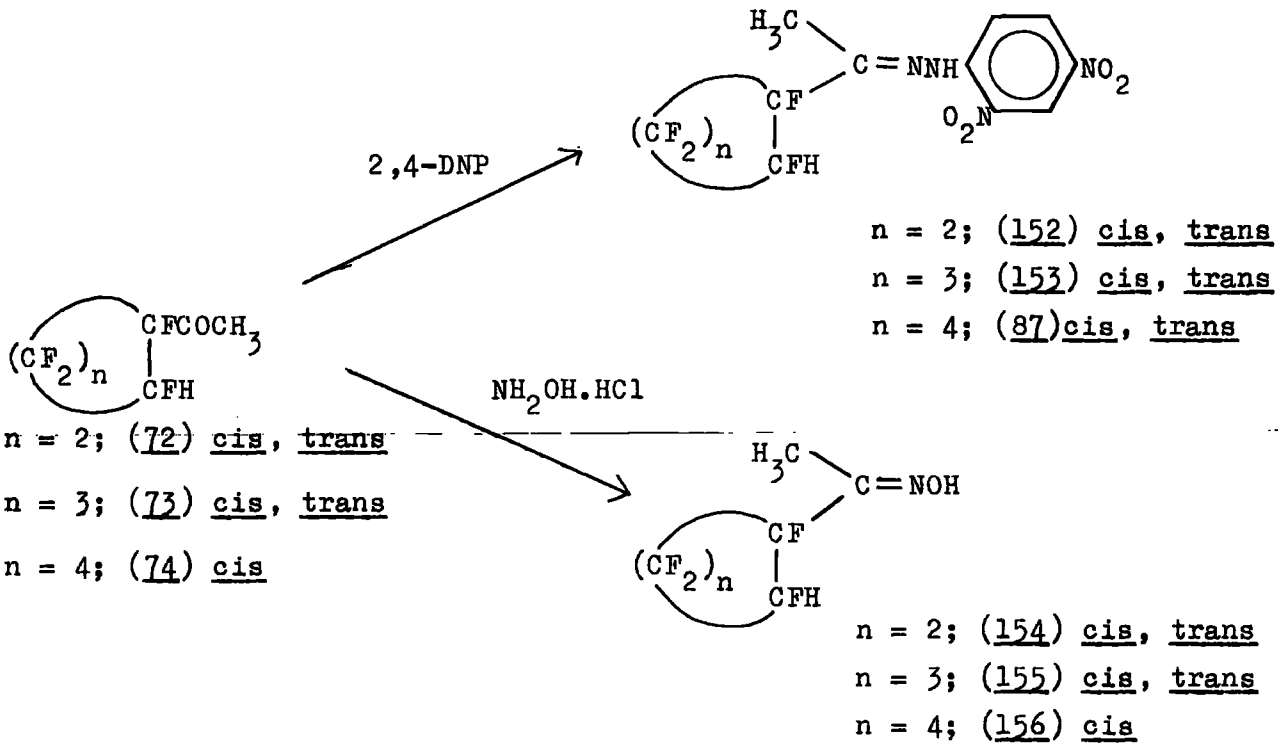
(d) Summary

Throughout the above pyrolysis experiments, the polyfluorocycloalkyl ring remained intact, testifying to the high stability of the C-F bond. As the ring size increased, the course of the reaction changed. In the cyclobutyl case, rearrangement only occurred; in the cyclopentyl ring case, there was specific loss of acetyl fluoride; in the cyclohexyl case, fragmentation was more random and resulted in a mixture of products.

5. Reactions of the Carbonyl Group

The inductive effect of the fluorine-containing substituent should enhance the susceptibility of the carbonyl to nucleophilic addition and thus it is to be expected that reaction of the methyl ketones with ammonia derivatives should proceed readily. The geometric isomers of

adducts (72), (73) and (74) were systematically reacted with 2,4-dinitrophenylhydrazine (2,4-DNP) and with hydroxylamine hydrochloride to give the corresponding 2,4-dinitrophenylhydrazone and oxime derivatives, (86) and (85) respectively.



Compounds (72) and (73) reacted readily with both reagents but (74) was notably slower to react and, indeed, this change in reactivity was even more pronounced in the reactions of (72) and (74) with (-)-menthydrazide (88), as described in Chapter III (the latter methyl ketone did not react at all). The poor reactivity of (74) is evidently caused by the steric effect of the polyfluorocyclohexyl group, although the smaller rings are obviously not having the same influence.

VI.B ALCOHOLS

1. Ether Formation

One of the primary objectives of this project was the formation of partly fluorinated ethers for testing as potential anaesthetic agents (see Section D). Apart from the direct method of radical addition of a

hydrocarbon ether to a fluoroalkene which was successfully exploited in earlier chapters, the alternative is chemical conversion of partly fluorinated alcohols.

Fluorine-containing alcohols are more acidic than their hydrocarbon analogues due to the strong inductive effect of the fluoroalkyl groups, as shown by the pKa values in Table 24[180]. It can be seen, however, that

Table 24 pKa Values of Fluorinated Alcohols[180]

Alcohol	pKa
CF_3CH_2OH	12.8
$(CF_3)_2CHOH$	9.3
$(CF_3)_3COH$	5.4
$(CF_3)_2C(OH)_2$	6.58

the effect of fluorine on the hydroxyl diminishes dramatically as it is further removed from the hydroxyl group.

In the presence of base, fluorine-containing alcohols would be expected to react readily with alkyl halides in a Williamson ether synthesis:

$$R\text{-}X + R_fCH_2OH \xrightarrow{\text{base}} R_fCH_2OR + HX$$

R_f = polyfluoro group

Unfortunately, the polyfluorocycloalkylmethanols tended to decompose in the presence of a strong base. Evidently dehydrofluorination leads to a reactive vinyl alkoxy species which polymerises to an involatile oil. This tendency to decompose excluded the Williamson synthesis and the use of dimethyl sulphate and dihalocarbenes generated by the base hydrolysis of haloforms[181] e.g. difluorocarbene from chlorodifluoromethane. Thus, reactions were limited to those which did not rely on the use of base.

(a) Pyrolysis of Sodium Trihaloacetates

Other workers have successfully generated difluorocarbene from sodium chlorodifluoroacetate[182-184] and dichlorocarbene from sodium trichloroacetate[185-187] although the carbene has usually been used to form a cyclopropane by reaction with a double bond rather than inserted into an O-H bond, e.g.,

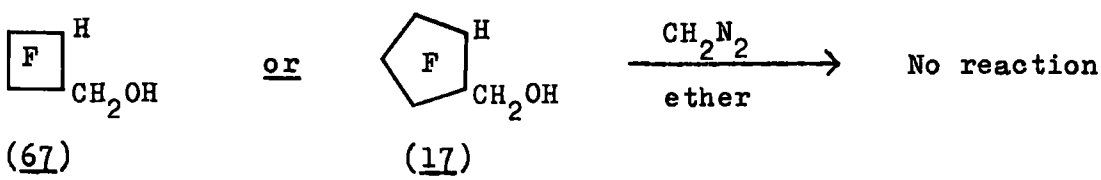
[183]

It was found that when a mixture of sodium chlorodifluoroacetate and one of the polyfluorocycloalkylmethanols (67, 17, or 68) was heated, several new components were observed by g.l.c. in the liquid recovered but they could not be isolated. A large volume of carbon monoxide was produced at the same time which made the pyrolysis (in a sealed Carius tube) potentially explosive. This factor renders the process impractical if a large quantity of liquid is required for separation of its components.

Dichlorocarbene insertion did not occur with (93) although some chloroform was recovered, indicating that the first stage in the reaction, decarboxylation of the acetate ion, had taken place.

(b) Diazomethane[188,189]

It is well known that hydrocarbon alcohols are not sufficiently acidic (e.g. the pKa of methanol is about 16) to be methylated by diazomethane without the addition of a Lewis acid. However, many fluorinated alcohols are acidic enough to react without a Lewis acid[190,191]. No methylation occurred when either (67) or (17) were stirred with



(67) (17)

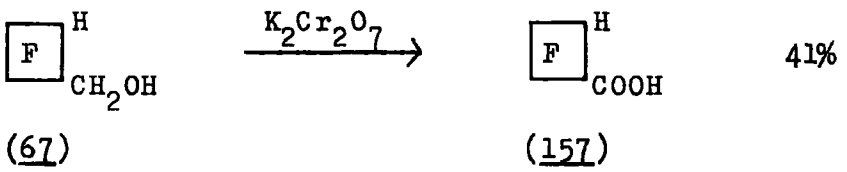
diazomethane solution, showing that these partly fluorinated alcohols are not appreciably acidic, i.e. their pKa's are greater than 13 (2,2,2-trifluoroethanol is sufficiently acidic to be directly methylated using diazomethane[190]: its pKa is 12.8 (Table 24)).

Addition of Lewis acids, e.g. aluminium tri-isopropoxide[190] or boron trifluoride etherate, gave no detectable amount of methylation.

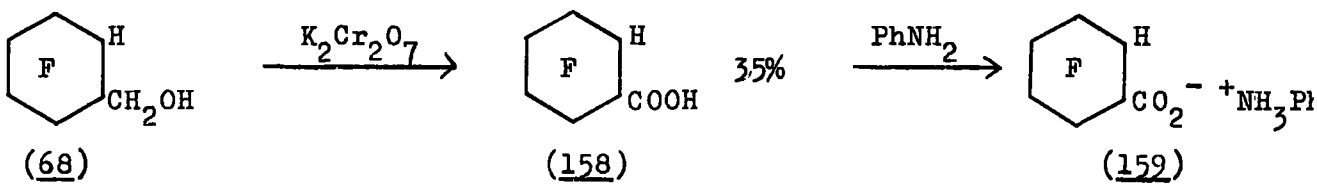
It is evident that the fluorine in these alcohols is removed far enough from the hydroxyl to have little or no effect on the acidity of the hydroxyl group but it is not clear why they are so inert to methylation in the presence of diazomethane and Lewis acid.

2. Oxidation

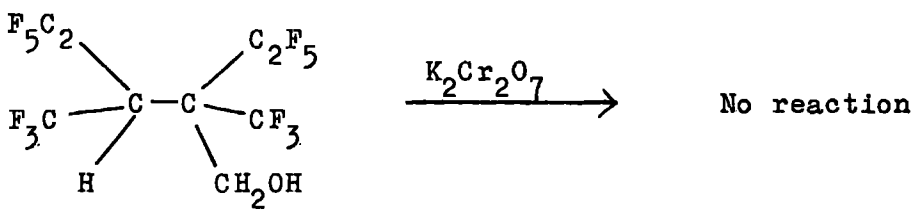
There are clear indications from the results that the dichromate oxidation of the alcohols is affected by the steric effect of the fluorine-containing substituent. Thus, the alcohol (67) readily gave the



(67) (157)



(68) (158) (159)



(93)

corresponding carboxylic acid (157) which has been reported previously[54] although no spectroscopic details were given. The acid (158) was only obtained as an impure oil and was characterised as the anilinium salt

(159) and (93) did not react at all, the orange dichromate solution not changing colour. As the fluorine-containing substituent increases in size, the initial stage in the oxidation, viz., formation of a chromate ester, clearly becomes more difficult and reactivity decreases.

3. Reaction with Base

Reaction of the polyfluorocycloalkylmethanols with base gave low recoveries of involatile oils which were not investigated.

In contrast, compound (93) reacted cleanly with tertiary amines to give a mixture of products identified as the tetra- and di-hydrofurans, (161) and (162) respectively. A proposed mechanism to account for the formation of these products is shown in Scheme 5 overleaf. After initial dehydrofluorination, intramolecular attack of alkoxide ion on the double bond gives the intermediate anion (160) which, to account for both products, is able to eliminate fluoride ion as readily from a CF_3 group as from a tertiary position.

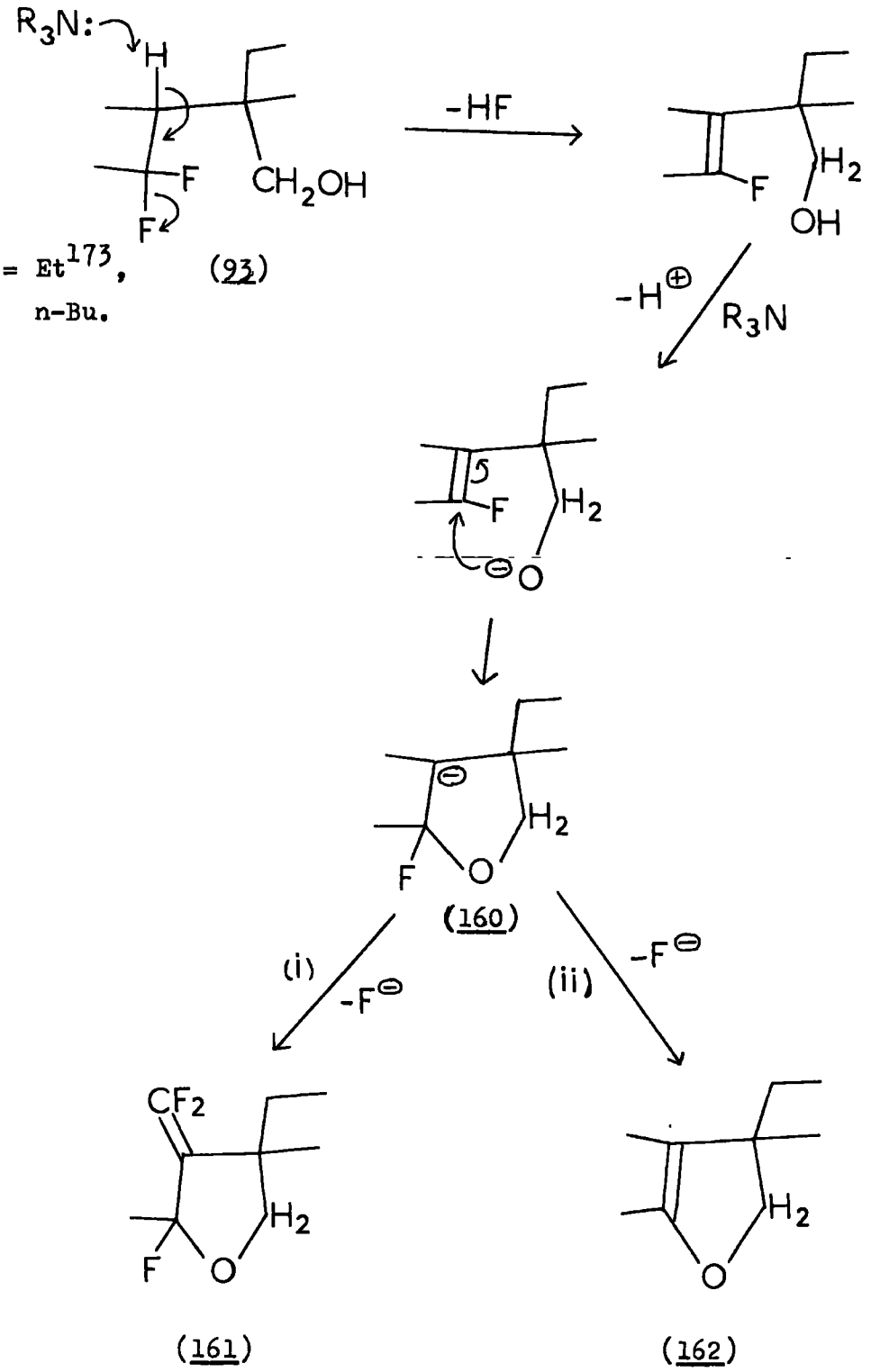
(a) Structural Assignments

Compounds (161) and (162) gave satisfactory elemental analysis. Their structures followed from their ^{19}F n.m.r. spectra. The information in Tables 22 and 23 were used for comparison.

Thus, for compound (161), it was readily established that it contained a difluoromethylene group and a C_2F_5 and two CF_3 groups attached to saturated carbon atoms.

The structure of (162) was assigned by comparison of its ^{19}F n.m.r. chemical shifts with those of the similar dihydrofuran (148) prepared in Section A.2.

Scheme 5



R = Et[173], n-Bu. (93)

(161) (162)

All unmarked bonds are to fluorine.

VI.C METHYL ETHERS

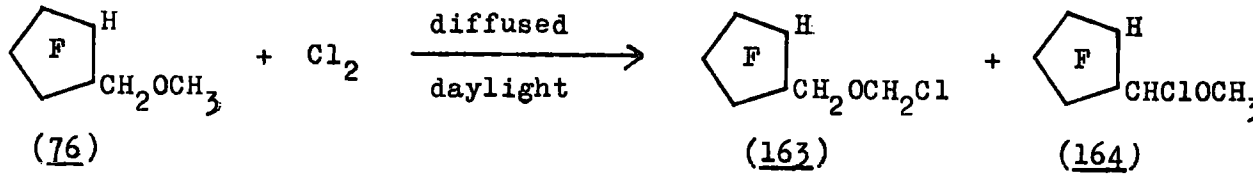
1. Halogenation

(a) Chlorine and Bromine

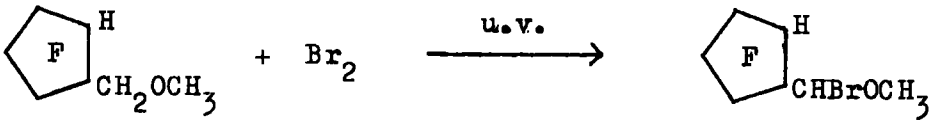
The photochemical chlorination of fluoroethers was studied extensively by Park and co-workers[192, 193]. It was established that chlorination proceeds with an initial attack on the non-fluorinated portion of the ethers, e.g. $C_2H_5OCF_2CFClH$ and the hydrogen of the fluoroalkyl portion is only substituted with difficulty. They found that, in general, chlorination is directed away from the methyl and methylene groups adjacent to CF_3 and CF_2 groups. This is not in general agreement with the directive effects of these groups in the chlorination of alkanes. For example, Henne and Renoll[194] found that chlorination of $CH_3CF_2CH_2Cl$ favoured replacement of hydrogen on the chlorine-containing carbon atom rather than on the carbon atoms not containing chlorine.

The reactions carried out are illustrated in Table 25. It was found that, like Park and co-workers, chlorination was directed away from the fluorinated part of the ether, the major product being (163). Based on this result, the activation energy for hydrogen atom abstraction at the methyl group is lower than at the methylene and thus bromination would be expected to occur preferentially at this site. However, the opposite occurred. Since bromination is a more selective process, it is clear that there is another factor involved in directing chlorination away from the site of preferential attack. By making the chlorination more selective, i.e. using carbon disulphide as a solvent to complex with chlorine atoms[195], attack was indeed preferred at the CH_2 site; a non-complexing solvent, for example carbon tetrachloride, also tended to alter the ratio of attack at the two sites. The results are shown in Table 26 (page 113). It is unclear at the moment why the chlorination of fluoroethers is directed away from the preferred site of attack.

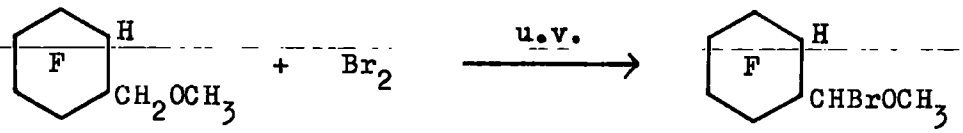
Table 25 Halogenation of Partly Fluorinated Ethers



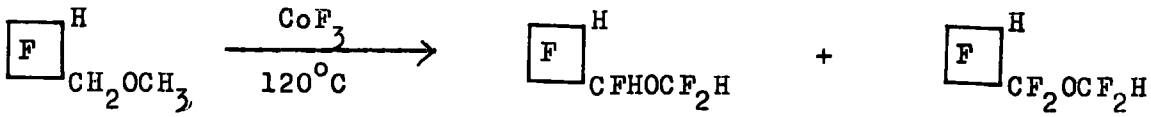
(76) (163) (164)



(76) (165)



(77) (166)



(75) (167) (168)

$CF_3CFHCF_2CH_2OCH_3$ $\xrightarrow[120^\circ C]{CoF_3}$ $CF_3CFHCF_2CH_2OCF_2H$

(105) (169)

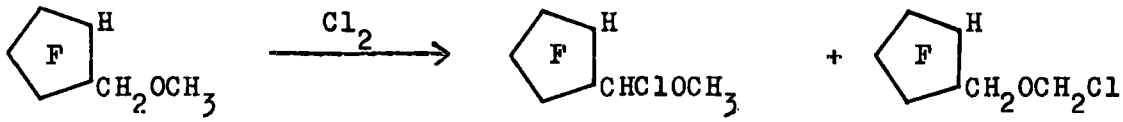
+ $CF_3CFHCF_2CFHOCF_2H$

(170)

+ $CF_3CFHCF_2CFHOCFH_2$

(171)

Table 26 Product Distribution in the Chlorination of (76)



(76) (164) (163)

Solvent	(164) %	(163) %
Compound (76)	9	91
CCl_4	44	56
CS_2	77	23

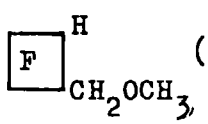
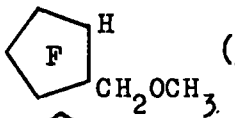
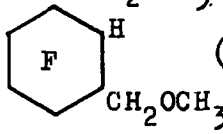
(b) Cobalt Trifluoride Fluorination

The fluorination reactions carried out are shown in Table 25. It is evident from the products obtained that the fluorine-containing substituent is stabilising the compound during reaction and fragmentation products are not observed.

2. Pyrolysis

Isomer mixtures of compounds (75), (76) and (77) were systematically pyrolysed. In each case the trans : cis isomer ratio decreased, indicating isomerisation but otherwise the ethers were recovered unchanged. The results are shown in Table 27 below.

Table 27 Pyrolysis of Partly Fluorinated Ethers

Ether	Temperature (°C)	Isomer Ratio (trans/cis) Before	After
 (75)	600	9.4	1.8
 (76)	650	1.6	1.2
 (77)	685	0.8	0.5

VI.D TESTING OF FUNCTIONAL COMPOUNDS

The co-operative aspect of this project was to provide novel, partly fluorinated organic compounds (especially ethers) for testing as potential anaesthetic agents by I.C.I. Ltd., Pharmaceuticals Division. The rationale for this is that the "ideal" anaesthetic has not yet been discovered[196] and the search is continuing by testing novel compounds for possible activity.

An "ideal" anaesthetic would produce rapid and smooth sleep, be non-interfering with respect to the cardio-respiratory system, be non-toxic, allow rapid emergence and, in the case of inhalation anaesthetic, be non-flammable.

Unfortunately, the compounds that were tested did not produce the desired effects on the test animals and were often toxic.

EXPERIMENTAL

INSTRUMENTATION

Infra-red spectra were recorded on a Perkin-Elmer 457 Grating Infra-red Spectrophotometer using conventional methods.

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

Mass spectra were recorded on an A.E.I. M.S.9 Spectrometer, or on a V.G. Micromass 12B Spectrometer fitted with a Pye Series 104 gas chromatograph. Latterly both spectrometers were linked with a V.G. Datasystem 2000.

Proton (^{1}H) and fluorine (^{19}F) nuclear magnetic resonance spectra were recorded either on a Varian A56/60D spectrometer, operating at 60 and 56.46 MHz respectively with an ambient probe temperature of 40°C or on a Brüker HX90E spectrometer operating at 90 and 84.67 MHz respectively with an ambient probe temperature of 22°C. Chemical shifts are quoted in p.p.m. relative to external T.M.S. and $CFCl_3$, upfield shifts positive.

Quantitative gas liquid chromatography (g.l.c.) analysis was carried out using a Griffin and George D6 or a Varian Aerograph Model 920 Gas Density Balance, 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 methyl silicone on chromosorb P (column Z) or 30% trixylenylphosphate on the same support (column T). Preparative-scale g.l.c. was carried out on a Varian Aerograph Model 920 or "Autoprep" instruments.

Fractional distillations of product mixtures were carried out using a small or a large concentric tube; Fischer-Spaltrohr MS 200 or HMS 500 systems respectively.

Carbon, nitrogen and hydrogen analyses were obtained using a Perkin-Elmer 240 Elemental Analyser. Analyses for halogens were performed by

the literature method[197].

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

Optical rotation measurements were carried out using a Bellingham and Stanley manual polarimeter taking 10cm cells or a Thorn Automation-NPL Automatic Polarimeter Type 243 taking 1cm cells (I.C.I. Ltd.).

CHAPTER VII

EXPERIMENTAL TO CHAPTER II

VII.A LITHIUM FLUORIDE DOSIMETRY

1. Dosemeter Irradiation.

For each irradiation position two sachets each containing six lithium fluoride in polytetrafluoroethene dosemeters were provided and a further sachet of six served as a control and thus were unirradiated. To obtain absorbed doses for accurate thermoluminescence measurements a set of dosemeters was irradiated for 30 seconds at the 3cm. position, another set for one minute at the 5cm. position, and the third set for 3 minutes at the 8cm. position, and then the irradiations were repeated with the duplicate sets of dosemeters. For such a short irradiation time, the source was placed in the irradiating position and the dosemeters lowered into their positions by means of lengths of nylon line from the outer room (Chapter II, Figure 2), irradiated, and then withdrawn. The distances were achieved by means of runways connected to the source's steel tube. These were constructed and attached by University Workshop personnel and the dosemeters were weighted with lead weights so they rested on the runway at the required distance from the source.

2. Absorbed Dose Rate.

The doses absorbed by the dosemeters at each distance were measured by the N.R.P.B. and converted to a dose rate in rads/minute. The results were as shown overleaf.

Using the expression $d = K.D^{-\frac{1}{2}} - x$, where d = measured distance from source (cm), K = constant, x = uncertainty in distance (cm), and D = absorbed dose rate at distance d (rads/min.), a graph was plotted of d versus $D^{-\frac{1}{2}}$ and the uncertainty x found to be 0.5cm. The formula for dose rate was thus:

$$D = \frac{8.22 \times 10^3}{(d - 0.5)^2} \quad \text{rads/minute}$$

Distance (cm.)	Time Irradiated (minutes)	Absorbed dose (rads)	Absorbed dose rate (rads/min.)
3	0.5	542	1085
		641	1281
5	1.0	407	407
		404	404
8	3.0	467	156
		405	135

From this expression, the dose rate was calculated to be 24360 rads/hour at 5cm. and 8760 rads/hour at 8cm. from the source.

VII.B FRICKE DOSIMETRY.

1. Dosimeter Solution Preparation.

Concentrated analytical reagent (A.R.) quality sulphuric acid ($22cm^3$) was added carefully to distilled water (about $600cm^3$) - not demineralized water. When cool, A.R. ferrous ammonium sulphate (0.56g) and A.R. sodium chloride (0.06g) were dissolved in the solution and the volume made up to one litre. This gives a solution of density 1.024 g/cm^3 which was used within a day of its preparation.

2. Dosimeter Irradiation.

Aliquots of approximately $20cm^3$ of solution were placed in cut down recovered Carius tubes to simulate irradiation conditions. Since the working limits of the Fricke dosimeter are 4-40 krad and the optimum is 15-20 krad, samples were irradiated to give an absorbed dose in this range.

3. Typical Calculation.

The worked example illustrates how the absorbed dose rate was calculated to give each of the sets of data shown overleaf.

Dose amd Dose Rate Data

Distance (cm.)	Time (mins.)	Temp. (°C)	Absorbance	Dose (krad)	Dose Rate (krad/hr)	Average
5	58	23	0.625	17.58	18.19	18.44
	58	23	0.642	18.06	18.68	
8	168	23	0.855	24.03	8.58	8.37
	120	23	0.580	16.30	8.15	

Example

20 cm^3 of dosimeter solution was irradiated for 58 minutes at 5cm. from the source. The absorbance was found as 0.625 at 304 nm. at 23°C using 1cm. cells.

Solution density 1.024 g/cm^3

Fe^{2+} ion concentration 1.43×10^{-3} mol/l.

ε at 25°C is 2193 $dm^3/mol/cm$.

The variation of ε with temperature is given by

$$\varepsilon_2 = \varepsilon_1[1 + 0.007(t_2 - t_1)]$$

hence $\varepsilon(23^\circ C) = 2162$

$\therefore$ Ferric ion concentration $= \frac{0.625}{2162} = 0.289 \times 10^{-3}$ mol/l.

1 Mrad or 1000 krad produces change of

$$G \times 1.036 \times 10^{-6} \text{ mol/g.}$$

or $$G \times 1.036 \times 1.024 \times 10^{-3} \text{ mol/l.}$$

where 1.024 g/cm^3 is dosimeter solution density.

For Fricke dosimeter $G(Fe^{3+}) = 15.5$

D krad produces change of 0.289×10^{-3} mol/l.

$\therefore$ Dose (D) is $1000 \times \frac{0.289}{15.5 \times 1.036 \times 1.024} = 17.58$ krad

$\therefore$ Absorbed dose rate is $\frac{17.58}{58}$ krad per minute = 18.19 krad/hour.

CHAPTER VIII

EXPERIMENTAL TO CHAPTER III

VIII. A REAGENTS

Perfluorocyclohexene was available within this laboratory and F-cyclo-pentene and -butene were prepared by technical staff by literature methods.

Methanol and cyclohexanol were purified and dried by refluxing a portion with magnesium turnings and iodine until the iodine colour disappeared, then adding the bulk of the alcohol and the lot being fractionally distilled after refluxing 1 - 2 hours.

Acetaldehyde was fractionally distilled through a 20cm Vigreux and stored over molecular sieve 4A under nitrogen in a fridge.

Dimethyl ether was taken directly from a large storage cylinder without further purification.

VIII. B GENERAL PROCEDURE

All addition reactions were carried out using glass Carius tubes of ca. 100cm^3 volume and the reactants were degassed thoroughly before sealing the tubes under vacuum. Evacuation of tubes and transfer of gaseous reagents were performed using conventional vacuum line techniques.

Approximately one per cent by weight of benzoyl peroxide was used in addition reactions chemically initiated at ca. 85^{o}C. Some of the addition reactions were performed on more than one occasion and a typical set of reaction conditions are given in such cases.

VIII. C ADDITIONS TO F-CYCLOHEXENE

1. By Gamma-Ray Initiation

(a) Methanol

A mixture containing F-cyclohexene (29.1g, 111 mmol) and methanol (47.7g, 1.49 mol) was irradiated to a total dose of 3.0 x 10^7 rad. The

mixture was then washed with water, the fluorocarbon lower layer separated, dried ($MgSO_4$) and filtered. Distillation provided 2H-decafluorocyclohexylmethanol (68), (25.9g, 79%), but failed to separate the geometric isomers: b.p. 148-150°C; (Found: C, 29.0; H, 1.4; F, 64.3%. $C_7H_4F_{10}O$ requires C, 28.59; H, 1.37; F, 64.59%); n.m.r. spectrum no.1; i.r. spectrum no.1; mass spectrum no. 1.

(b) Cyclohexanol

A mixture containing F-cyclohexene (13.44g, 51.3 mmol) and cyclohexanol (15.31g, 153 mmol) was irradiated to a dose of 1.33×10^7 rad. Cyclohexanol was then distilled off and the residue fractionally sublimed to give 1-(2'H-decafluorocyclohexyl)-cyclohexanol (71), (2.28g, 12%), but failed to separate the geometric isomers: (Found: C, 39.4; H, 4.1%. $C_{12}H_{12}F_{10}O$ requires C, 39.78; H, 3.31; F, 52.49%); n.m.r. spectrum no.2; i.r. spectrum no.2; mass spectrum no. 2.

(c) Acetaldehyde

A mixture containing F-cyclohexene (21.8g, 83.2 mmol) and acetaldehyde (37.04g, 842 mmol) was irradiated to a dose of 3.0×10^7 rad. Distillation of the mixture gave only cis-2H-decafluorocyclohexyl methyl ketone (74), (22.10g, 87%): b.p. 128°C; (Found: C, 31.4; H, 1.1; F, 61.8%. $C_8H_4F_{10}O$ requires C, 31.37; H, 1.31; F, 62.09%); n.m.r. spectrum no. 3; i.r. spectrum no. 3; mass spectrum no. 3.

(d) Dimethyl Ether

A mixture containing F-cyclohexene (13.98g, 53.4 mmol) and dimethyl ether (7.57g, 164.6 mmol) was irradiated to a dose of 1.5×10^7 rad. The work up procedure when using dimethyl ether is described later in Chapter IX.D.1. Distillation of the liquid recovered gave 2H-decafluorocyclohexyl methoxymethane (77), (12.78g, 78%), as an isomer mixture which showed as a single peak on all g.l.c. columns available: b.p. 143°C; (Found: C, 31.3; H, 2.3, F, 61.5%. $C_8H_6F_{10}O$ requires C, 31.17; H, 1.95; F, 61.69%.); n.m.r. spectrum no.4; i.r. spectrum no. 4; mass spectrum no. 4.

2. By Benzoyl Peroxide Initiation

(a) Methanol

A mixture containing F-cyclohexene (41.2g, 157 mmol), methanol (23.5g, 734 mmol) and benzoyl peroxide (0.75g) was heated at 95°C for 24½ hours. Work-up as described in Section C.1(a) gave (68), (30.94g, 67%).

(b) Acetaldehyde

A mixture containing F-cyclohexene (32.4g, 124 mmol), acetaldehyde (14.32g, 325 mmol) and benzoyl peroxide (0.64g) was heated at 90°C for 23½ hours. Fractional distillation gave (74, cis), (30.64g, 81%) and from the pot residue a further amount of this isomer (1.40g, 3.7%) was separated by preparative-scale g.l.c. (column Z, 150°C) as well as trans-2H-decafluorocyclohexyl methyl ketone (74), (1.37g, 3.6%): m.p. 36°C, b.p. 143°C; (Found: C, 31.6; H, 1.1%. $C_8H_4F_{10}O$ requires C, 31.37; H, 1.31; F, 62.09%); n.m.r. spectrum no. 5, i.r. spectrum no. 5, mass spectrum no. 5.

(c) Dimethyl Ether

A mixture containing F-cyclohexene (15.4g, 58.8 mmol), dimethyl ether (6.77g, 147.2 mmol) and benzoyl peroxide (0.38g) was heated at 85°C for 68 hours. Distillation of the liquid remaining after allowing excess dimethyl ether to evaporate gave (77), (10.2g, 56%) and from the pot residue a further amount of this compound (3.15g, 17%) was separated by preparative g.l.c. (column Z, 200°C) as well as di-(2'H-decafluorocyclohexyl)-methyl ether (78) as an isomer mixture, (2.29g, 14%): m.p. 81°C; (Found: C, 29.6; H, 0.9; F, 66.3%. $C_{14}H_6F_{20}O$ requires C, 29.47; H, 1.05; F, 66.66%); n.m.r. spectrum no 6, i.r. spectrum no. 6, mass spectrum no. 6.

VIII. D ADDITIONS TO F-CYCLOPENTENE

1. By Gamma-Ray Initiation

(a) Methanol

A mixture containing F-cyclopentene (34.73g, 164 mmol) and methanol (17.29g, 540 mmol) was irradiated to a dose of 1.6×10^7 rad. The mixture was then washed with water, the fluorocarbon lower layer separated, dried ($MgSO_4$) and filtered. Distillation gave 2H-octafluorocyclopentylmethanol (17), (24.7g, 68%) but failed to separate the geometric isomers. A pure sample of trans-2H-octafluorocyclopentylmethanol (17) was separated by preparative g.l.c. (column Z): b.p. 139°C ; (Found: C, 29.5; H, 1.7; F, 61.9%. Analysis was carried out on the isomer mixture. $C_6H_4F_8O$ requires C, 29.51; H, 1.64; F, 62.30%); n.m.r. spectrum no. 7, i.r. spectrum no. 7, mass spectrum no. 7.

(b) Cyclohexanol

A mixture containing F-cyclopentene (14.8g, 69.8 mmol) and cyclohexanol (15.3g, 153 mmol) was irradiated to a dose of 1.16×10^7 rad. Removal of unchanged starting materials by distillation left a pot residue which was distilled at reduced pressure through a 10cm. Vigreux to give 1-(2'H-octafluorocyclopentyl)-cyclohexanol (70), (3.53g, 16%) but failed to separate the geometric isomers: m.p. 48°C; (Found: C, 42.6; H, 3.8; F, 48.4%. $C_{11}H_{12}F_8O$ requires C, 42.31; H, 3.85; F, 48.72%); n.m.r. spectrum no. 8, i.r. spectrum no. 8, mass spectrum no. 8.

(c) Acetaldehyde

A mixture containing F-cyclopentene (19.08g, 90 mmol) and acetaldehyde (19.25g, 440 mmol) was irradiated to a dose of 1.59×10^7 rad. Fractional distillation gave cis-2H-octafluorocyclopentyl methyl ketone (73), (10.2g, 44%): b.p. 112°C; (Found: C, 33.0; H, 1.2; F, 59.6%. $C_7H_4F_8O$ requires C, 32.81; H, 1.56; F, 59.38%); n.m.r. spectrum no. 9, i.r. spectrum no. 9, mass spectrum no. 9; and trans-2H- octafluoro-

cyclopentyl methyl ketone (73), (8.47g, 36.8%): b.p. 128°C; (Found: C, 32.8; H, 1.8; F, 59.6%. $C_7H_4F_8O$ requires C, 32.81; H, 1.56; F, 59.38%); n.m.r. spectrum no. 10, i.r. spectrum no. 10, mass spectrum no. 10.

(d) Dimethyl Ether

A mixture containing F-cyclopentene (10.50g, 49.5 mmol) and dimethyl ether (6.87g, 149 mmol) was irradiated to a dose of 1.5×10^7 rad. After allowing dimethyl ether to evaporate off, the liquid remaining was fractionally distilled to give trans-2H-octafluorocyclopentyl methoxymethane (76), (7.4g, 58% total yield of both isomers) : b.p. 121°C; (Found: C, 32.4; H, 2.6; F, 58.7%. $C_7H_6F_8O$ requires C, 32.56; H, 2.32; F, 58.91%); n.m.r. spectrum no. 11, i.r. spectrum no. 11, mass spectrum no. 11; and cis-2H-octafluorocyclopentyl methoxymethane (76): b.p. 127°C; (Found: C, 32.4; H, 2.6; F, 58.7%. $C_7H_6F_8O$ requires C, 32.56; H, 2.32; F, 58.91%); n.m.r. spectrum no. 12, i.r. spectrum no. 12, mass spectrum no. 12. Analysis was carried out on the isomer mixture.

2. By Benzoyl Peroxide Initiation

(a) Methanol

A mixture containing F-cyclopentene (41.5g, 196 mmol), methanol (25.3g, 790 mmol) and benzoyl peroxide (0.60g) was heated at 95°C for 24 hours. Work-up as described in Section D.1(a) gave (17), (30.60g, 64%) as an isomer mixture.

(b) Acetaldehyde

A mixture containing F-cyclopentene (59.26g, 279 mmol), acetaldehyde (49.05g, 1.11 mol) and benzoyl peroxide (0.74g), divided between two Carius tubes, was heated at 80°C for 115 hours. Fractional distillation gave (73, cis), (21.94g, 30.6%), b.p. 112°C and (73, trans), (13.85g, 19.4%), b.p. 128°C.

(c) Dimethyl Ether

A mixture containing F-cyclopentene (10.3g, 48.6 mmol), dimethyl

ether(7.23g, 157 mmol), and benzoyl peroxide (0.26g) was heated at 85°C for 68 hours. Distillation of the liquid recovered gave (76), (6.33g, 50.5%), as an isomer mixture. The two-to-one adduct, analogous to (78), was detected by g.l.c. in the distillation pot residue but was not separated.

VIII.E ADDITIONS TO F-CYCLOBUTENE

1. By Gamma-Ray Initiation

(a) Methanol[54]

A mixture containing F-cyclobutene (18.5g, 114 mmol) and methanol (11.58g, 362 mmol) was irradiated to a dose of 5.6×10^6 rad. The mixture was then washed with water, the fluorocarbon lower layer separated, dried ($MgSO_4$) and filtered. Distillation at reduced pressure gave 2H-hexafluorocyclobutylmethanol (67), (18.83g, 85%) but failed to separate the geometric isomers. Preparative-scale g.l.c. (column A) gave trans-2H-hexafluorocyclobutylmethanol (67) : b.p. 128°C; (Found: C, 30.7; H, 2.1; F, 58.3%. Calc. for $C_5H_4F_6O$: C, 30.93; H, 2.06; F, 58.76%); n.m.r. spectrum no.13, i.r. no. 13, mass spectrum no. 13; and cis-2H-hexafluorocyclobutylmethanol (67) : b.p. 141°C; (Found: C, 31.0; H, 2.5; F, 58.2%. Calc. for $C_5H_4F_6O$: C, 30.93; H, 2.06; F, 58.76%); n.m.r. spectrum no. 14 , i.r. spectrum no. 14, mass spectrum no. 14.

(b) Cyclohexanol

A mixture containing F-cyclobutene (8.8g, 54.3 mmol) and cyclohexanol (18.81g,188 mmol) was irradiated to a dose of 1.33×10^7 rad. After removing unchanged F-cyclobutene, cyclohexanol was distilled off and the pot residue then redistilled at reduced pressure through a 10 cm. Vigreux. This gave 1-(2'H-hexafluorocyclobutyl)-cyclohexanol (69) but failed to separate the geometric isomers. Preparative-scale g.l.c. (column Z) gave 1-(trans-2'H-hexafluorocyclobutyl)-cyclohexanol (69) :

b.p. 194°C; (Found: C, 46.1; H, 4.9; F, 43.3%. $C_{10}H_{12}F_6O$ requires C, 45.80; H, 4.58; F, 43.51%); n.m.r. spectrum no. 15, i.r. spectrum no. 15 ,, mass spectrum no. 15; and 1-(cis-2'H-hexafluorocyclobutyl)-cyclohexanol (69) : m.p. 54°C; (Found: C, 46.1; H, 4.9; F, 43.3%. $C_{10}H_{12}F_6O$ requires C, 45.80; H, 4.58; F, 43.51%); n.m.r. spectrum no. 16, i.r. spectrum no. 16. Analysis was performed on the isomer mixture.

(c) Acetaldehyde[54]

A mixture containing F-cyclobutene (20.51g, 127 mmol) and acetaldehyde (23.28g, 530 mmol) was irradiated to a dose of 1.46×10^7 rad. Fractional distillation gave cis-2H-hexafluorocyclobutyl methyl ketone (72), (4.0g, 15%): b.p. 100°C; (Found: C, 35.1; H, 2.2; F, 54.9%. Calc. for $C_6H_4F_6O$: C, 34.95; H, 1.94; F, 55.34%); n.m.r. spectrum no. 17, i.r. spectrum no. 17, mass spectrum mo. 16; and trans-2H-hexafluorocyclobutyl methyl ketone (72), (13.7g, 52.5%) : b.p. 116°C; (Found: C, 34.7; H, 1.9; F, 55.9%. Calc. for $C_6H_4F_6O$: C, 34.95; H, 1.94; F, 55.34%); n.m.r. spectrum no. 18, i.r. spectrum no. 18, mass spectrum no. 17.

(d) Dimethyl Ether

A mixture containing F-cyclobutene (14.9g, 93 mmol) and dimethyl ether (11.0g, 239 mmol) was irradiated to a dose of 1.23×10^7 rad. Distillation of the liquid recovered gave 2H-hexafluorocyclohexyl methoxymethane (75), (14.20g, 74%). A portion was separated by preparative g.l.c. (column A, 135°C) to give trans-2H-hexafluorocyclo-butyl methoxymethane (75): b.p. 106°C; (Found: C, 34.4; H, 3.2; F, 54.5%. $C_6H_6F_6O$ requires C, 34.62; H, 2.88; F, 53.85%); n.m.r. spectrum no. 19, i.r. spectrum no. 19, mass spectrum no. 18; and cis-2H-hexafluorocyclo-butyl methoxymethane (75): b.p. 124°C; (Found: C, 34.4; H, 3.2; F, 54.5%. $C_6H_6F_6O$ requires C,34.62; H, 2.88; F, 53.85%); n.m.r. spectrum no. 20, i.r. spectrum no. 20. Analysis was performed on the isomer mixture.

2. By Benzoyl Peroxide Initiation

(a) Methanol

A mixture containing F-cyclobutene (11.1g, 68 mmol), methanol (9.48g, 296 mmol) and benzoyl peroxide (0.17g) was heated at 80°C for 19½ hours. Work-up as described in Section E.1(a) gave the alcohol (67), (7.52g, 57%), as an isomer mixture.

(b) Acetaldehyde

A mixture containing F-cyclobutene (9.4g, 58 mmol), acetaldehyde (10.11g, 230 mmol) and benzoyl peroxide (0.2g) was heated at 80°C for 19½ hours. Fractional distillation gave (72, cis), (3.13g, 24%), b.p. 100°C and (72, trans), (8.24g, 64%), b.p. 116°C.

(c) Dimethyl Ether

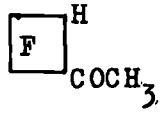
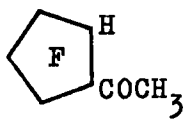
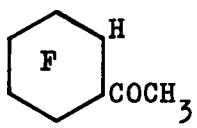
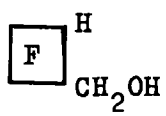
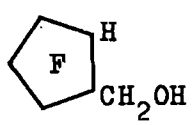
A mixture containing F-cyclobutene (11.9g, 73.5 mmol), dimethyl ether (8.17g, 177.6 mmol) and benzoyl peroxide (0.27g) was heated at 80°C for 64½ hours. Distillation gave (75), (7.88g, 51%), as an isomer mixture. The two-to-one adduct, analogous to (78), was detected by g.l.c. in the pot residue but was not separated.

VIII. F IRRADIATION OF STEREOISOMERS

In order to show that the product mixtures arise from kinetic control, samples of stereoisomers were placed in Pyrex n.m.r. tubes with an excess of methanol (for an alcohol adduct) or acetaldehyde (for a methyl ketone adduct) and degassed before sealing under vacuum. The high field ^{19}F n.m.r. spectra of the samples were recorded and they were then irradiated before the spectra were recorded again. In no case was a signal due to the alternative isomer detected.

The quantities of sample and solvent used and the total dose of radiation received by each mixture is summarized overleaf in Table 28.

Table 28 Experimental Conditions for Stereoisomer Irradiations

Compound	Isomer	Fluorocarbon g, mmol	Solvent[a] g, mmol	Irradiation Dose, rad
 (72)	cis	0.34, 1.65	1.50, 34.1	7×10^6
	trans	0.27, 1.3	1.50, 34.1	7×10^6
 (73)	cis	0.55, 2.1	0.95, 21.6	7×10^6
	trans	0.49, 1.91	0.95, 21.6	7×10^6
 (74)	trans	0.24, 0.8	0.70, 15.9	1.5×10^7
 (67)	trans	0.56, 2.9	0.46, 14.4	1.5×10^7
 (17)	trans	0.2, 0.8	0.2, 6.2	7×10^6

a Acetaldehyde for (72), (73) and (74); methanol for (67) and (17).

VIII.G RESOLUTION OF ENANTIOMERS

1. Preparation of (-)-Menthydrazide (88)[141]

This was a two stage operation. Natural (-)-menthol (187.5g, 1.202 mol), ethyl chloroformate (442.5g, 4.078 mol), and six drops of pyridine were refluxed for twenty hours. The mixture was doubly distilled to give ethyl (-)-menthyl carbonate,(199.8g, 73%), b.p. 73°C, 0.1 mmHg, which was then refluxed at 130°C for 89 hours with hydrazine hydrate (71.2g, 1.424 mol) and diglyme (250 cm^3) as solvent. (The literature solvent is 2-methoxyethanol). Fractional distillation at reduced pressure left a residue (90g) which solidified on cooling. Two recrystallisations from 60-80 petrol gave (-)-menthydrazide (88), (29g, 15%), m.p. 91-93°C, $[\alpha]_D^{25} = -80.4°$. Literature: m.p. 101° [141] or 96-98°C[138], $[\alpha]_D^{25} = -79°$ [138].

2. Formation of Menthydrazones

(a) Compound (74)

Formation of the menthydrazone of (74) was attempted under a variety of increasingly vigourous reaction conditions as outlined below.

(i) (-)-Menthydrazide (88) (0.49g, 2.3 mmol) and (74) (0.70g, 2.3 mmol) were stirred in neutral ethanol at room temperature for three days. At the end of this time no precipitate had formed, thus no reaction.

(ii) Compound (88) (0.96g, 4.5 mmol) and (74) (1.37g, 4.5mmol) were dissolved in the minimum volume of ethanol buffered with sodium acetate and glacial acetic acid and the mixture refluxed for 15 hours. No precipitate formed, thus no reaction.

(iii) Compound (88) (2.14g, 10.0 mmol) and (74) (3.05g, 10.0 mmol) were dissolved in a xylene/ 2-methoxyethanol solution and refluxed for six hours. No precipitate formed, thus no reaction.

(b) Compound (72, trans)

Reaction with (88) occurred readily under mild conditions. Thus,

(88) (15.62g, 73 mmol) was dissolved in buffered ethanol (75 cm^3) and (72) (15.05g, 73 mmol) was added. The mixture was refluxed for 30 minutes and left to cool overnight. A light-yellow solid mass had formed. It was filtered off, dried in the air and recrystallised from ethanol containing 10% added water to give trans-2H-hexafluorocyclobutyl methyl ketone (-)-menthydrazone (89), (19.73g, 67%): m.p. 166-8°C, decomposition; (Found: C, 50.5; H, 6.2; N, 7.1%. $C_{17}H_{24}F_6N_2O_2$ requires C, 50.75; H, 5.97; N, 6.97%); n.m.r. spectrum no. 21, i.r. spectrum no. 21.

3. Polarimeter Measurements

All rotation measurements quoted are specific rotations, that is $[\alpha]_D^T$, where T is the ambient temperature around the polarimeter at the time of measurements. The product obtained above after one recrystallisation from ethanol gave a polarimeter reading of -52.7°. After a further recrystallisation from ethanol, the reading was -52.1° and after a third it was -52.7°. The specific rotations obtained after recrystallising from cyclohexane, carbon tetrachloride, toluene and benzene were -52.6°, -53.7°, -53.2° and -53.0° respectively. The discrepancies in these values are due to errors in polarimeter readings or, more likely, incomplete solution of (89) in the solvent.

4. T.l.c. Data

Samples of (89) were run 15 cm. along plates to enhance the possibility of separation. The R_f values obtained with a variety of solvents and solvent systems are shown overleaf in Table 29. It was noted that when ammonia was included in a solvent system, two spots were observed, one under short wavelength ultraviolet light only and the other under long wavelength light only.

5. Chemical Shift Reagents

Two optishift reagents were tried, Eud_3 which causes signals to shift downfield away from TMS and Prd_3 which causes signals to shift in

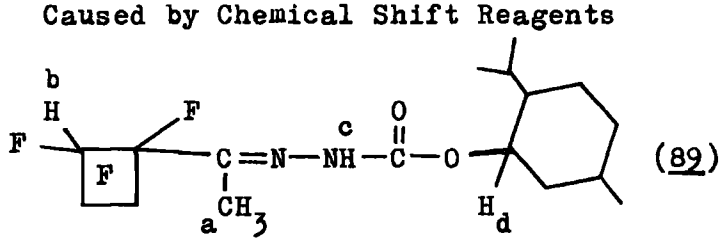
Table 29 R_f Values for (89) with Different Mobile Phases

Solvent/ Solvent System	R_f Value (a) 366nm.	(b) 254nm.	Observation
Hexane	0.02	0.04	
Toluene	0.05	0.10	
Dichloromethane		0.28	No spot using 366 nm.
Ether		0.64	No spot using 366 nm.
Ethyl acetate	0.69	0.69	No spreading of spot.
Toluene/Ether 50:50		0.65	No spot using 366 nm.
Toluene/Ethyl acetate/ Ammonia 10:10:1	0.72	0.32-0.51	Decomposition product at 0.72.
Special mixture*	0.73	0.6-0.7	Decomposition as above.

* Toluene/Ethyl acetate/880 Ammonia/Ethanol 60:20:10:35

the other direction towards TMS. The methyl signal (marked 'a' below) remained a singlet throughout these experiments. The results are summarized in Table 30 below.

Table 30 Changes in Chemical Shifts of Particular Signals in (89) Caused by Chemical Shift Reagents



(89)

Signal	Before, p.p.m.	Eud_3 After 1st addition	Eud_3 After 2nd addition	Prd_3 After 1st addition	Prd_3 After 2nd addition
a	1.96	1.97	1.89	1.88	1.94
b	5.33	5.37	5.31	5.19	5.05
c	8.36	8.53	8.92	7.85	6.86
d	4.67	4.94	5.62	3.98	*

* No longer observed.

6. Formation of Optically Active Amine Bisulphite

Sulphur dioxide was bubbled through a mixture of (-)-1-phenyl ethylamine (1.26g, 10.4 mmol) and 5cm^3 of ether to which had been added some water. Gas was bubbled in until the initially formed white solid was replaced by a homogeneous yellow liquid. To this optically active amine bisulphite was added (74) (4.00g, 13.1 mmol). For reaction to occur, the solution should immediately be decolourised with the evolution of heat and sulphur dioxide. However, a white paste formed only slowly, did not solidify, and was therefore not investigated further.

CHAPTER IX

EXPERIMENTAL TO CHAPTER IV

IX.A GENERAL

The unsaturated fluorocarbons used were either available within the laboratory, or were prepared by technical staff, or were personally prepared by literature methods.

The general procedure for addition reactions was employed, as described on page 120.

IX.B ADDITIONS TO ALCOHOLS

1. Methanol

(a) F-3,4-dimethyl hex-3-ene (92)

A mixture containing (92) (31.0g, 77.5 mmol) and methanol (13.58g, 424 mmol) was irradiated to a dose of 1.45×10^7 rad. The mixture was then washed with water, the lower fluorocarbon layer separated, dried ($MgSO_4$) and filtered. Reduced pressure distillation gave 1,1,3-trihydro-F-2,3-dimethyl-2-ethyl-pentan-1-ol (93), (22.30g, 66%): b.p. 167-9°C; (Found: C, 24.8; H, 1.3; F, 70.0%. $C_9H_4F_{16}O$ requires C, 25.00; H, 0.93; F, 70.37%); n.m.r. spectrum no. 22, i.r. spectrum no. 22, mass spectrum no. 19.

(b) F-1,2-bis(cyclobutyl)cyclobutene

A mixture containing the trimer (4.35g, 8.95 mmol) and methanol (1.04g, 32.5 mmol) was irradiated to a dose of 1.64×10^7 rad. The liquid recovered (5.36g) was a two phase mixture, the lower layer being shown (column A) to be essentially unchanged trimer and the upper layer to be unchanged methanol.

(c) F-2-butyne

A mixture containing F-2-butyne (17.0g, 105 mmol) and methanol

(12.18g, 380 mmol) was irradiated to a dose of 5.4×10^6 rad. On opening the tube, 2.42g of unchanged acetylene was recovered and 23.84g of liquid was collected. Of this liquid, 12.82g was transferred off under vacuum and found to be mainly trans-2-methoxy 3-hydro-F-but-2-ene (94) which was identified by comperison of its infra-red and n.m.r. spectra with those of authentic sample spectra[150]. The residual 10.52g of liquid was washed with water, the lower layer separated, dried ($MgSO_4$) and filtered to give, after removal of minor impurities by preparative g.l.c. (column O, 115°C), (E)-(2-trifluoromethyl)-4,4,4-trifluorobut-2-en-1-ol (95), (2.4g, 12%): b.p. 104°C; (Found: C, 30.7; H,2.3; F, 58.3%. $C_5H_4F_6O$ requires C,30.92; H, 2.06; F, 58.76%); n.m.r. spectrum no. 23, i.r. spectrum no. 23, mass spectrum no. 20.

(d) F-2,3-dimethyl buta-1,3-diene

A mixture containing the diene (7.84g, 30.0 mmol) and methanol (4.0g, 125 mmol) was irradiated to a dose of 1.22×10^7 rad. On opening the tube, the mixture was washed with water, the fluorocarbon separated, dried ($MgSO_4$) and filtered. By comparison of g.l.c. retention times, the components in the 5.07g of liquid recovered were shown to be the products of nucleophilic addition and substitution[143].

2. Other Alcohols

(a) Ethanol and Cyclohexanol

(i) Ethanol and (92)

A mixture of (92) (22.06g, 55.2 mmol) and ethanol (19.84g, 430 mmol) was irradiated to a dose of ca. 10^8 rad. After this time, the liquid interface had not moved and g.l.c. (column O) showed the fluorocarbon layer to be unchanged (92) only.

(ii) Cyclohexanol and (92)

A mixture of (92) (17.63g, 44 mmol) and cyclohexanol (12.35g, 123.5 mmol) was irradiated to a dose of 1.33×10^7 rad. As in the previous experiment, g.l.c. (column Z) showed the fluorocarbon layer to

be unchanged (92) only.

(b) Glucose

(i) Glucose and F-propene

A mixture containing anhydrous glucose (18.72g, 104 mmol) and F-propene (5.0g, 33 mmol) was irradiated to a dose of 1.5×10^7 rad. On adding the recovered solid to water, no lower layer separated, indicating no incorporation of F-propene.

(ii) Using dimethyl sulphoxide as a solvent

A mixture of glucose (13.1g, 72.8 mmol) dissolved in dry dimethyl sulphoxide (20 cm^3) and F-propene (7.9g, 52.7 mmol) was irradiated to a dose of 1.2×10^7 rad. On opening the tube, 3.7g of gas was recovered and the liquid residue added to water. No lower layer separated, indicating no reaction had occurred.

(c) Sorbitol and F-propene using Dimethyl Sulphoxide as a Solvent

A mixture of sorbitol (19.95g, 109.6 mmol) dissolved in dry dimethyl sulphoxide (30 cm^3) and F-propene (7.2g, 48 mmol) was irradiated to a dose of 3.4×10^7 rad and was heated at 85°C for a part of this irradiation (ca. 9×10^6 rad). On opening the tube, work-up as in the preceding experiment gave 2.3g of unchanged gas and no lower layer.

IX.C ADDITIONS TO ACETALDEHYDE

1. F-3,4-dimethyl hex-3-ene (92)

Divided between two Carius tubes, a mixture of (92) (80.55g, 201.3 mmol) and acetaldehyde (31.00g, 704.5 mmol) was irradiated to a dose of 1.4×10^7 rad. The mixture was then heated (125°C) for six hours to distill off unchanged starting materials and the residue was transferred off intractable tar under vacuum to give 3-pentafluoroethyl-3,4-bis (trifluoromethyl)-5,5,6,6,6-pentafluorohexan-2-one (96), (84.79g, 94%): b.p. 150°C, decomposition; (Found: C, 27.0; H, 0.8; F, 68.1%. $C_{10}H_4F_{16}O$

requires C, 27.02; H, 0.90; F, 68.47%); n.m.r.spectrum no. 24, i.r. spectrum no. 24, mass spectrum no. 21.

2. F-bicyclobutylidene

A mixture of dimer (1.75g, 5.3 mmol) and acetaldehyde (0.75g, 17 mmol) was irradiated to a dose of 3.4×10^6 rad. Separation of the one-to-one adduct (97) by preparative g.l.c. (column A, 110°C) caused decomposition to a mixture of two components, the second of longer g.l.c. retention time being the one-to-one adduct. The decomposition product was separated by preparative g.l.c. (column T, 115°C) to give 1-(F-cyclobutenyl)-hexafluorocyclobutyl methyl ketone(98): analysis was unsatisfactory; n.m.r. spectrum no. 25, i.r. spectrum no. 25, mass spectrum no. 22.

3. F-bicyclopentylidene

(a) Without a Cosolvent

A mixture containing the dimer (7.25g, 17 mmol) and acetaldehyde (3.13g, 71 mmol) was irradiated to a dose of 6.7×10^6 rad. The level of the interface was unchanged and the upper layer had taken on a dark brown colouration during this time. Only unchanged dimer was recovered.

(b) Using (72, trans) as a Cosolvent

It was noted that both the dimer and acetaldehyde would dissolve separately in (72). However, when the three components were placed together , the dimer separated as a lower layer although it is possible that it was partially miscible in the cosolvent.

Thus, a mixture containing dimer (5.80g, 13.7 mmol), acetaldehyde (2.49g, 56.6 mmol) and (72) (0.30g, 1.5 mmol) was irradiated to a dose of 4×10^6 rad. The hydrocarbon layer had again tarred up and 4.24g of non-black liquid was recovered and identified by g.l.c. (column O) as unchanged dimer only.

4. F-1,2-bis(cyclobutyl)cyclobutene

A mixture containing trimer (5.37g, 11.1 mmol) and acetaldehyde

(1.5g, 34.0 mmol) was irradiated to a dose of 1.22 x 10^7 rad. The upper layer had formed a black tar and 4.96g of liquid was recovered and identified by g.l.c. (column O) as unchanged trimer only.

5. F-2-butyne

A mixture containing F-2-butyne (24.0g, 148 mmol) and acetaldehyde (19.0g, 432 mmol) was irradiated to a dose of 5.5 x 10^6 rad. The mixture was poured into water, separated the lower layer, dried it ($MgSO_4$) and filtered to give 8.85g of liquid. This was distilled to give (E)-3-trifluoromethyl-1,1,1-trifluoropent-2-en-4-one (99), (5.74g, 19%): b.p. 88-89°C; (Found: C, 35.2; H, 2.3; F, 54.8%. $C_6H_4F_6O$ requires C, 34.95; H, 1.94; F, 55.34%); n.m.r. spectrum no. 26, i.r. spectrum no. 26, mass spectrum no. 23.

6. F-2,3-dimethyl buta-1.3-diene

A mixture containing the diene (12.19g, 46.5 mmol) and acetaldehyde (14.53g, 330 mmol) was irradiated to a dose of 1.2 x 10^7 rad. The mixture was washed with water, the lower layer separated, dried ($MgSO_4$) and filtered to give 12.75g of fluorocarbon which on distillation gave 2,3-bis(trifluoromethyl)-1,1,4,4-tetrafluorohex-1-en-5-one (100), (4.43g, 31%): b.p. 116°C; (Found: C, 31.5; H, 1.3; F, 61.6%. $C_8H_4F_{10}O$ requires C, 31.37; H, 1.31; F, 62.09%); n.m.r. spectrum no. 27, i.r. spectrum no. 27, mass spectrum no. 24; and 4,5-bis(trifluoromethyl)-3,3,6,6-tetrafluorooctan-2,7-dione (101), (4.85g, 30%): analysis was unsatisfactory; n.m.r. spectrum no. 28, i.r. spectrum no. 28, mass spectrum no. 25.

IX.D ADDITIONS TO DIMETHYL ETHER

1. General Procedure

Because of the highly volatile nature of the ether, a rather different work-up method was developed for these reactions. The Carius tube was cooled in liquid air, opened and the tube left to warm up to room temperature of its own accord. In this way, the ether was allowed to

evaporate gently without flushing out products with it but it did mean that unchanged fluoroalkene was, in general, not recovered if its boiling point was below room temperature and in such cases only the yield of recovered product is quoted and not conversions. The residual material was then either fractionally distilled if it was a liquid or sublimed or recrystallised in the case of solids.

2. F-ethene

Before use, the F-ethene was passed through a column of silica gel to remove from it stabilisers and radical inhibitors.

A mixture of F-ethene (3.6g, 36 mmol) and dimethyl ether (9.3g, 202 mmol) was irradiated within a steel cylinder jacket near the source for 880 hours. A waxy viscous liquid (2.82g) was recovered which gave a small quantity of colourless mobile liquid under vacuum transfer. G.l.c. (column O, 175°C) showed this to be a mixture of four components which were identified as the telomers (102) from their mass spectra, nos. 26, 27 and 28 respectively.

3. Chlorotrifluoroethene

A mixture containing the alkene (9.5g, 89.2 mmol) and dimethyl ether (19.9g, 432.6 mmol) was irradiated to a dose of 2.1×10^7 rad. A colourless liquid (11.49g) was recovered which, on vacuum transfer, gave 1.30g of volatile material which contained the the two components of shortest g.l.c. retention time. These were separated by preparative g.l.c. (column Z, 170°C) and identified as 3-chloro-2,2,3-trifluoropropyl methyl ether (103): b.p. 103°C; (Found: C, 29.8; H, 4.0; F, 34.3; Cl, 22.6%. $C_4H_6F_3ClO$ requires C, 29.54; H, 3.69; F, 35.08; Cl, 21.85%); n.m.r. spectrum no. 29, i.r. spectrum no. 29, mass spectrum no. 29; and 3,5-dichloro-2,2,3,4,4,5-hexafluoropentyl methyl ether (104): b.p. 169°C; (Found: C, 26.1; H, 2.4; F, 41.6; Cl, 24.9%. $C_6H_6F_6Cl_2O$ requires C, 25.81; H, 2.15; F, 40.86; Cl, 25.45%); n.m.r. spectrum no. 30, i.r. spectrum no. 30, mass spectrum no. 30.

4. F-propene

(a) Gamma-ray Initiation

A mixture containing F-propene (10.4g, 69.3 mmol) and dimethyl ether (8.7g, 189.1 mmol) was irradiated to a dose of 1.4×10^7 rad. The liquid recovered (14.54g) was distilled to give 2,2,3,4,4,4-hexafluorobutyl methyl ether (105), (8.0g, 59%): b.p. 87°C (lit.[67] 87°C); (Found: C, 30.9; H, 3.0; F, 57.8%. Calc. for $C_5H_6F_6O$: C, 30.61; H, 3.06; F, 58.16%); n.m.r. spectrum no 31, i.r. spectrum no. 31, mass spectrum no 31; and a pot residue (3.2g) which was not investigated.

(b) Benzoyl Peroxide Initiation

A mixture of F-propene (17.0g, 113.3 mmol), dimethyl ether (13.7g, 298 mmol) and benzoyl peroxide (0.23g) was heated at 80°C for 17 hours. The liquid recovered (22.4g) was distilled to give (105), (15.2g, 68%) and left a pot residue (4.1g) which was not investigated.

5. F-2-butene

A mixture of F-2-butene (8.3g, 41.5 mmol) and dimethyl ether (5.7g, 124 mmol) was irradiated to a dose of 1.25×10^7 rad. The liquid recovered (10.7g) was distilled to give 2-trifluoromethyl-2,3,4,4,4-pentafluorobutyl methyl ether (106), (3.04g., 30%): b.p. 97°C; (Found: C, 29.0; H, 2.8; F, 62.2%. $C_6H_6F_8O$ requires C, 29.27; H, 2.44; F, 61.79%); n.m.r. spectrum no. 32, i.r. spectrum no. 32; and a pot residue (5.1g) which was not investigated.but probably contained the two-to-one adduct.

6. F-2,3-dimethyl but-2-ene

A mixture containing the butene (3.68g, 12.3 mmol) and dimethyl ether (2.9g , 63 mmol) was irradiated to a dose of 1.75×10^7 rad. The liquid recovered (3.64g) was shown by g.l.c. (column O, 160°C) to be a 1 : 4.2 molar ratio of two components. These were separated by preparative g.l.c. (column O, 150°C) and respectively identified as 2,2,3-tris(trifluoromethyl)-4,4,4-trifluorobutyl methyl ether (107), (0.34g,8%): b.p. 124°C; analysis was unsatisfactory; n.m.r. spectrum no.

33, i.r. spectrum no 33, mass spectrum no 32; and bis-[2,2,3-tris(trifluoromethyl)-4,4,4-trifluorobutyl] ether (108), (1.33g, 33%): m.p. 70-72°C; (Found: C, 25.9; H, 1.3%. $C_{14}H_6F_{24}O$ requires C, 26.00; H, 0.93; F, 70.59%); n.m.r. spectrum no. 34, i.r. spectrum no. 34.

7. F-3,4-dimethyl hex-3-ene (92)

(a) Gamma-ray Initiation

A mixture containing (92) (21.21g, 53 mmol) and dimethyl ether (8.17g, 177.6 mmol) was irradiated to a dose of 1.5×10^7 rad. The liquid recovered (21.2g) was fractionated under vacuum at room temperature to remove unchanged (92) and the residue was distilled to give bis-[2-pentafluoroethyl-2,3-bis(trifluoromethyl)-4,4,5,5,5-pentafluoropentyl] ether (109), (6.22g, 28%): b.p.91-94°C, 1 mmHg; (Found: C, 25.5; H, 0.5; F, 71.5%. $C_{18}H_6F_{32}O$ requires C, 25.53; H, 0.71; F, 71.87%); n.m.r. spectrum no. 35, i.r. spectrum no. 35, mass spectrum no. 33.

(b) Benzoyl Peroxide Initiation

A mixture containing (92) (20.54g, 51.4 mmol), dimethyl ether (8.91g, 194 mmol) and benzoyl peroxide (0.31g) was heated at 80°C for 64½ hours. The liquid recovered (20.1g) was treated as in the preceding experiment to give (109), (4.70g, 21%), b.p. 69°C, 0.015 mmHg.

8. F-bicyclopentylidene

A mixture containing the dimer (4.26g, 10 mmol) and dimethyl ether (2.4g, 52.1 mmol) was irradiated to a dose of 1.78×10^7 rad. The crude white solid recovered (4.2g) was recrystallised from chloroform to give bis-[1-spirooctafluorocyclopentyl-1-(2',2',3',3',4',4',5',5'-octafluorocyclopentyl)]-methyl ether (110), (2.57g, 61%): m.p. 60°C; (Found: C, 29.3; H, 0.7; F, 67.6%. $C_{22}H_6F_{32}O$ requires C, 29.53; H, 0.67; F, 68.00%); n.m.r. spectrum no. 36, i.r. spectrum no. 36, mass spectrum no.34.

9. F-2-butyne

A mixture containing F-2-butyne (11.6g, 71.6 mmol) and dimethyl ether (8.1g, 176 mmol) was irradiated to a dose of 1.38×10^7 rad. Only

unchanged gases were recovered.

10. F-2,3-dimethyl buta-1,3-diene

A mixture containing the diene (6.55g, 25 mmol) and dimethyl ether (3.5g, 76 mmol) was irradiated to a dose of 1.75×10^7 rad. The recovered liquid (5.53g) was shown by g.l.c. (column O, 160°C) to be essentially unchanged diene only.

CHAPTER X

EXPERIMENTAL TO CHAPTER V

X.A GENERAL

The general procedure for addition reactions, as described on page 120, was employed. The functional hydrocarbons were purified and dried by conventional tachniques before use.

X.B ADDITIONS TO COMPOUNDS OF THE TYPE X-CH_2OCH_3

1. The Addition of F-propene to Dimethoxymethane at Room Temperature

A mixture containing F-propene (15.2g, 101.3 mmol) and dimethoxymethane (17.68g, 232.6 mmol) was irradiated to a dose of 1.16×10^7 rad. On opening, gas (3.0g) and liquid (28.55g) were recovered. The liquid was washed with water and the lower fluorocarbon layer separated. This was shown by g.l.c. (column O, 140°C) to be a mixture of three components in the ratio 66 : 18 : 16 (taking account of differing molecular weights). The major component was separated by distillation and shown to be 1,1,1,2,3,3-hexafluoro-5,7-dioxaoctane (118): b.p. 128°C; (Found: C, 32.1; H, 3.7; F, 49.9%. $C_6H_8F_6O_2$ requires C, 31.86; H, 3.54; F, 50.44%); n.m.r. spectrum no. 37, i.r. spectrum no. 37, mass spectrum no. 35. The minor components were separated as a mixture by preparative g.l.c. (column O, 160°C) and identified from their mass spectra, in increasing order of g.l.c. retention time, as respectively 1-methoxy di-2,2,3,4,4,4-hexafluorobutyl ether (119) and 2',2',3',4',4',4'-hexafluorobutoxymethyl 2,2,3,4,4,4-hexafluorobutyl ether (120): (Found: C, 28.6; H, 2.2%. $C_9H_8F_{12}O_2$ requires C, 28.73; H, 2.13; F, 60.64%); mass spectra nos. 36 and 37 respectively.

2. The Addition of F-propene to Dimethoxyethane at Room Temperature

A mixture containing F-propene (16.1g, 107.3 mmol) and

dimethoxyethane (26.6g, 296 mmol) was irradiated to a dose of 5.2×10^6 rad. On opening the tube, gas (6.74g) and liquid (34.96g) was collected. The liquid was washed with water, the lower layer separated, dried ($MgSO_4$) and filtered to give 21.5g of product mixture. Fractional distillation gave the two products in the ratio 53 : 47 and they were respectively identified as 2-methoxy-3,3,4,5,5,5-hexafluoropentyl methyl ether (121), (9.71g, 38%): b.p. 138°C; (Found: C, 35.3; H, 4.2; F, 47.0%. $C_7H_{10}F_6O_2$ requires C, 35.00; H, 4.17; F, 47.50%); n.m.r. spectrum no. 38, i.r. spectrum no. 38, mass spectrum no. 38; and 1,1,1,2,3,3-hexafluoro-5,8-dioxanonane (122), (8.7g, 34%): b.p. 150°C; (Found: C, 35.2; H, 4.5; F, 47.0%. $C_7H_{10}F_6O_2$ requires C, 35.00; H, 4.17; F, 47.50%); n.m.r. spectrum no. 39, i.r. spectrum no. 39, mass spectrum no. 39. The distillation pot residue was found to contain a mixture of two-to-one adducts identified as 1-methoxymethyl di-2,2,3,4,4,4-hexafluorobutyl ether (123) and 2-methoxy-3,3,4,5,5,5-hexafluoropentyl 2,2,3,4,4,4-hexafluorobutyl ether (124) from their mass spectra, nos 40 and 41 respectively.

3. The Addition of F-propene to 2-methoxyethanol at Room Temperature

A mixture containing F-propene (11.0g, 73.3 mmol) and 2-methoxyethanol (15.80g, 208 mmol) was irradiated to a dose of 1.1×10^7 rad. The mixture gave unchanged gas (0.26g) and a liquid (21.33g) which was washed with water to leave fluorocarbon (12.41g, 75% conversion). G.l.c. (column Z, 180°C) showed this to be a mixture of three products in the ratio 1 : 1 : 1. Using preparative-scale g.l.c. (column Z, 140°C), the product of shortest retention time was able to be separated into its constituent diastereomers (ratio 3 : 2) and at higher temperature (180°C) the two other one-to-one adducts were isolated. A mixture of components (probably two-to-one adducts) of much longer retention time were not investigated. The compounds thus isolated were, in increasing order of

g.l.c. retention times:- 2-hydroxy-3,3,4,5,5,5-hexafluoropentyl methyl ether (Diastereomer A) (125): m.p. 37°C; (Found: C, 32.1; H, 3.8; F, 50.8%. $C_6H_8F_6O_2$ requires C, 31.86; h, 3.54; F, 50.44%); n.m.r. spectrum no. 40, i.r. spectrum no. 40, mass spectrum no. 42; 2-hydroxy-3,3,4,5,5,5-hexafluoropentyl methyl ether (Diastereomer B) (125): b.p. 155°C; (Found: C, 32.0; H, 3.9; F, 50.8%. $C_6H_8F_6O_2$ requires C, 31.86; H, 3.54; F, 50.44%); n.m.r. spectrum no. 41, i.r. spectrum no. 41; 2-methoxy-3,3,4,5,5,5-hexafluoropentan-1-ol (126): b.p. 164°C; (Found: C, 31.9; H, 3.9; F, 50.8%. $C_6H_8F_6O_2$ requires C, 31.86; H, 3.54; F, 50.44%); n.m.r. spectrum no. 42, i.r. spectrum no. 42, mass spectrum no. 43; and 4-(2'-hydroxyethoxy)-1,1,1,2,3,3-hexafluorobutane (127): (Found: C,H analysis unsatisfactory; F, 50.8%. $C_6H_8F_6O_2$ requires C, 31.86; H, 3.54; F, 50.44%); n.m.r. spectrum no. 43, i.r. spectrum no. 43, mass spectrum no 44.

4. The Addition of Compound (77) to F-cyclobutene at Room Temperature

A mixture containing F-cyclobutene (0.44g, 2.7 mmol) and (77) (2.00g, 6.5 mmol) was irradiated to a dose of 2.47×10^7 rad. On opening, 2.05g of liquid was recovered which g.l.c. (column O, 160°C) showed to contain only unchanged (77) and a small quantity of dissolved F-cyclobutene.

5. The Addition of Compound (77) to F-cyclohexene at 80°C

A mixture containing (77) (3.50g, 11.4 mmol) and F-cyclohexene (1.7g, 6.5 mmol) was irradiated to a dose of 1.2×10^7 rad whilst being heated at 80°C. Volatile liquid (3.53g) was gently evaporated from the mixture at reduced pressure to leave a residue which was sublimed to give a white solid, identified by comparison of g.l.c. retention times, as being the two-to-one adduct (78), (0.57g, 15%); see n.m.r. spectrum no. 6, i.r. spectrum no. 6, mass spectrum no. 6.

6. The Addition of Benzyl Methyl Ether to F-propene at Room Temperature

A mixture containing benzyl methyl ether (8.90g, 73 mmol) and F-propene (5.10g, 33.3 mmol) was irradiated to a dose of 1.32×10^7 rad. On opening F-propene (5.1g, 100%) and liquid (8.55g) was recovered, indicating that no reaction had occurred.

7. The Addition of Ethylene Oxide to F-cyclopentene

(a) Irradiation at Room Temperature

A mixture containing ethylene oxide (6.46g, 147 mmol) and F-cyclopentene (10.9g, 51.4 mmol) was irradiated to a dose of 1.85×10^7 rad. The mixture was poured into water but no lower layer separated, indicating that no addition product had been formed.

(b) Benzoyl Peroxide Initiation

A mixture containing ethylene oxide (4.60g, 104.5 mmol), F-cyclopentene (7.94g, 37.4 mmol) and benzoyl peroxide (0.10g) was heated at 80°C for 23 hours. The mixture gave on cooling a white viscous upper layer (1.56g) which gave no signals in the ^{19}F n.m.r. spectrum and so was not investigated further. The rest of the liquid was treated as in the preceding experiment with the same result.

8. The Addition of 18-Crown-6 Polyether to F-propene at Room Temperature

A mixture containing the polyether (11.10g, 42 mmol) and F-propene (2.6g, 17.3 mmol) was irradiated to a dose of 1.46×10^7 rad. Recovered was gas (2.6g) and unchanged ether (11.02g). Quantitative recovery of F-propene indicates no addition has occurred.

X.C ADDITIONS TO COMPOUNDS OF THE TYPE $X\text{-}OCH_3$

Additions to several of this class of compound have been recorded in the previous section, namely dimethoxymethane, dimethoxyethane, 2-methoxyethanol, compound (77), benzyl methyl ether. For convenience, these reactions are not described again; further examples of the reactions of $X\text{-}OCH_3$ are reported below.

1. The Addition of Anisole to F-propene at 160°C

A mixture containing anisole (19.68g, 182.2 mmol) and F-propene (7.55g, 50.3 mmol) was irradiated to a dose of 3.2×10^7 rad whilst being heated at 160°C. On opening, F-propene(5.56g) and liquid (19.8g) were recovered. The liquid was shown by g.l.c. (column O, 180°C) and

by n.m.r. to be only unchanged anisole.

2. The Additions of Dimethoxybenzenes to F-cyclobutene at 100°C

(a) 1,3-dimethoxybenzene

A mixture containing 1,3-dimethoxybenzene (16.0g, 116 mmol) and F-cyclobutene (9.8g, 60.5 mmol) was irradiated to a dose of 4.6×10^6 rad whilst being heated at 100°C. On opening, F-cyclobutene (9.74g) and liquid (15.01g) were recovered : quantitative recovery of the former indicates no addition had occurred.

(b) 1,4-dimethoxybenzene

A mixture containing 1,4-dimethoxybenzene (18.22g, 132 mmol) and F-cyclobutene (10.1g, 62.3 mmol) was irradiated to a dose of 2.3×10^7 rad, whilst being heated at 100°C. On opening, F-cyclobutene (9.96g) and liquid (17.91g) were recovered: quantitative recovery of the former indicates no addition had occurred.

3. The Addition of Trimethyl Borate to F-cyclopentene at Room Temperature

A mixture containing trimethyl borate (16.8g, 161.5 mmol) and F-cyclopentene (16.5g, 77.8 mmol) was irradiated to a dose of 1.38×10^7 rad. No F-cyclopentene was obtained when the mixture was warmed gently under vacuum. The liquid was distilled to give as the only product tri-(2H-1,2,3,3,4,4,5,5-octafluorocyclopentyl)-methyl borate (131), (9.44g, 49%): b.p. 133-136°C, 3mmHg, as a mixture of cis and trans isomers; (Found: C,H analysis gave a significant nitrogen figure due to incomplete combustion of the borate; B, 1.7; F, 61.7%. $C_{18}BH_9F_{24}O_3$ requires C, 29.19; H, 1.21; B, 1.49; F, 61.62%); n.m.r. spectrum no. 44, i.r. spectrum no. 44, mass spectrum no. 45.

(a) Quantitative Hydrolysis of (131)

Compound (131) (0.86g) was added to excess water and the mixture shaken periodically over thirty minutes to dissolve the boric acid that had formed on hydrolysis. Fluorocarbon (0.79g) was recovered as a lower

layer and shown by comparison of g.l.c. retention times (column Z, 160°C) to be the alcohol (17) isomer mixture. For a one-to-one adduct, about 0.66g of (17) would have been recovered and for the three-to-one adduct (131) the mass of alcohol would be 0.80g.

4. The Addition of Trimethyl Phosphate to F-propene

(a) Irradiation at Room Temperature

A mixture containing trimethyl phosphate (24.37g, 174.1 mmol) and F-propene (11.3g, 75.3 mmol) was irradiated to a dose of 2.8×10^7 rad. On opening, F-propene (7.78g) and liquid (27.23g) were recovered. The liquid was poured into water and the lower layer that resulted was separated and molecularly distilled off P_2O_5 to give 2,2,3,4,4,4-hexafluorobutyl dimethyl phosphate (132), (2.91g, 13%): (Found: C, 24.9; H, 2.9; P, 7.7%. $C_6H_9F_6O_4P$ requires C, 24.83; H, 3.10; P, 10.69; F, 39.31%); n.m.r. spectrum no. 45, i.r. spectrum no. 45, mass spectrum no. 46.

(b) Irradiation at 100°C

A mixture containing trimethyl phosphate (14.02g, 100 mmol) and F-propene (7.62g, 50.8 mmol) was irradiated to a dose of 1.6×10^7 rad. Treatment as in the preceding experiment gave (132), (7.44g, 50%), identified by comparison of its i.r. spectrum with that of an authentic sample.

(c) Benzoyl Peroxide Initiation

A mixture containing trimethyl phosphate (28.72g, 205 mmol), F-propene (12.3g, 82 mmol) and benzoyl peroxide (0.19g) was heated at 80°C for 69½ hours. Work-up as previously described gave F-propene (8.16g) and (132),(0.64g, 3%).

5. The Addition of Trimethyl Methoxy Silane to F-propene at Room Temperature

A mixture containing the silane (4.10g, 39.4 mmol) and F-propene (2.7g,

18 mmol) was irradiated to a dose of 1.16 x 10^7 rad. F-propene (0.38g) and liquid (5.26g) was recovered. From g.l.c. (column O, 200°C), this contained one product, a sample of which was separated by preparative g.l.c. (column O, 140°C) and identified as trimethyl 2,2,3,4,4,4-hexafluorobutoxy silane (133), (2.83g, 62% by g.l.c.): (Found: C, 33.4; H,5.0; F, 44.7%. $C_7H_{12}F_6OSi$ requires C, 33.07; H, 4.72; F, 44.88; Si, 11.02%); n.m.r. spectrum no. 46, i.r. spectrum no. 46, mass spectrum no. 47.

6. The Addition of Methyl Benzoate to F-cyclobutene at Room Temperature

A mixture containing F-cyclobutene (9.2g, 56.8 mmol) and methyl benzoate (12.14g, 89.3 mmol) was irradiated to a dose of 5.9 x 10^7 rad. F-cyclobutene (8.88g) and liquid (11.23g) were recovered: high recovery of unchanged F-cyclobutene implies that no addition occurred.

7. Addition of Methyl Formate to (92) at Room Temperature

A mixture containing methyl formate (13.04g, 217 mmol) and (92) (15.95g, 39.9 mmol) was irradiated to a dose of 4.2 x 10^7 rad. The mixture was poured into water, the lower layer separated, dried ($MgSO_4$) and filtered. The fluorocarbon (12.05g) was distilled at reduced pressure to give, in addition to unchanged (92), a liquid product which was identified by comparison of its n.m.r. and i.r. spectra as the alcohol (93), (5.12g, 30%) - see n.m.r. spectrum no. 22 and i.r. spectrum no. 22.

8. The Addition of γ-Butyrolactone to F-propene at Room Temperature

A mixture containing F-propene (8.5g, 56.7 mmol) and the lactone (15.86g, 184.4 mmol) was irradiated to a dose of 1.9 x 10^7 rad. F-propene (7.37g) and liquid (16.68g) were recovered. The liquid was poured into a large quantity of water and, after washing several times, the lower layer (0.88g) was separated and molecularly distilled off P_2O_5 to give γ-[2-(1',1',2',3',3',3'-hexafluoropropyl)]-butyrolactone (134), (0.88g, 6.4%): Analysis unsatisfactory; n.m.r. spectrum no. 47, i.r. spectrum no. 47, mass spectrum no. 48.

X.D ADDITIONS TO COMPOUNDS OF THE TYPES X-CH_2OH AND X-CHO

The reaction of 2-methoxyethanol was described in Section B.3, and will not be repeated here.

1. Additions to X-CH_2OH

(a) The Addition of Benzyl Alcohol to F-cyclobutene at Room Temperature

A mixture containing the alcohol (12.87g, 119 mmol) and F-cyclobutene (6.77g, 41.8mmol) was irradiated to a dose of 1.8×10^7 rad. On opening, F-cyclobutene (6.33g) and liquid (12.76 g) were recovered: the high recovery of the former unchanged implies no addition occurred.

(b) The Addition of 2-pentafluorophenyl ethanol to F-cyclobutene at Room Temperature

A mixture containing the alcohol (4.86g, 22.9 mmol) and F-cyclobutene (2.3g, 14.2 mmol) was irradiated to a dose of 5.4×10^6 rad. F-cyclobutene (1.34g) and liquid (4.78g) were recovered. The liquid was shown by ^{19}F n.m.r. to consist of unchanged alcohol and dissolved F-cyclobutene only.

2. Additions to X-CHO

(a) The Addition of Acetaldehyde to F-propene

(i) Irradiation at room temperature

A mixture containing acetaldehyde (17.95g, 408 mmol) and F-propene (19.6g, 130.7 mmol) was irradiated to a dose of 1.34×10^7 rad. The mixture was distilled twice to give 1,1,1,2,3,3-hexafluoropentan-4-one(136), (7.78g, 31%): b.p. 78°C; (Found: C, 30.7; H, 2.1; F, 59.1%. $C_5H_4F_6O$ requires C, 30.93; H, 2.06; F, 58.76%); n.m.r. spectrum no. 48, i.r. spectrum no. 48, mass spectrum no. 49.

The ketone was further characterised as the 2,4-dinitrophenylhydrazone derivative: m.p. 122°C; (Found: C, 35.3; H,2.4; N, 15.2%. $C_{11}H_8F_6N_4O_4$ requires C, 35.29; H, 2.14; N, 14.97; F, 30.48%).

(ii) Benzoyl Peroxide Initiation

A mixture containing F-propene (23.8g, 159 mmol) and acetaldehyde

(24.2g, 550 mmol) was heated at 80°C for 23 hours. The mixture was then distilled to give (136), (19.53g, 63%), b.p. 78°C.

(b) The Addition of Benzaldehyde to F-cyclobutene at 80°C.

A mixture containing benzaldehyde (24.6g, 232 mmol) and F-cyclobutene (14.4g, 89 mmol) was irradiated to a dose of 1.18×10^7 rad whilst being heated at 80°C. F-cyclobutene (13.2g) and liquid (23.82g) were recovered: high recovery of thr former implies that no addition occurred.

CHAPTER XI

EXPERIMENTAL TO CHAPTER VI

XI.A REACTIONS OF METHYL KETONES

1. Halogenation

(a) Chlorination of (74)

A mixture containing (74) (3.03g, 9.9 mmol) and chlorine (2.01g, 28.3 mmol) was irradiated in a small Pyrex Carius tube fitted with a Rotaflo tap for four hours by a Hanovia high pressure mercury vapour lamp. The liquid recovered (3.44g) was shown by g.l.c. (column O, 200°C) to contain, besides a good deal of unchanged starting material, two products . Samples of these were separated by preparative g.l.c. (column O, 175°C) and shown to be respectively cis-2H-decafluorocyclohexyl chloromethyl ketone (137): b.p. 154°C; (Found: C, 28.5; H, 1.2%; insufficient for halogen. $C_8H_3ClF_{10}O$ requires C, 28.19; H, 0.88; Cl, 10.42; F, 55.80%); n.m.r. spectrum no. 49, i.r. spectrum no. 49, mass spectrum no. 50; and cis-2H-decafluorocyclohexyl dichloromethyl ketone (138): b.p. 170°C; (Found: C, 25.5; H, 0.4%; insufficient for halogen. $C_8H_2Cl_2F_{10}O$ requires C, 25.60; H, 0.53; Cl, 18.93; F, 50.67%); n.m.r. spectrum no. 50, i.r. spectrum no. 50, mass spectrum no. 51.

(b) Bromination of (74)

A mixture containing (74) (2.01g, 6.5 mmol) and bromine (1.12g, 7 mmol) was degassed in container as described above and irradiated for five hours by a Hanovia high pressure mercury vapour lamp. The clear, slightly red liquid recovered (2.39g) was shown by g.l.c. (column O, 200°C) to contain, besides unchanged (74), two products, the first of which was in great excess of the other. This major product was separated by preparative g.l.c. (column O, 200°C) and identified as cis-2H-decafluorocyclohexyl bromomethyl ketone (139), (0.70g, 28%): (Found: C, 24.9;

H, 0.6; Br, 21.7; F, 48.5%. $C_8H_3BrF_{10}O$ requires C, 24.94; H, 0.78; Br, 20.78; F, 49.35%); n.m.r. spectrum no. 51, i.r. spectrum no. 51.

(c) Fluorination of (74)

Compound (74) (6.18g, 20.2 mmol) was passed in a stream of nitrogen (60 cm^3/min.) over the cobalt trifluoride bed heated at 140°C during a period of 45 minutes. The liquid recovered (4.89g) was shown by g.l.c. (column O, 160°C) to consist of a single pure product identified as cis-2H-decafluorocyclohexyl acyl fluoride (140), (4.89g, 78%): b.p. 84°C; (Found: C, 26.8; H, 0.1; F, 66.9%. $C_7HF_{11}O$ requires C, 27.10; H, 0.32; F, 67.42%); n.m.r. spectrum no. 52, i.r. spectrum no. 52, mass spectrum no. 52.

(i) Hydrolysis of the acyl fluoride (140)

The acid fluoride (140) (1.31g, 4.2 mmol) was stirred with an excess of water (1.64g, 91 mmol) at room temperature for 2½ hours. The organic lower layer was dissolved in ether, the ether solution separated, dried ($MgSO_4$), filtered and the ether evaporated at reduced pressure. The residue was sublimed to give a white solid identified as cis-2H-decafluorocyclohexyl carboxylic acid (141), (0.66g, 51%): m.p. 46°C, b.p. 161°C; (Found: C, 27.6; H, 0.8; F, 62.1%. $C_7H_2F_{10}O_2$ requires C, 27.27; H, 0.65; F, 61.69%); n.m.r. spectrum no. 53, i.r. spectrum no. 53, mass spectrum no. 53.

(ii) Formation of the anilinium salt of (141)

The acid (141) derived from stirring (140) (0.8g, 2.6 mmol) with excess water was dissolved in ether, separated from the water and excess aniline added to the solution. Evaporation of the solvent left a brown oil which solidified on standing. Two recrystallisations from toluene gave anilinium cis-2H-decafluorocyclohexyl carboxylate (142), (0.42g, 42%): m.p. 151°C; (Found: C, 39.0; H, 2.5; N, 3.5%. $C_{13}H_9F_{10}NO_2$ requires C, 38.90; H, 2.24; N, 3.49; F, 47.38%); i.r. spectrum no. 54, mass spectrum no. 54.

(d) Fluorination of (96)

Compound (96) (17.33g, 39.0 mmol) was passed in a flow of nitrogen (60 cm^3/min.) over CoF_3 heated to 170°C. After dropwise addition, the bed was purged for a further hour and 14.07g of liquid was recovered. From g.l.c. (column A, 80°C) this was shown to contain two products which were fractionally distilled apart and identified as 4H-perfluoro-3-ethyl-3,4-dimethyl-hexan-2-one (144), (5.5g, 28%): b.p. 140°C; (Found: C, 23.8; H, 0.0; F, 72.8%. $C_{10}HF_{19}O$ requires C, 24.10; H, 0.20; F, 72.49%); n.m.r. spectrum no. 54, i.r. spectrum no. 55, mass spectrum no. 55; and 1,4-dihydro-F-3-ethyl-3,4-dimethyl- hexan-2-one (143),(8.6g, 46%) : b.p. 151°C; (Found: C, 25.2; H, 0.1; F, 71.0%. $C_{10}H_2F_{18}O$ requires C, 25.00; H, 0.42; F, 71.25%); n.m.r. spectrum no.55, i.r. spectrum no. 56, mass spectrum no. 56.

(e) Fluorination of (136)

Compound (136) (6.13g, 31.6 mmol) was passed dropwise over CoF_3 heated to 110°C in a stream of nitrogen (60 cm^3/min.). After purging for 30 minutes, the mixture recovered was warmed to room temperature. The material appeared to evaporate quickly and only 2.28g of gases was recovered and shown by g.l.c. to be mainly two components which were not investigated. A less volatile residue (0.4g) was collected which had the odour of an acetic acid.

2. Reactions with Base

(a) Reaction of (74) with aqueous NaOH

A mixture of (74) (5.87g, 19.2 mmol) and NaOH solution (2g, 50 mmol in 40 cm^3 water) was stirred at room temperature for 30 hours. Dilute hydrochloric acid was then added and a lower layer was separated and shown by g.l.c. to be a single component identified as 1-hydro-F-cyclohexene (147), (1.91g, 41%), by comparison of its n.m.r. spectrum (recorded for convenience as no. 56) and i.r. spectrum with literature values[169,170].

(b) Reaction of (96) with Tri-n-butylamine

Compound (96) (20.97g, 47.2 mmol) was added to tri-n-butylamine (29.3g, 158.4 mmol) dissolved in tetraglyme (24 cm^3) and the mixture stirred at room temperature for 4½ hoyrs. Excess dilute HCl was added and the fluorocarbon lower layer separated, washed with water, separated, dried ($MgSO_4$), filtered and distilled to give as the only product 2-methylideno-F-3,4,5-trimethyl-3-ethyl-dihydrofuran (148), (15.92g, 83%): b.p. 126°C; (Found: C, 30.0; H, 0.1; F, 65.3%. $C_{10}F_{14}H_2O$ requires C, 29.7; H, 0.5; F, 65.84%); n.m.r. spectrum no. 57, i.r. spectrum no. 57, mass spectrum no. 57.

(i) Pyrolysis of (148)

Compound (148) (6.01g, 14.9 mmol) was passed in a stream of nitrogen (60 cm^3/min.) through a platinum lined and packed tube heated to 600°C during 6 hours and 4.43g of liquid was recovered and shown by g.l.c. to be essentially one component with a small amount of breakdown products. A sample of the product was isolated by preparative g.l.c. (column O, 160°C) and identified as 2',3,4-tris(trifluoromethyl)-5-(1',1'-dihydro-pentafluoropropyl)-furan (149): b.p. 137°C; (Found: C,29.5; H, 0.2; F, 66.2%. $C_{10}H_2F_{14}O$ requires C, 29.70; H, 0.50; F, 65.84%); n.m.r. spectrum no. 58, i.r. spectrum no. 58, mass spectrum no. 58.

3. Reduction Experiments

(a) Reduction of (96) with Sodium Borohydride

Sodium borohydride (0.48g, 12.6 mmol) was suspended in dry ether (6 cm^3) and (96) (3.17g, 7.1 mmol) was added slowly. The mixture was stirred at room temperature for 3½ hours before water was added. The Fluorocarbon recovered after removal of solvent (2.0g, 63%) was shown by its n.m.r. spectrum to be unchanged (96) only.

(b) Photochemical Reduction of (74)

A mixture of (74) (2.03g, 6.6 mmol) and dry isopropanol (6 cm^3) were degassed and irradiated in a silica Carius tube for 88½ hours with

a Hanovia high-pressure mercury vapour lamp. The mixture was shown by g.l.c. to contain only unchanged starting material.

(c) Bimolecular Reduction of (72)

Magnesium (0.2g, 8 mmol) was placed in dry toluene (3 cm^3) and from a dropping funnel a mixture of (72) (4.25g, 21 mmol), mercuric chloride (0.5g) and toluene (5 cm^3) was added dropwise. No solid mass formed (indicative of pinacolate formation) and the reaction was discontinued.

4. Pyrolysis Experiments

(a) Pyrolysis of (72)

(i) Pyrolysis of (72, trans) over quartz at 535°C

Compound (72, trans) (5.18g, 25.1 mmol) was passed in a flow of nitrogen (50 cm^3/min.) through a silica tube packed with quartz wool and heated to 535°C during 5½ hours. The liquid recovered (3.34g, 64%) was shown by integration of ^{19}F n.m.r. high field signals to contain (72) trans and cis in a ratio of 66 : 34.

(ii) Pyrolysis of (72, trans) over platinum at 535°C

Compound (72, trans) (2.86g, 13.9 mmol) was passed in a stream of nitrogen (50 cm^3/min.) through a platinum lined and packed tube heated to 535°C during 5 hours. The liquid recovered (1.97g, 69%) was shown as in the preceding experiment to contain (72) trans and cis in a ratio of 70 : 30.

(iii) Pyrolysis of (72, cis) over platinum at 575°C

Compound (72, cis) (2.21g, 10.7 mmol) when treated as in (ii) above resulted in recovery of liquid (1.63g, 74%) which was mainly (72) trans and cis in the ratio 25 : 75 as measured by ^{19}F n.m.r. signal integration as previously.

(iv) Pyrolysis of (72) over platinum at 620°C

The isomer mixture (72) (4.5g, 21.8 mmol) was treated as before over 6 hours to give recovered liquid (2.69g) which was shown by g.l.c.

(column O, 115°C) to consist of two new components and a little unchanged starting material. These were separated by preparative g.l.c. (column O, 120°C) and identified as cis-3H-hexafluorocyclobutyl methyl ketone (149): n.m.r. spectrum no. 59; and trans-3H-hexafluorocyclobutyl methyl ketone (149): b.p. 104°C; n.m.r. spectrum no. 60, i.r. spectrum no. 59.

(b) Pyrolysis of (73) at 660°C over Platinum

Isomer mixture (73) (2.51g, 9.8 mmol) was treated as above to give, after 3 hours, a liquid (1.05g) which was shown by g.l.c. to consist of one major component and a small quantity of starting material. The major product was separated by preparative g.l.c. and shown by comparison of its n.m.r. chemical shifts with those quoted in the literature[179] to be 1-hydro-F-cyclopentene (151), (1.81g, 52% by g.l.c.): n.m.r. spectrum no. 61.

(c) Pyrolysis of (74) over Platinum at 700°C

Compound (74) (3.09g, 10.1 mmol) was treated as before to give, after 4¾ hours, a liquid (1.62g) which contained a mixture of volatile components and some unchanged (74). The volatiles were separated en masse by preparative g.l.c. (column O, 150°C) and then isolated into its constituent four components (column O, 80°C). The first eluted was lost during removal from its g.l.c. trap and the third appeared from its ^{19}F n.m.r. spectrum to be a mixture of two components at least. The second compound eluted was identified from its n.m.r. spectra as 1-hydro-F-cyclohexene (147): n.m.r. spectrum no. 56; and the fourth compound was identified as F-cyclohexene by comparison of its ^{19}F n.m.r. spectrum with that from an authentic sample.

5. Reactions of the Carbonyl Group

(a) Formation of 2,4-dinitrophenylhydrazones

(i) General procedure

A stock solution of 2,4-dinitrophenylhydrazine (2,4-DNP) was prepared by dissolving 10g of the solid in 280 cm^3 of methanol and 20 cm^3

concentrated sulphuric acid, filtering the solution and using it at the rate of 30 cm^3 (containing 1.0g, 5 mmol 2,4-DNP) of solution for each 5 mmol of methyl ketone used. After stirring for a few minutes, the derivative precipitated (except in the case of (74) when evaporation of the solvent was first performed) and was then filtered off and recrystallised from meths.

(ii) Results

Using the afore described method, the 2,4-DNP's whose physical data are recorded in Table 31 were prepared.

Table 31 2,4-DNP Derivatives - Physical Properties

Starting Material		2,4-dinitriphenylhydrazone				
				Elemental Analysis		
		m.p. (°C)	Formula	% C Found (Calc.)	% H Found (Calc.)	% N Found (Calc.)
 (72)	cis	175-6	$C_{12}H_8F_6N_4O_4$	37.3 (37.31)	1.9 (2.07)	15.6 (14.51)
	trans	113-5		36.2 (37.31)	2.1 (2.07)	14.9 (14.51)
 (73)	cis	121-3	$C_{13}H_8F_8N_4O_4$	36.1 (35.78)	1.4 (1.83)	13.8 (12.84)
	trans	139-41		36.0 (35.78)	1.9 (1.83)	13.5 (12.84)
 (74)	cis	153-5	$C_{14}H_8F_{10}N_4O_4$	34.2 (34.57)	1.7 (1.65)	11.8 (11.52)

(b) Formation of Oximes

(i) General procedure

A stock solution of hydroxylamine hydrochloride was prepared by dissolving 10g up to a volume of 40 cm^3 of solution which gives 1g, 14.4 mmol of reagent in 4 cm^3 of solution. Then the methyl ketone (10 mmol) was dissolved in 5 cm^3 of ethanol and refluxed with 4 cm^3 of stock solution for three hours. After this time, water (20 cm^3) was added, the lower layer dissolved in ether, the organic phase separated, dried ($MgSO_4$), filtered and the solvent evaporated. The residue was then either molecularly distilled (for a liquid oxime) or sublimed (for a solid). The solid oximes could, if necessary, be recrystallised from 60-80 petrol.

(ii) Results

Using the method outlined above, the following oximes were prepared.

From (72, cis)(2.03g, 9.9 mmol) was obtained cis-2H-hexafluorocyclobutyl methyl ketone oxime (154), (0.52g, 24%): (Found: C, 32.9; H, 2.0; N, 6.5%. $C_6H_5F_6NO$ requires C, 32.58; H, 2.26; N, 6.33%); n.m.r. spectrum no. 62, i.r. spectrum no. 60.

From (72, trans) (4.14g, 20.1 mmol) was obtained trans-2H-hexafluorocyclobutyl methyl ketone oxime (154), (2.33g, 52%) : b.p. 164°C; (Found: C, 32.9; H, 2.0; N, 6.5%. $C_6H_5F_6NO$ requires C, 32.58; H, 2.26; N, 6.33%); n.m.r. spectrum no. 63, i.r. spectrum no. 61, mass spectrum no. 59.

From (73, cis) (5.14g, 20.1 mmol) was obtained cis-2H-octafluorocyclopentyl methyl ketone oxime (155), (2.08g, 38%) : m.p. 45-7°C; (Found: C, 30.9; H, 2.1; N, 4.9%. $C_7H_5F_8NO$ requires C, 31.00; H, 1.85; N, 5.17%); n.m.r. spectrum no. 64, i.r. spectrum no. 62, mass spectrum no. 60.

From (73, trans) (3.81g, 14.9 mmol) was obtained trans-2H-octafluorocyclopentyl methyl ketone oxime (155) , (2.46g, 64%): m.p. 60-2°C;

(Found: C, 31.2; H, 2.0; N, 4.9%. $C_7H_5F_8NO$ requires C, 31.00; H, 1.85; N, 5.17%); n.m.r. spectrum no. 65, i.r. spectrum no. 63.

No product was formed when the solvent was methanol but when meths was used, (74, cis) (4.04g, 13.2 mmol) gave cis-2H-decafluorocyclohexyl methyl ketone oxime (156) , (0.42g, 10%): m.p. 55-7°C; (Found: C, 30.2; H, 1.6; N, 4.2%. $C_8H_5F_{10}NO$ requires C,29.9; H, 1.56; N, 4.36%); n.m.r. spectrum no. 66, i.r. spectrum no. 64, mass spectrum no. 61.

XI.B REACTIONS OF ALCOHOLS

1. Attempted Formation of Ethers

(a) Difluorocarbene Insertion

Each of the polyfluorocycloalkylmethanol isomer mixtures was reacted with sodium chlorodifluoroacetate with similar results. For convenience, the reaction of (68) is described.

A mixture containing (68) (3.25g, 11 mmol) and sodium chlorodifluoroacetate (6.53g, 42.8 mmol) was degassed, sealed in and heated in a Carius tube at 160°C for 25½ hours. On opening, a large quantity of a gas identified as carbon monoxide and a colourless liquid (3.81g) were recovered. G.l.c. (column Z, 175°C) showed this to contain, in addition to unchanged alcohol, a mixture of at least eight components. The mixture was not investigated further.

(b) Dichlorocarbene Insertion

A mixture of (93) (6.66g, 15.4 mmol), tetrachloroethene (20 cm^3), diglyme (5 cm^3) and sodium trichloroacetate (15.48g, 83.5 mmol) was heated together in a 100 cm^3 flask fitted with reflux condenser for 6½ hours. Distillation of the mixture produced liquid boiling at under 80°C (4.85g) which was identified as chloroform. Hence the trichloroacetate ion was not losing chloride to give the carbene but instead protonating and the insertion reaction did not take place.

(c) Methylene Insertion

The diazomethane was generated as described in the literature[188].

(i) The Reaction of (17) with Diazomethane

The alcohol (17) (3.64g, 14.9 mmol) was added to the diazomethane solution produced from 3.80g, 17.7 mmol of p-tolylsulphonyl methylnitrosamide (precursor). The brown colour of the carbene persisted even after stirring for some time, indicating no reaction. Addition of several drops of BF_3-etherate caused the solution to immediately decolourise with the evolution of a gas preumed to be nitrogen. G.l.c. (column O) on the reaction mixture showed that only unchanged (17) was present in the ether solution.

A similar reaction occurred with (67).

2. Dichromate Oxidation Experiments

(a) Oxidation of (67)[54]

A mixture containing (67) (1.91g, 9.8 mmol), potassium dichromate (4.19g), concentrated sulphuric acid (3 cm^3) and water (15 cm^3) was refluxed for 3 hours. On cooling, the mixture was extracted with ether, the extracts separated, dried and the ether evaporated. The residue was molecularly distilled to give a liquid which solidified on standing. This was identified as 2H-hexafluorocyclobutyl carboxylic acid (157), (0.85g, 41%), as a mixture of isomers: (Found: C, 29.1; H, 1.2%. Calc. for $C_5H_2F_6O_2$: C, 28.85; H, 0.96; F, 54.81%); n.m.r. spectrum no. 67, i.r. spectrum no. 65.

(b) Oxidation of (68)

A mixture containing (68) (5.05g, 17 mmol), potassium dichromate (4.2g), concentrated sulphuric acid (8.8g) and water (20 cm^3) was refluxed for $2\frac{1}{2}$ hours. Treatment as described above gave an impure viscous liquid (1.88g, 35%). The carboxylic acid (158) was characterised as the anilinium salt (159): m.p. 141°C; (Found: C, 38.9; H, 2.3; N,3.7%.

$C_{13}H_9F_{10}NO_2$ requires C, 38.90; H, 2.24; N, 3.49%); the i.r. spectrum of (159) was almost identical to that of (142), i.r. spectrum no. 54. The salt was prepared as described on page 152.

(c) Oxidation of (93)

A mixture containing (93) (3.90g, 9 mmol), potassium dichromate (3.33g), concentrated sulphuric acid (2.5g) and water (10cm^3) was refluxed for 3 hours. Work-up as described in (a) above gave a liquid (2.68g, 69%) which was identified from its n.m.r. spectra as unchanged (93) only.

3. Reactions with Base

(a) Reaction of (68) with aqueous NaOH solution

A mixture containing (68) (6.52g, 22.2 mmol) and aqueous NaOH (2.0g, 50 mmol in 50 cm^3 of water) was stirred for 20 hours at room temperature. Excess dilute HCl was added and a viscous yellow lower layer (2.62g) was separated. It was not investigated further.

(b) Reaction of (93) with Tri-n-butylamine

Compound (93) (6.47g, 15 mmol) was added to tri-n-butylamine (11.0g, 59.5 mmol) dissolved in dry ether (10 cm^3) and the mixture stirred at room temperature for 22 hours. Excess dilute HCl was added, the ether extract separated after washing, dried (Na_2SO_4), filtered and the solvent evaporated to leave a light yellow residue (4.3g). G.l.c. (column A) showed this to contain four components. Preparative g.l.c. (column A, 65°C) was unable to separate the two components of shortest retention time but the third and fourth compounds were isolated and respectively identified as 5,5-dihydro-F-2,4-dimethyl-3-methylideno-4-ethyl-tetrahydrofuran (161), (0.7g, 11%) : b.p. 123°C; (Found: C, 27.5; H, 0.9; F, 67.4%. $C_9H_2F_{14}O$ requires C, 27.55; H, 0.51; F, 67.86%); n.m.r. spectrum no. 68, i.r. spectrum no. 66; and 5,5-dihydro-F-2,3,4-trimethyl-4-ethyl-dihydrofuran (162), (0$7g, 11%): (Found: C,H analyses for N;

F, 67.3%. $C_9H_2F_{14}O$ requires C, 27.55; H, 0.51; F, 67.86%); n.m.r. spectrum no. 69, i.r. spectrum no. 67, mass spectrum no. 62.

XI.C REACTIONS OF METHYL ETHERS

1. Halogenation

(a) Chlorination of (76)

(i) Using no solvent

A mixture of (76) (3.49g, 13.5 mmol), degassed beforehand and chlorine (1.10g, 15.5 mmol) was sealed in a Carius tube fitted with a Rotaflo tap and left to stand in ambient daylight. The chlorine colour rapidly disappeared and on opening a large volume of HCl fumes was evolved and a colourless liquid (3.92g) was recovered. This contained some unchanged (76) and two major products. The latter were separated by preparative g.l.c. (column O, 190°C) and, in order of elution, identified as 2H-octafluorocyclopentyl methoxy chloromethane (164) , (0.2g, 5%), as an isomer mixture: (Found: C, 29.0; H, 2.0; Cl, 12.5; F, 51.5%. $C_7H_5ClF_8O$ requires C, 28.72; H, 1.71; Cl, 12.14; F, 51.97%); n.m.r spectrum no. 70, i.r. spectrum no. 68, mass spectrum no. 63; and 2H-octafluorocyclopentyl chloromethoxy methane (163), (2.00g, 51%) , as an isomer mixture: b.p. 163°C; (Found: C, 29.0; H, 2.0; Cl, 12.5; F, 51.5%. $C_7H_5ClF_8O$ requires C, 28.72; H, 1.71; Cl, 12.14; F, 51.97%); n.m.r. spectrum no. 71, i.r. spectrum no. 69, mass spectrum no 64. Analysis was performed on a mixture of (163) and (164). An impure sample of the third product was tentatively identified from its n.m.r. spectra as the dichloroether which had substituted a chlorine at each of the methyl and methylene sites.

The experiment was repeated on several occassions and the ratio of (163) : (164) varied between 10 : 1 (as in the example described) and 20 : 1.

(ii) Using carbon tetrachloride as solvent

A degassed mixture containing (76) (1.35g, 5.3 mmol), chlorine

(0.52g, 7.4 mmol) and CCl_4 (3.79g, 24.3 mmol) was treated as in (i) above to give a colourless liquid (4.94g). From g.l.c. (column O, 200°C) the ratio of (163) : (164) was 56 : 43.

(iii) Using carbon disulphide as solvent

A degassed mixture containing (76) (0.90g, 3.5 mmol), chlorine (0.61g, 9mmol) and CS_2 (2.62g, 34.5 mmol) was treated as in (i) above to give a recovered fluorocarbon layer (0.68g). From g.l.c. (column O, 220°C), the ratio (163) : (164) was 23 : 77.

(b) Bromination of (76)

A mixture containing (76) (4.41g, 17.1 mmol) and bromine (3.70g, 23.1 mmol) was degassed and sealed in a small Carius tube fitted with a Rotaflo tap. The mixture was irradiated for 2½ hours by a Hanovia high-pressure mercury vapour lamp. A light-red tinged liquid (5.92g) was recovered which contained one major product and a second minor product of longer retention time. A sample of the major product was separated by preparative g.l.c. (column O, 200°C) and identified as 2H-octafluorocyclopentyl methoxy bromomethane (165) as an isomer mixture: b.p. 164°C; (Found: C, 25.2; H, 1.5; Br, 24.4; F, 44.5%. $C_7H_5BrF_8O$ requires C, 24.93; H, 1.48; Br, 23.74; F, 45.10%); n.m.r. spectrum no.72, i.r. spectrum no. 70, mass spectrum no. 65.

(c) Bromination of (77)

A mixture containing (77) (6.06g, 19.7 mmol) and bromine (3.61g, 22.6 mmol) was degassed and sealed in a small Carius tube fitted with a Rotaflo tal. The mixture was irradiated for 1¾ houre by a Hanovia high-pressure mercury vapour lamp. The liquid recovered (7.47g) had a composition similar to that described in (b) above. Distillation gave the major product which was identified as 2H-decafluorocyclohexyl methoxy bromomethane (166) , (5.88g, 77%) : b.p. 183°C; (Found: C, 24.7; H, 1.1; Br, 21.3; F, 48.7%. $C_8H_5BrF_{10}O$ requires C, 24.81; H, 1.29; Br, 20.67;

F, 49.10%); n.m.r. spectrum no. 73, i.r. spectrum no 71.

(d) Fluorination of (75)

Compound (75) (4.32g, 20.8 mmol) was passed in a stream of nitrogen (50 cm^3/min.) over CoF_3 heated to 120°C during 1¾ hours and the bed was then purged a further 30 minutes to give a colourless liquid (4.3g) which was shown by g.l.c. to contain two products. These were separated by preparative g.l.c. (column O, 110°C) and identified, in order of elution, as 2H-hexafluorocyclobutyl difluoromethoxy difluoromethane (168), (0.46g, 8%): b.p. 87°C; (Found: C, 25.9; H, 1.1%. $C_6H_2F_{10}O$ requires C, 25.71; H, 0.71; F, 68.86%); n.m.r. spectrum no. 74, i.r. spectrum no. 72; and 2H-hexafluorocyclobutyl difluoromethoxy fluoromethane (167), (0.92g, 17%) : b.p. 107°C; (Found: C, 27.6; H, 1.1; F, 65.5%. $C_6H_3F_9O$ requires C, 27.48; H, 1.15; F, 65.27%); n.m.r. spectrum no 75, i.r. spectrum no. 73.

(e) Fluorination of (105)

Compound (105) (6.53g, 33.3 mmol) was passed dropwise in a stream of nitrogen (50 cm^3/min.) over CoF_3 heated to 120°C during 1¾ hours to give a colourless liquid (6.14g) which g.l.c. showed to contain three products in equal proportion. Samples of each were separated by preparative g.l.c. (column Z, 50°C) and identified, in order of elution, as 2,2,3,4,4,4-hexafluorobutyl difluoromethyl ether (169) : (Found: C, 26.1; H, 1.9%; insufficient for F. $C_5H_4F_8O$ requires C, 25.86; H, 1.72; F, 65.52%); n.m.r. spectrum no. 76, i.r. spectrum no. 74; 1,2,2,3,4,4,4-heptafluorobutyl difluoromethyl ether (170) : Analysis unsatisfactory; n.m.r. spectrum no. 77, i.r. spectrum no. 75; and 1,2,2,3,4,4,4-heptafluorobutyl fluoromethyl ether (171) : (Found: C, 26.0; H, 1.6%; insufficient for F. $C_5H_4F_8O$ requires C, 25.80; H, 1.72; F, 65.52%); n.m.r. spectrum no. 78, i.r. spectrum no. 76.

2. Pyrolysis of Methyl Ethers

(a) Pyrolysis of (75) at 600°C

Compound (75) (2.07g, 10 mmol) was passed in a stream of nitrogen (50 cm^3/min.) through a platinum lined and packed tube heated to 600°C during 3½ hours. Collected was a liquid (1.13g, 54%) which g.l.c. (column A, 110°C) showed to contain the geometric isomers of (75). The trans/cis isomer ratio had changed (^{19}F n.m.r. high field signal integration) from 9.36 to 1.76.

(b) Pyrolysis of (76) at 650°C

Compound (76) (2.08g, 8 mmol), on treatment at 650°C as above, gave, after 4½ hours, a liquid (1.21g, 58%) which g.l.c. (column A, 95°C) showed to contain a mixture of fragmentation components and mainly the geometric isomers of (76). The trans/cis isomer ratio had changed (as measured above) from 1.58 to 1.15.

(c) Pyrolysis of (77) at 685°C

Compound (77) (2.85g, 9.3 mmol), on treatment at 685°C as in (a) above, gave, after 3¾ hours, a liquid (1.04g) which g.l.c. (column A, 100°C) to contain a mixture of fragmentation components and mainly (77). The trans/cis isomer ratio had changed (^{19}F n.m.r. high field signal integration) from 0.79 to 0.48.

APPENDICES

APPENDIX I

N.M.R. SPECTRA

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27. 2,3-bis(trifluoromethyl)-1,1,4,4-tetrafluorohex-1-en-5-one (100).
28. 4,5-bis(trifluoromethyl)-3,3,6,6-tetrafluorooctan-2,7-dione (101).
29. 3-chloro-2,2,3-trifluoropropyl methyl ether (103).
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38. 2-methoxy-3,3,4,5,5,5-hexafluoropentyl methyl ether (121).
39. 1,1,1,2,3,3-hexafluoro-5,8-dioxanonane (122).
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71. 2H-octafluorocyclopentyl chloromethoxy methane(163) isomer mixture.
72. 2H-octafluorocyclopentyl methoxy bromomethane(165) isomer mixture.
73. 2H-decafluorocyclohexyl methoxy bromomethane(166) isomer mixture.
74. 2H-hexafluorocyclobutyl difluoromethoxy difluoromethane(168).
75. 2H-hexafluorocyclobutyl difluoromethoxy fluoromethane(167).

76. 2,2,3,4,4,4-hexafluorobutyl difluoromethyl ether(169).

77. 1,2,2,3,4,4,4-heptafluorobutyl difluoromethyl ether(170).

78. 1,2,2,3,4,4,4-heptafluorobutyl fluoromethyl ether(171).

Abbreviations

The following abbreviations are used in this appendix:

S = singlet

D = doublet

T = triplet

Q = quartet

AB = AB quartet

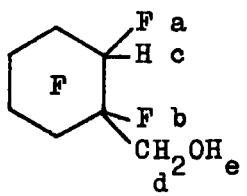
P = pentet (quintet)

St = sextet

Sp = septet

M = multiplet

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
1. 2H-decafluorocyclohexylmethanol (68) isomer mixture			
^{19}F			
232.4	Broad D, J_{ac}=40	1	cis a
209.8	Broad D, J_{ac}=40		trans a
195.1	Broad S	1	cis b
189.1	Broad S		trans b
Signals between 115 and 146 p.p.m. (equivalent to 8F, CF_2 region) which were not assigned.			
^{1}H			
3.09	S	1	e
4.16	M	2	d
5.23	Broad D (unresolved)	1	c



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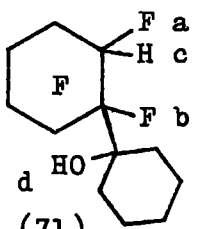


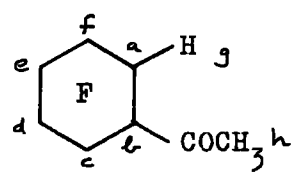
(71)

2. 1-(2'H-decafluorocyclohexyl)-cyclohexanol (71) isomer mixture			
^{19}F			
226.0	Broad	1	cis a
208.0	Broad		trans a
194.8	Broad	1	cis b
186.9	Broad		trans b
Signals between 111 and 150 p.p.m. (equivalent to 8F, CF_2 region) which were not assigned.			
^{1}H			
2.70		1	d
4.6 - 4.8	Broad	1	c
Signals centred around 2.0 p.p.m. (equivalent to 10H) which were not assigned.			

Recorded in $CDCl_3$ solution.

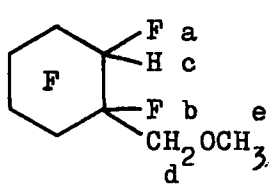
Shift p.p.m.	Fine Structure Coupling Constants in Hz,	Relative Intensity	Assignment
3. Cis-2H-decafluorocyclohexyl methyl ketone (74)			
^{19}F			
231	D, J_{ag}=45	1	a(equatorial)
193		1	b(axial)
120	All S	8	c(ax.)
134			c(eq,)
124			d(ax.)
139			d(eq.)
123			e(ax.)
145			e(eq.)
128			f(ax.)
128			f(eq.)
^{1}H			
2.64	D, J_{hb}=6	3	h
5.78	D, J_{ga}=45	1	g

cis



(74)

Shift p.p.m.	Fine Structure Coupling Constants on Hz.	Relative Intensity	Assignment
4. 2H-decafluorocyclohexyl methoxymethane (77) isomer mixture			
^{19}F			
234.3	D, J_{ac}=43	1	cis a
210.8	Broad unresolved		trans a
193.5	Broad S	1	cis b
187.0	Broad S		trans b
Signals between 115 and 149 p.p.m. (equivalent to 8F, CF_2 region) which were not assigned.			
^{1}H			
3.62, 3.68	Both S	3	e, each isomer
3.96, 4.13, 4.35	All Broad S	2	d
5.42	Broad D, J_{ca}=44	1	c
5. Trans-2H-decafluorocyclohexyl methyl ketone (74)			
^{19}F			
213.3	Broad	1	a
175.5	Broad	1	b
Signals between 118 and 139 p.p.m. (equivalent to 8F, CF_2 region) which were not assigned.			
^{1}H			
2.49	D, J_{db}=4	3	d
5.19	Broad D, J_{ca}=45	1	c



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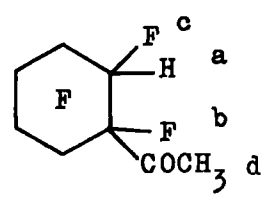
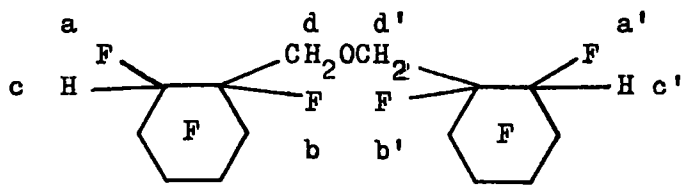


(74)

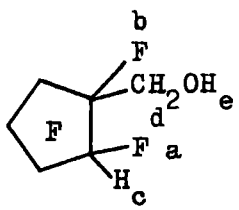
Shift p.p.m.	Fine Structure Coupling constants in Hz.	Relative Intensity	Assignment
6. Di-(2'H-decafluorocyclohexyl)-methyl ether (78) isomer mixture			
^{19}F			
232.4	Broad	2	cis a,a'
209.4	Broad		trans a,a'
193.3	Broad	2	cis b,b'
186.5	Broad		trans b,b'
Signals between 115 and 147 p.p.m. (equivalent to 16F, CF_2 region) which were not assigned.			
^{1}H			
4.10	Assymetric D	2	d,d'
4.30	S		
4.78	Broad S	1	c,c'
5.53	Broad S		

Recorded as a solution in $CDCl_3$.



(78)

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
7. Trans-2H-octafluorocyclopentylmethanol (17)			
^{19}F			
213.9	D, J_{ac}=47	1	a
181.1	S	1	b
122.1, 136.1	AB, J=264	8	Ring CF_2's
125.5, 132.4	AB, J=263		
126.8, 131.4	AB, J=128		
^{1}H			
4.08, 4.48	Both S	2	d
4.65	Broad S	1	e
5.63	Broad D	1	c
8. 1-(2'H-octafluorocyclopentyl)-cyclohexanol (70) isomer mixture			
^{19}F			
219.4	D, J_{ac}=44	1	cis a
207.6	D, J_{ac}=46		trans a
190.0	Broad S	1	cis b
176.7	Broad S		trans b
Signals between 114 and 135 p.p.m. (equivalent to 6F, CF_2 region) which were not assigned.			
^{1}H			
1.7-1.9	Broad	10	Ring CH_2
2.04	S	1	d
5.2-5.6	Broad	1	c



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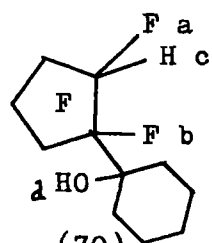
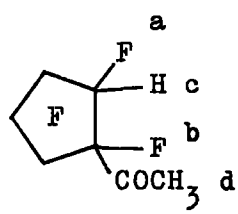


(70)

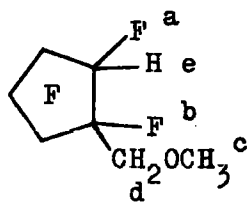
Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
9. Cis-2H-octafluorocyclopentyl methyl ketone (73)			
^{19}F			
228.4	D, J_{ac}=44 of D, J=10	1	a
191.8	S	1	b
131.1	S	6	Ring CF_2
119.5, 130.3	AB, J=253		
122.8, 134.0	AB, J=270		
^{1}H			
2.55	D, J_{bd}=5	3	d
5.83	M	1	c



(73)

10. Trans-2H-octafluorocyclopentyl methyl ketone (73)			
^{19}F			
215.5	D, J_{ac}=48	1	a
174.3	S	1	b
117.5, 129.7	AB, J=260	6	Ring CF_2
127.6, 133.3	AB, J=252		
124.3, 130.4	AB, J=266		
^{1}H			
2.48	D, J_{bd}=5	3	d
5.45	Broad D, J_{ca}=47	1	c

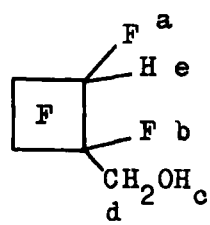
Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
11. Trans-2H-octafluorocyclopentyl methoxymethane (76)			
^{19}F			
212.0	D, J_{ae}=48	1	a
180.9	S	1	b
120.6, 133.0	AB, J=267	6	Ring CF_2
125.0, 134.8	AB, J=260		
124.9, 130.6	AB, J=150		
^{1}H			
3.67	S	3	c
3.88, 4.30	Both S	2	d, each H
5.28	Broad D	1	e



(76)

12. Cis-2H-octafluorocyclopentyl methoxymethane (76)			
^{19}F			
226.6	D, J_{ae}=49	1	a
192.7	S	1	b
118.4, 130.2	AB, J=235	6	Ring CF_2
125.8, 135.5	AB, J=271		
131.3	S		
^{1}H			
3.67	S	3	c
3.88, 4.22	Both S	2	d
5.35	Broad D	1	e

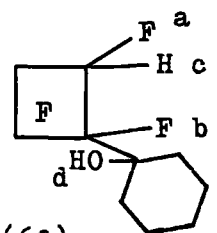
Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
13. Trans-2H-hexafluorocyclobutylmethanol (67)			
^{19}F			
219.7	D, J_{ae}=50	1	a
182.6	S	1	b
122.3, 136.5	AB, J=238	4	Ring CF_2
128.9, 133.6	AB, J=236		
^{1}H			
4.2, 4.67	Both S	2	d, each H
4.77	S	1	c
5.68	Broad D, J_{ea}=50	1	e



(67)

14. Cis-2H-hexafluorocyclobutylmethanol (67)			
^{19}F			
225.2	D, J_{ae}=51	1	a
198.9	S	1	b
118.5, 134.3	AB, J=233	4	Ring CF_2
126.7, 132.6	AB, J=235		
^{1}H			
3.73	S	1	c
3.98, 4.38	Both S	2	d, each H
5.33	Broad D	1	e

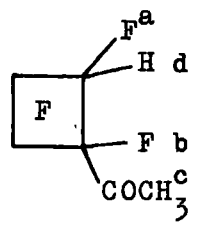
Shift p.p.m.	Fine Structure Coupling Constants in Hz.,	Relative Intensity	Assignment
15. 1-(trans-2'H-hexafluorocyclobutyl)-cyclohexanol (69)			
^{19}F			
214.3	D, J_{ac}=46	1	a
194.5	S	1	b
119.2, 135.5	AB, J=230	4	Ring CF_2
125.3, 128.4	AB, J=140		
^{1}H			
1.8	Broad S	10	Ring CH_2
2.95	Broad S	1	d
5.52	Broad D	1	c



(69)

16. 1-(cis-2'H-hexafluorocyclobutyl)-cyclohexanol (69)			
^{19}F			
221.3	D, J_{ac}=52	1	a
194.5	S	1	b
118.4, 135.2	AB, J=224	4	Ring CF_2
124.3	M		
^{1}H			
1.8	Broad S	10	Ring CH_2
3.30	Broad S	1	d
5.52	Broad D	1	c

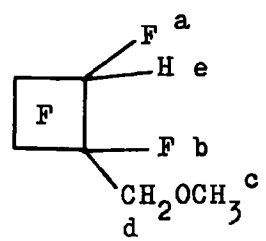
Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
17. Cis-2H-hexafluorocyclobutyl methyl ketone (72)			
^{19}F			
223.4	D, J_{ad}=48 of T, J=4	1	a
196.9	S	1	b
119.3, 135.4	AB, J=226	4	Ring CF_2
126.1, 133.2	AB, J=238		
^{1}H			
2.39	D, J_{bc}=5	3	c
4.01	D, J_{da}=49 of P, J=8	1	d



(72)

18. Trans-2H-hexafluorocyclobutyl methyl ketone (72)			
^{19}F			
214.8	D, J_{ad}=49	1	a
173.4	M, J=6	1	b
118.7, 139.2	AB, J=223	4	Ring CF_2
128.3	T, J=181		
^{1}H			
2.50	D, J_{bc}=5	3	c
5.6	D, J_{da}=50 of M, J=5	1	d

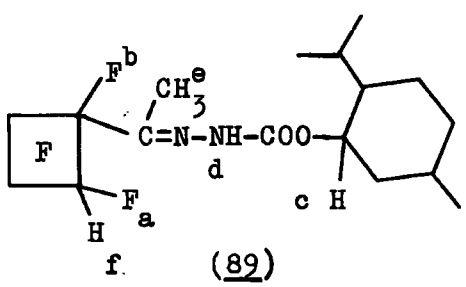
Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
19. Trans-2H-hexafluorocyclobutyl methoxymethane (75)			
^{19}F			
217.4	D, J_{ae}=49 of T, J=18	1	a
179.4	S	1	b
121.0, 135.0	AB, J=232	4	Ring CF_2
129.9	Broad		
^{1}H			
3.70	S	3	c
3.9, 4.3	Both S	2	d, each H
5.5	Broad Q	1	e



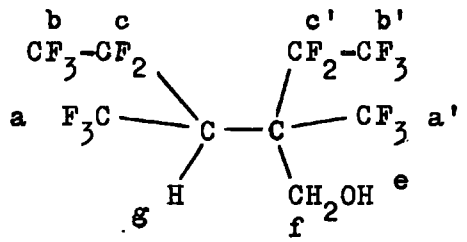
(75)

20. Cis-2H-hexafluorocyclobutyl methoxymethane (75)			
^{19}F			
221.8	D, J_{ae}=47	1	a
197.3	S	1	b
119.6, 135.7	AB, J=231	4	Ring CF_2
128.0, 134.2	AB, J=228		
^{1}H			
3.7	S	3	c
4.0, 4.2	Both S	2	d, each H
5.4	Broad D	1	e

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
21. Trans-2H-hexafluorocyclobutyl methyl ketone (-)-menthydrazide (89)			
^{19}F			
211.9	D	1	a
165.8	S	1	b
120.1, 133.6	AB, J=220	4	Ring CF_2
125.6, 126.1	AB, J=40		
^{1}H			
0.7-0.9	Several S	9	Ring CH_3
1.64	Broad	6	Ring CH_2
1.96	S	3	e
4.69	T, J=12 of D, J=5	1	c
5.33	Broad D	1	f
8.15	S	1	d



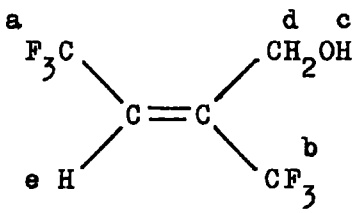
(89)



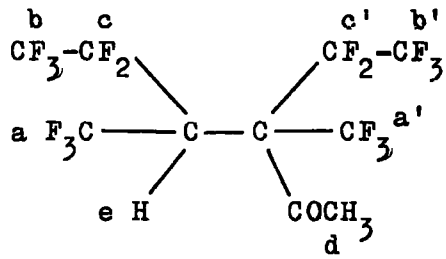
(93)

22. 1,1,3-trihydro-F-2,3-dimethyl-2-ethyl-pentan-1-ol (93)			
^{19}F			
57.8	S	3	a or a'
62.0	Assymetric D	3	a' or a
80.4	S	3	b or b'
83.9	S	3	b' or b
108.9	Assymetric D	4	c, c'
^{1}H			
3.15	S	1	e
4.17	Broad M	1	g
4.75	S	2	f

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
23. (E)-(2-trifluoromethyl)-4,4,4-trifluorobut-2en-1-ol (95)			
^{19}F			
60.4	D, J_{ae}=8	3	a
69.2	T, J=2	3	b
^{1}H			
4.32	Broad S	1	c
4.53	S	2	d
6.42	Q, J_{ea}=8	1	e



(95)

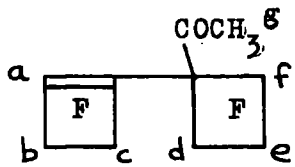


(96)

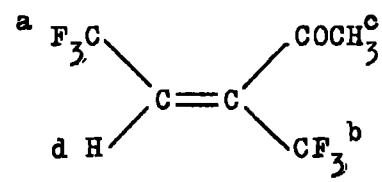
24. 3-pentafluoroethyl-3,4-bis(trifluoromethyl)-5,5,6,6,6-pentafluorohexan-2-one (96)

^{19}F			
57.4	D, J=91	3	a or a'
60.6	Broad S	3	a' or a
77.3	S	3	b or b'
84.5	M	3	b' or b
96.9, 114.4	AB, J=310	2	c or c'
105.2	S	2	c' or c
^{1}H			
2.70	S	3	d
5.10	D, J=46 of Q, J=8	1	e

Shift p.p.m.	Fine Structure Coupling Constants in Hz,	Relative Intensity	Assignment
25. 1-(F-cyclobutenyl)-hexafluorocyclobutyl methyl ketone (98)			
^{19}F			
99.6	S	1	a
115.3	S	2	b or c
119.3, 125.7	AB, J=230	4	d, f
121.3	S	2	c or b
131.6, 135.4	AB, J=220	2	e
^{1}H			
2.12	S		g



(98)

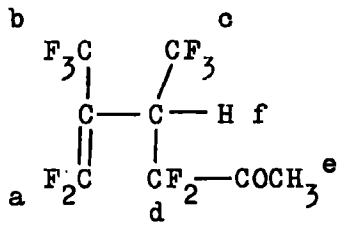


(99)

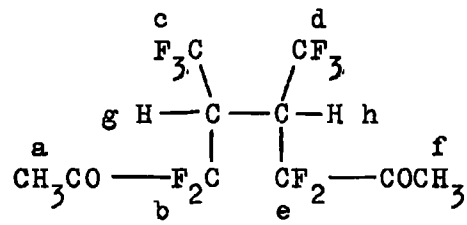
26. (E)-(3-trifluoromethyl)-1,1,1-trifluoropent-2-en-4-one (99)

^{19}F			
63.0	D, J_{ad}=7.5	3	a
67.3	T, J=1.8	3	b
^{1}H			
2.38	S	3	c
6.40	Q, J_{da}=7.5 of Q, J=1.8	1	d

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
27. 2,3-bis(trifluoromethyl)-1,1,4,4-tetrafluorohex-1-en-5-one (100)			
^{19}F			
60.6, 62.4	Assymetric D	] 8	a + b + c
66.5	S		
103.5, 113.8	AB, J=304	2	d
^{1}H			
2.30	S	3	e
4.47	Broad S	1	f



(100)



(101)

28. 4,5-bis(trifluoromethyl)-3,3,6,6-tetrafluorooctan-2,7-dione (101)			
^{19}F			
62.8	S	6	c + d
102.3, 113.1	AB, J=304	4	b + e
^{1}H			
2.50	D, J=4	6	a + f
4.38	Broad S	2	g + h

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
29. 3-chloro-2,2,3-trifluoropropyl methyl ether (103)			
^{19}F			
121.3	M	2	c
157.6	D, J_{ab}=48 of T, J=12	1	a
^{1}H			
3.57	S	3	e
3.90	T	2	d
6.50	D, J_{ba}=48 of T, J=8	1	b

b a c d e
$HCFCl-CF_2-CH_2OCH_3$

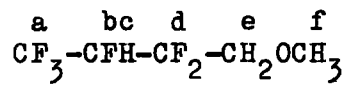
(103)

b a c d e f g
$HCFCl-CF_2-CFCl-CF_2-CH_2OCH_3$

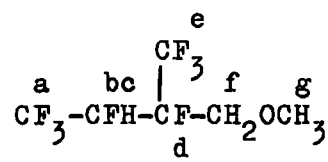
(104)

30. 3,5-dichloro-2,2,3,4,4,5-hexafluoropentyl methyl ether (104)			
^{19}F			
114	Broad		c
121	Broad		e
136	D, J=49		d
152	Broad		a
^{1}H			
3.95	S	3	g
4.42	T, J=14	2	f
7.15	Broad	1	b

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
31. 2,2,3,4,4,4-hexafluorobutyl methyl ether (105)			
^{19}F			
76.3	M, J=6	3	a
120.4	M, J=6	2	d
121.5	M, J=10		
216.7	D, J_{bc}=43 of M	1	b
^{1}H			
3.48	S	3	f
3.67-4.28	Broad	2	e
5.10	D, J_{cb}=43 of M, J=4	1	c



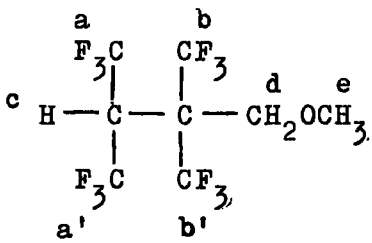
(105)



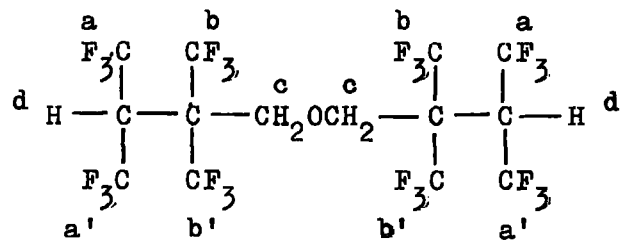
(106)

32. 2-trifluoromethyl-2,3,4,4,4-pentafluorobutyl methyl ether (106)			
^{19}F			
58.0	Broad S	3	a or e
59.7	Broad S	3	e or a
187.6	Broad S	1	d
191.2	Broad S		
216.8	Broad D, J_{bc}=32	1	b
^{1}H			
3.58	S	3	g
3.90, 4.15	Both S	2	f
5.48	Broad D	1	c

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
33. 2,2,3-tris(trifluoromethyl)-4,4,4-trifluorobutyl methyl ether (107)			
^{19}F			
60.8	M,J=9	1	a, a'
65.9	M, J=9	1	b, b'
^{1}H			
3.10	S	3	e
3.68	Broad S	2	d
4.10	T, J=9	1	c



(107)



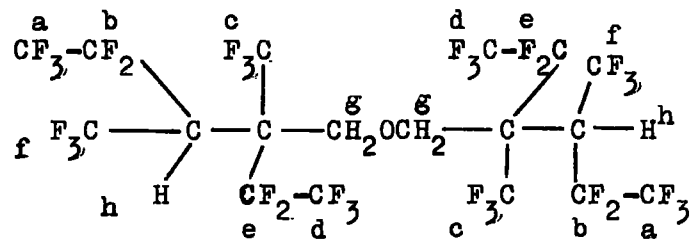
(108)

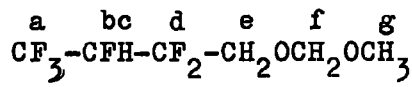
34. Bis-[2,2,3-tris(trifluoromethyl)-4,4,4-trifluorobutyl] ether (108)

^{19}F			
59.3	St, J=8	1	a , a'
64.4	P , J=8	1	b, b'
^{1}H			
4.46	S	2	c
4.90	Sp	1	d

Recorded as a dilute solution in d_6-acetone.

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
35. Bis-[2-pentafluoroethyl-2,3-bis(trifluoromethyl)-4,4,5,5,5-pentafluoropentyl] ether (109)			
^{19}F			
57.5	S	3	c or f
59.1	Assymetric D	3	f or c
80.4	S	3	a or d
83.4	Assymetric D	3	d or a
108.3	Broad S	2	b, e
^{1}H			
4.70	Broad S		g, h



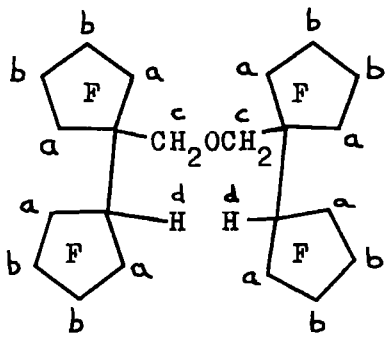


(118)

37. 1,1,1,2,3,3-hexafluoro-5,7-dioxaoctane (118)			
^{19}F			
75.9	M, J=6	3	a
117.3, 123.7	AB, J=283	2	d
127.2	M, J=10		
216.0	D, J_{bc}=43 of M	1	b
^{1}H			
3.55	S	3	g
3.73	S	2	e
4.17	M		
4.85	S	2	h
5.35	D of M, broad	1	c

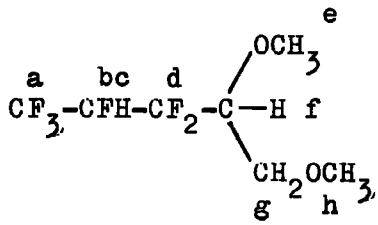
Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
36. Bis-[1-spirooctafluorocyclopentyl-1-(2',2',3',3',4',4',5',5'-octafluorocyclopentyl)]-methyl ether (110)			
^{19}F			
106.7	Broad S	1	a
110.5	S		
111.5	S		
115.1	S		
119.1	S		
123.8	S		
126.1	S	1	b
130.8	Broad S		
136.0	D, J=40		
140.9			
^{1}H			
4.40	S		c, d

Recorded as a solution in acetone for ^{19}F and in $CDCl_3$ for ^{1}H.

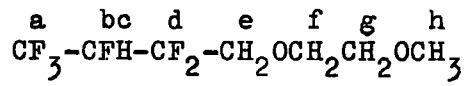


(110)

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
38. 2-methoxy-3,3,4,5,5,5-hexafluoropentyl methyl ether (121)			
^{19}F			
75.7	M	3	a
121.5	D, J=56	2	d
125.5	D, J=46		
215.6	D, J=134 of D, J_{bc}=43	1	b
^{1}H			
3.62	S	3	h
3.82	S	3	e
3.93	Broad D	2	g
4.08	Broad	1	f
5.43	D, J_{cb}=43 of M	1	c



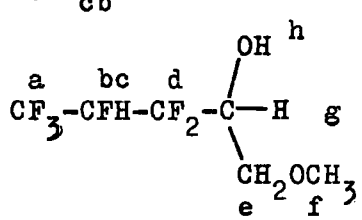
(121)



(122)

39. 1,1,1,2,3,3-hexafluoro-5,8-dioxanonane (122)			
^{19}F			
75.6	M	3	a
117.6, 123.6	AB, J=275	2	d
216.3	D, J_{bc}=42	1	b
^{1}H			
3.42	S	3	h
3.70	D, J=5	4	f, g
4.05	Broad D, J=16	2	e
5.28	D, J_{cb}=43 of M	1	c

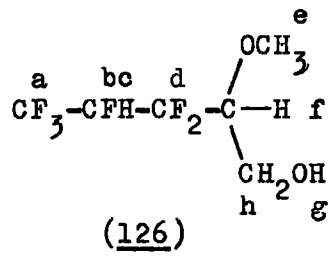
Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
40. 2-hydroxy-3,3,4,5,5,5-hexafluoropentyl methyl ether (125) (Diastereomer A)			
^{19}F	Recorded as a liquid at 60°C.		
75.4	Q, J=6 of D, J=10	3	a
127.6	Broad S	2	d
214.7	D, J_{bc}=42 of M	1	b
^{1}H			
3.70	S	3	f
4.00	D	2	e
4.43	Broad S	1	g
4.77	S	1	h
5.62	D, J_{cb}=43 of M	1	c



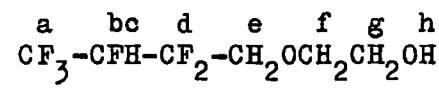
(125)

41. 2-hydroxy-3,3,4,5,5,5-hexafluoropentyl methyl ether (125) (Diastereomer B)			
^{19}F			
75.7	Broad M	3	a
123.0	D, J=74 of M, J=11	2	d
217.0	M, J=11	1	b
^{1}H			
3.68	S	3	f
3.95	D	2	e
4.65	Broad S	1	g
4.85	S	1	h
5.55	D of M, unresolved	1	c

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
42. 2-methoxy-3,3,4,5,5,5-hexafluoropentan-1-ol (126)			
^{19}F			
75.3	Broad M	3	a
120.1	D, J=98	2	d
124.5	Broad S		
214.7	D, J=104 of D, J_{bc}=44	1	b
^{1}H			
3.83	S		e
4.13	Broad S		h
4.30	Broad S		g
5.43	D, J_{cb}=43 of M, J=7		c
Signal due to proton f not observed			



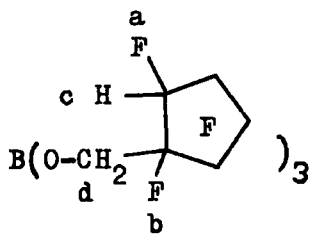
(126)



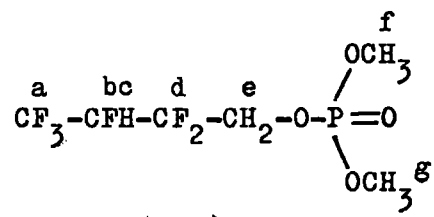
(127)

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
43. 4-(2'-hydroxyethoxy)-1,1,1,2,3,3-hexafluorobutane (127)			
^{19}F			
75.3	Broad M	3	a
120.3	Broad D, J=66	2	d
123.3	Broad D, J=176		
215.1	Broad D of D	1	b
^{1}H			
3.47	S		h
3.73	S		f, g
3.83	S		
3.97	Broad S		e
5.33	Broad D		c

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
44. Tri-(2H-1,2,3,3,4,4,5,5-octafluorocyclopentyl)-methyl borate (131)			
^{19}F			
226.5	D, J_{ac}=46	1	cis a
214.8	D, J_{ac}=44		trans a
195.1	Broad S	1	cis b
180.6	Broad S		trans b
Signals between 116 and 140 p.p.m. (equivalent to 6F, CF_2 region) which were not assigned.			
^{1}H			
4.39, 4.76	Both S		d
5.4	Broad		c



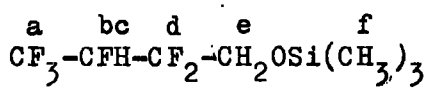
(131)



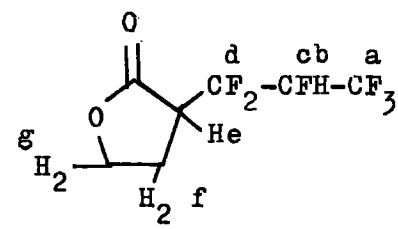
(132)

45. 2,2,3,4,4,4-hexafluorobutyl dimethyl phosphate (132)			
^{19}F			
75.7	Broad S	3	a
121.1	Broad D	2	d
215.4	Broad S	1	b
^{1}H			
4.05	S	3	f, g
4.23	S	3	
4.80	Broad S	2	e
5.77	Broad D, J_{cb}=44	1	c

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
46. Trimethyl 2,2,3,4,4,4-hexafluorobutoxy silane (133)			
^{19}F			
73.4	M, J=6	3	a
118.1, 125.8	AB, J=270	2	d
216.1	Broad D, J_{bc}=44	1	b
^{1}H			
0.25	S	9	f
4.07	M	2	e
5.17	D, J_{cb}=44 of M, J=6	1	c



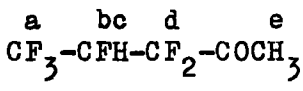
(133)



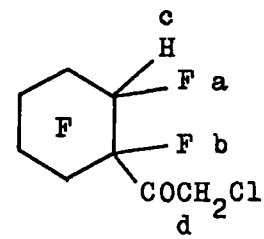
(134)

47. γ-[2-(1',1',2', 3',3',3'-hexafluoropropyl)]-butyrolactone (134)			
^{19}F			
75.6	M	3	a
124.7	M	2	d
129.3	M		
214.3	D, J_{bc}=43 of M	1	c
217.3	D, J_{bc}=43 of M		
^{1}H			
2.92	S		f
4.55	Broad M		g
5.13	Broad M		e
5.80	Broad M		b

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
48. 1,1,1,2,3,3-hexafluoropentan-4-one (136)			
^{19}F			
76.5	Broad M	3	a
117.5, 125.5	AB, J=298	2	d
218.1	D, J_{bc}=43 of M, J=11	1	b
^{1}H			
2.32	S	3	e
5.32	D, J_{cb}=43 of M, J=5-7	1	c



(136)



(137)

49. Cis-2H-decafluorocyclohexyl chloromethyl ketone (137)

^{19}F

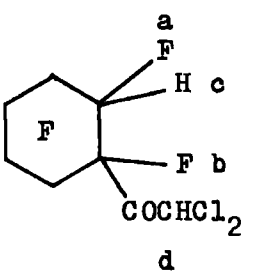
227.9		1	a
197.9	S	1	b

Signals between 118 and 147 p.p.m. (equivalent to 8F, CF_2 region) which were not assigned.

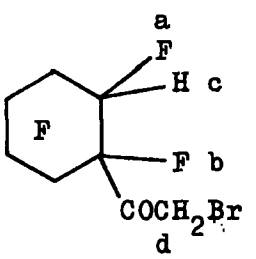
^{1}H

4.50	S	2	d
5.50	D of M, J=12	1	c

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
50. Cis-2H-decafluorocyclohexyl dichloromethyl ketone (138)			
^{19}F			
225.3	D, J_{ac}=45	1	a
188.6	S	1	b
Signals between 117 and 147 p.p.m. (equivalent to 8F, CF_2 region) which were not assigned.			
^{1}H			
5.42	M		c, d



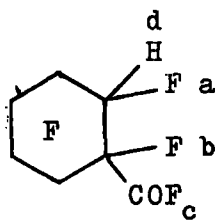
(138)



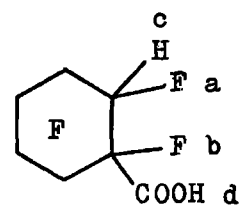
(139)

51. Cis-2H-decafluorocyclohexyl bromomethyl ketone (139)			
^{19}F			
230.4	D, J_{ac}=44 of M	1	a
194.6	Broad S	1	b
Signals between 117 and 149 p.p.m. (equivalent to 8F, CF_2 region) which were not assigned.			
^{1}H			
4.77	D, J=4	2	d
5.92	D of M, J=12	1	c

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
52. Cis-2H-decafluorocyclohexyl acyl fluoride (140)			
^{19}F			
230.6	D, J_{ad}=44 of M	1	a
192.6	S	1	b
-23.6	Broad D, J=18	1	c
Signals between 116 and 150 p.p.m. (equivalent to 8F, CF_2 region) which were not assigned.			
^{1}H			
5.47	M, J=10		d



(140)

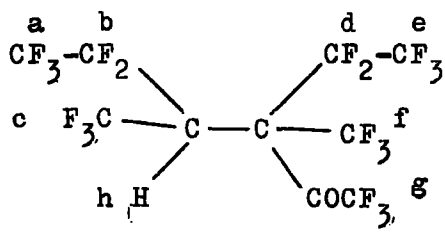


(141)

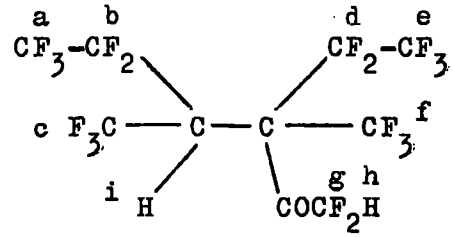
53. Cis-2H-decafluorocyclohexyl carboxylic acid (141)			
^{19}F			
231.1	Broad D, J_{ac}=39	1	a
192.7	Broad S	1	b
Signals between 117 and 150 p.p.m. (equivalent to 8F, CF_2 region) which were not assigned.			
^{1}H			
5.53	Broad S	1	c
10.23	S	1	d

Recorded with ether as solvent.

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
54. 4H-perfluoro-3-ethyl-3,4-dimethyl-hexan-2-one (144)			
^{19}F			
57.9	D	6	c, f
73.0	S	3	g
77.0	D, J=44	3	e or a
84.7	M, J=11	3	a or e
97.8, 114.9	AB, J=295	4	b, d
103.7	Broad S		
^{1}H			
5.08	Broad		h



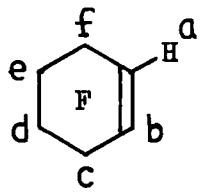
(144)



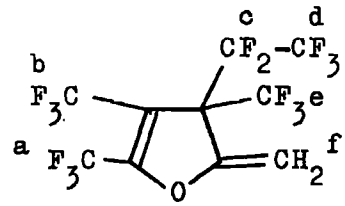
(143)

55. 1,4-dihydro-F-3-ethyl-3,4-dimethyl-hexan-2-one (143)			
^{19}F			
57.8, 58.9	Assymetric D	6	c, f
77.4	D, J=46	3	e or a
84.8	M	3	a or e
97.0, 114.6	AB, J=291	4	b, d
103.8	Broad D, J=116		
125.6	D, J_{gh}=52	2	g
^{1}H			
5.32	Broad M		i
6.55	T, J_{hg}=53		h

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
56. 1-hydro-F-cyclohexene (147)[170]			
^{19}F			
108.8	S	2	f
122.8	S	2	c
124.1	S	1	b
136.4	S	4	d, e
^{1}H			
6.10	S		a



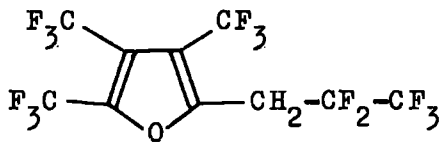
(147)



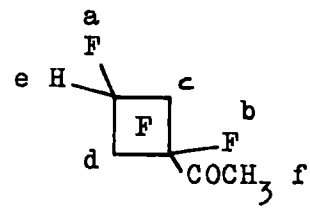
(148)

57. 2-methylideno-F-3,4,5-trimethyl-3-ethyl-dihydrofuran (148)			
^{19}F			
56.5	Broad S	3	b
68.3	Q, J=10	3	a
70.3	M, J=7	3	e
82.1	S	3	d
118.4	Assymetric D	2	c
^{1}H			
5.32	S		f

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
58. 2,3,4-tris(trifluoromethyl)-5-(1',1'-dihydro-pentafluoropropyl)-furan (149)			
^{19}F			
59.3	Sp, J=8	3	b
59.8	Broad S	3	c
64.6	Q, J=8	3	a
87.8	S	3	d
117.4	T, J_{ef} of Q, J=4	2	e
^{1}H			
3.78	T, J_{fe}=16		f



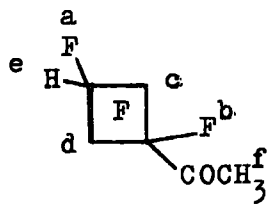
(149)



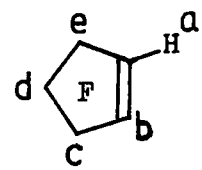
(150)

59. Cis-3H-hexafluorocyclobutyl methyl ketone (150)			
^{19}F			
195.1	S	1	b
163.2	D, J_{ae}=25	1	a
93.6, 101.4	AB, J=162	2	c, d
124.5, 137.4	AB, J=287	2	
^{1}H			
1.95	T, J=6	3	f
5.09	Broad	1	e

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
60. Trans-3H-hexafluorocyclobutyl methyl ketone (150)			
^{19}F			
181.5	S	1	b
152.3	D, J_{ae}=50	1	a
114.6, 136.8	AB, J=275	2	c, d
127.4, 141.0	AB, J=277	2	
^{1}H			
2.0	M	3	f
5.58	D, J_{ea}=50	1	e



(150)

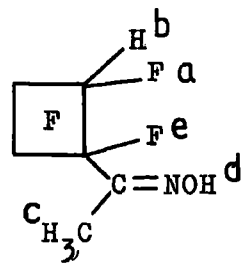


(151)

61. 1-hydro-F-cyclopentene (151)[179]

^{19}F			
109.0	D, J=12	2	e
122.2	D, J=13	2	c
127.4	Broad S	1	b
132.3	D, J=3	2	d
^{1}H			
5.97	S		a

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
62. Cis-2H-hexafluorocyclobutyl methyl ketone oxime (154)			
^{19}F			
223.6	D, J_{ab}=49 of T, J=7	1	a
191.9	Broad S	1	e
118.2, 135.6	AB, J=228	4	Ring CF_2
126.6, 133.1	AB, J=230		
^{1}H			
2.73	S	3	c
5.37	D, J_{ba}=49 of P, J=9	1	b
8.62	S	1	d

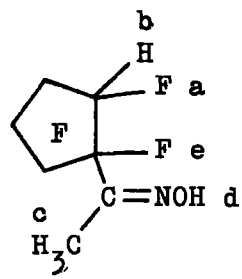


(154)

63. Trans-2H-hexafluorocyclobutyl methyl ketone oxime (154)			
^{19}F			
213.4	D, J_{ab}=50	1	a
167.9	D, J=10 of D, J=18	1	e
121.1, 134.8	AB, J=233	4	Ring CF_2
127.2	D, J=23		
^{1}H			
2.0	S	3	c
5.32	D, J_{ba}=50 of M	1	b
9.95	S	1	d

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
64. Cis-2H-octafluorocyclopentyl methyl ketone oxime (155)			
^{19}F			
227.2	Broad D, J_{ab}=46	1	a
188.6	Broad S	1	e
116.9, 128.6	AB, J=250	6	Ring CF_2
119.9, 136.2	AB, J=270		
129.8	D, J=30		
^{1}H			
2.33	S	3	c
5.82	D	1	b
8.67	Broad S	1	d

Recorded in ether solution.



(155)

65. Trans-2H-octafluorocyclopentyl methyl ketone oxime (155)

^{19}F

205.0	Broad D, J_{ab} =47	1	a
169.7	Broad S	1	e

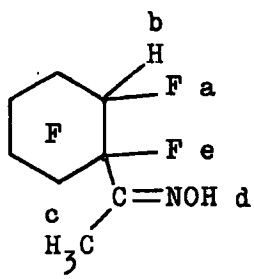
Signals between 113 and 134 p.p.m. (equivalent to 6F, CF_2 region) which were not assigned.

^{1}H

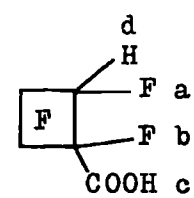
2.37	S	3	c
5.42	Broad D, J_{ba}=47	1	b
9.80	S	1	d

Recorded in $CDCl_3$ solution.

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
66. Cis-2H-decafluorocyclohexyl methyl ketone oxime (156)			
^{19}F			
230.0	Broad D	1	a
191.4	Broad S	] 1	e
182.5	Broad S	]	
Signals between 114 and 149 p.p.m. (equivalent to 8F, CF_2 region) which were not assigned.			
^{1}H			
2.42	S	3	c
5.93	D, J_{ba}=52 of M, J=12	1	b
7.30	S	1	d
Recorded in ether solution.			



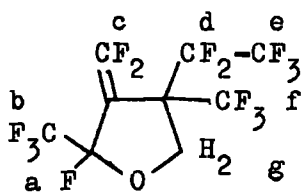
(156)



(157)

67. 2H-hexafluorocyclobutyl carboxylic acid(157) isomer mixture			
^{19}F			
218.0	D, J_{ad}=50	] 1	cis a
210.3	S	]	trans a
194.7		] 1	cis b
172.6	S	]	trans b
116.0, 135.0	AB, J=230	] 4	Ring CF_2
123.0, 127.5	AB, J=230	]	
^{1}H			
5.27	Broad D	1	d
9.17	S	1	c

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
68. 5,5-dihydro-F-2,4-dimethyl-3-methylideno-4-ethyl-tetrahydrofuran (161)			
^{19}F			
65.6	D, J_{ca}=62 of AB, J=17	2	c
69.5	M	3	f
71.6	St, J=6	3	b
82.4	S	3	e
104.5	Broad S	1	a
115.8	D, J=27 of Q, J=12	2	d
^{1}H			
4.52	Broad S		g



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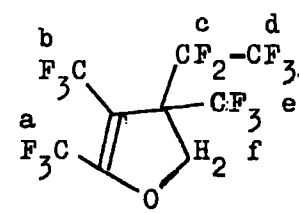
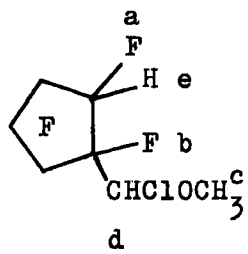


(162)

69. 5,5-dihydro-F-2,3,4-trimethyl-4-ethyl-dihydrofuran (162)			
^{19}F			
56.1	Broad S	3	b
68.9	Q, J=10	3	a
70.0	M	3	e
82.2	S	3	d
119.5	Broad S	2	c
^{1}H			
4.85	Broad S		f

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
70. 2H-octafluorocyclopentyl methoxy chloromethane (164) isomer mixture			
^{19}F			
211.9	Broad	1	a
190.1	Broad	1	b
Signals between 115 and 138 p.p.m. (equivalent to 6F, CF_2 region) which were not assigned.			
^{1}H			
3.90	S	3	c
4.81	Broad	1	e
6.00	Broad	1	d



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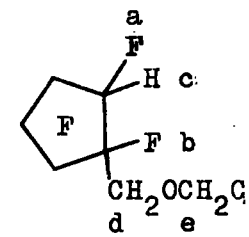
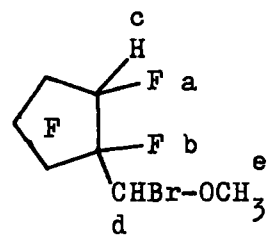


(163)

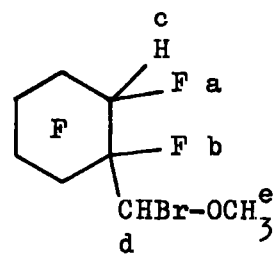
71. 2H-octafluorocyclopentyl chloromethoxy methane (163) isomer mixture			
^{19}F			
225.9	D, J_{ac}=46	1	cis a
212.3	D, J_{ac}=46		trans a
192.8	Broad S	1	cis b
180.4	Broad S		trans b
Signals between 115 and 138 p.p.m. (equivalent to 6F, CF_2 region) which were not assigned.			
^{1}H			
3.07	S	3	d
3.43	S		d
3.78	S		c
5.75	Broad S	2	e

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
72. 2H-octafluorocyclopentyl methoxy bromomethane (165) isomer mixture			
^{19}F			
222.6	Broad S	1	a
212.3	D		
210.8	D		
190.0	S	1	b
185.4	S		
183.6	S		
180.7	S		
Signals between 116 and 135 p.p.m. (equivalent to 6F, CF_2 region) which were not assigned.			
^{1}H			
3.75	S	3	e
4.45	S	2	c
4.90	S		
5.80	S		d
6.07	S		
6.42	S		



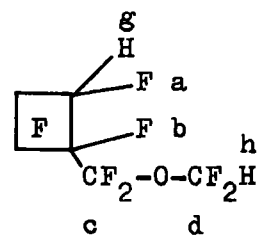
(165)

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
73. 2H-decafluorocyclohexyl methoxy bromomethane (166) isomer mixture			
^{19}F			
233.4	D		
231.8	D	1	a
211.7	S		
188.5	Assymetric D		
183.5	S	1	b
178.7	S		
Signals between 116 and 149 p.p.m. (equivalent to 8F, CF_2 region) which were not assigned.			
^{1}H			
3.85	S	3	e
5.61	D		c
6.32	D	2	
6.48	S		d
6.70	S		



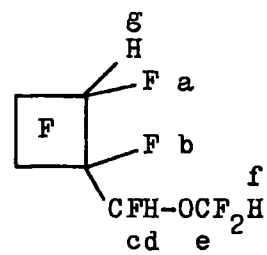
(166)

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
74. 2H-hexafluorocyclobutyl difluoromethoxy difluoromethane (168)			
^{19}F			
223.3	Broad D	1	cis a
218.3	Broad D, J_{ag}=47		trans a
202.2	T, J=11	1	cis b
182.7	M, J=4		trans b
79.2	M, J=4	2	c
87.1	D, J_{dh}=70 of T, J=5	2	d
119.5, 138.7	AB, J=232	2	Ring CF_2
129.1	M	2	
^{1}H			
5.37	Broad D, J_{ga}=50		g
6.77	T, J_{hd}=70		h



(168)

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
75. 2H-hexafluorocyclobutyl difluoromethoxy fluoromethane (167)			
^{19}F			
219.0	D, J_{ag}=47	1	a
217.9	d, J_{ag}=52 of D, J=17		
192.4	S	1	b
144.2	Broad S	1	c
122.2, 136.7	AB, J=236	4	Ring CF_2
129.9	D, J=11		
88.0	M	2	e
^{1}H			
7.32	Broad D	1	g
8.19	D, J=43 of T, J=11	1	d
8.4	T, J_{fe}=72	1	f



(167)

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
76. 2,2,3,4,4,4-hexafluorobutyl difluoromethyl ether (169)			
^{19}F			
76.3	M	3	a
88.4	D, J_{fg}=71	2	f
120.9	Broad D, J=106	2	d
215.7	D, J_{bc}=43	1	b
^{1}H			
4.52	Complex M	2	e
5.23	D, J_{cb}=45	1	c
6.55	T, J_{gf}=73	1	g

a bc d e f g
CF_3-CFH-CF_2-CH_2OCF_2H

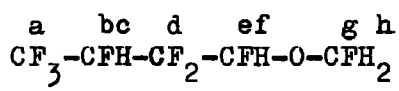
(169)

a bc d ef g h
CF_3-CFH-CF_2-CHF-O-CF_2H

(170)

77. 1,2,2,3,4,4,4-heptafluorobutyl difluoromethyl ether (170)			
^{19}F			
76.5	M	3	a
87.9	D, J_{gh}=72 of M	2	g
130.0	Broad S	2	d
145.7	Broad D	1	f
152.1	Broad D		
217.5	Broad M	1	b
^{1}H			
5.47	Broad D, J_{cb}=48		c
6.38	D, J=55 of T, J=6		e
6.80	T, J_{hg}=70		h

Shift p.p.m.	Fine Structure Coupling Constants in Hz.	Relative Intensity	Assignment
78. 1,2,2,3,4,4,4-heptafluorobutyl fluoromethyl ether (171)			
^{19}F			
76.3	D of M	3	a
130.0	D of M	2	d
146.7	Broad D	1	e
154.1	Broad D		
159.2	Broad M	1	g
217.8	Broad M	1	b
^{1}H			
5.78	Broad D, J_{cb}=54		c
6.08	Broad D, J=53		f, h



(171)

APPENDIX II

INFRA-RED SPECTRA

Index

25. 1-(F-cyclobutenyl)-hexafluorocyclobutyl methyl ketone (98).

26. (E)-(3-trifluoromethyl)-1,1,1-trifluoropent-2-en-4-one (99).

27. 2,3-bis(trifluoromethyl)-1,1,4,4-tetrafluorohex-1-en-5-one (100).

28. 4,5-bis(trifluoromethyl)-3,3,6,6-tetrafluorooctan-2,7-dione (101).

29. 3-chloro-2,2,3-trifluoropropyl methyl ether (103).

30. 3,5-dichloro-2,2,3,4,4,5-hexafluoropentyl methyl ether (104).

31. 2,2,3,4,4,4-hexafluorobutyl methyl ether (105).

32. 2-trifluoromethyl-2,3,4,4,4-pentafluorobutyl methyl ether (106).

33. 2,2,3-tris(trifluoromethyl)-4,4,4-trifluorobutyl methyl ether (107).

34. Bis-[2,2,3-tris(trifluoromethyl)-4,4,4-trifluorobutyl] ether (108).

35. Bis-[2-pentafluoroethyl-2,3-bis(trifluoromethyl)-4,4,5,5,5-pentafluoropentyl] ether (109).

36. Bis-[1-spirooctafluorocyclopentyl-1-(2',2',3',3',4',4',5',5'-octafluorocyclopentyl)]-methyl ether (110).

37. 1,1,1,2,3,3-hexafluoro-5,7-dioxaoctane (118).

38. 2-methoxy-3,3,4,5,5,5-hexafluoropentyl methyl ether (121).

39. 1,1,1,2,3,3-hexafluoro-5,8-dioxanonane (122).

40. 2-hydroxy-3,3,4,5,5,5-hexafluoropentyl methyl ether (Diastereomer A) (125).

41. 2-hydroxy-3,3,4,5,5,5-hexafluoropentyl methyl ether (Diastereomer B) (125).

42. 2-methoxy-3,3,4,5,5,5-hexafluoropentan-1-ol (126).

43. 4-(2'-hydroxyethoxy)-1,1,1,2,3,3-hexafluorobutane (127).

44. Tri-(2H-1,2,3,3,4,4,5,5-octafluorocyclopentyl)-methyl borate (131).

45. 2,2,3,4,4,4-hexafluorobutyl dimethyl phosphate (132).

46. Trimethyl 2,2,3,4,4,4-hexafluorobutoxy silane (133).

47. γ-[2-(1',1',2',3',3',3'-hexafluoropropyl)]-butyrolactone (134).

48. 1,1,1,2,3,3-hexafluoropentan-4-one (136).

49. Cis-2H-decafluorocyclohexyl chloromethyl ketone (137).

50. Cis-2H-decafluorocyclohexyl dichloromethyl ketone (138).

51. Cis-2H-decafluorocyclohexyl bromomethyl ketone (139).
52. Cis-2H-decafluorocyclohexyl acyl fluoride (140).
53. Cis-2H-decafluorocyclohexyl carboxylic acid (141).
54. Anilinium cis-2H-decafluorocyclohexyl carboxylate (142).
55. 4H-perfluoro-3-ethyl-3,4-dimethyl-hexan-2-one (144).
56. 1,4-dihydro-F-3-ethyl-3,4-dimethyl-hexan-2-one (143).
57. 2-methylideno-F-3,4,5-trimethyl-3-ethyl-dihydrofuran (148).
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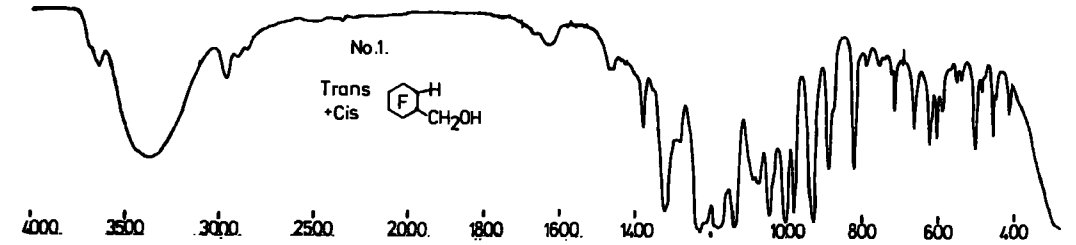
59. Trans-3H-hexafluorocyclobutyl methyl ketone (150).
60. Cis-2H-hexafluorocyclobutyl methyl ketone oxime (154).
61. Trans-2H-hexafluorocyclobutyl methyl ketone oxime (154).
62. Cis-2H-octafluorocyclopentyl methyl ketone oxime (155).
63. Trans-2H-octafluorocyclopentyl methyl ketone oxime (155).
64. Cis-2H-decafluorocyclohexyl methyl ketone oxime (156).
65. 2H-hexafluorocyclobutyl carboxylic acid (157) isomer mixture.
66. 5,5-dihydro-F-2,4-dimethyl-3-methylideno-4-ethyl-tetrahydrofuran (161).
67. 5,5-dihydro-F-2,3,4-trimethyl-4-ethyl-dihydrofuran (162).
68. 2H-octafluorocyclopentyl methoxy chloromethane (164) isomer mixture.
69. 2H-octafluorocyclopentyl chloromethoxy methane (163) isomer mixture.
70. 2H-octafluorocyclopentyl methoxy bromomethane (165) isomer mixture.
71. 2H-decafluorocyclohexyl methoxy bromomethane (166) isomer mixture.
72. 2H-hexafluorocyclobutyl difluoromethoxy difluoromethane (168).
73. 2H-hexafluorocyclobutyl difluoromethoxy fluoromethane (167).
74. 2,2,3,4,4,4-hexafluorobutyl difluoromethyl ether (169).
75. 1,2,2,3,4,4,4-heptafluorobutyl difluoromethyl ether (170).
76. 1,2,2,3,4,4,4-heptafluorobutyl fluoromethyl ether (171).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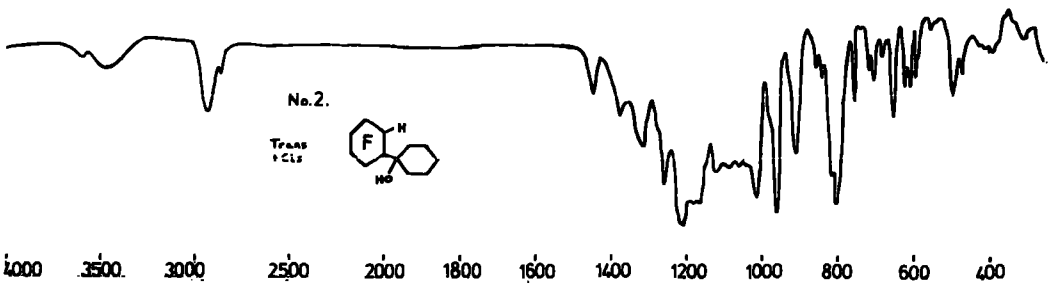
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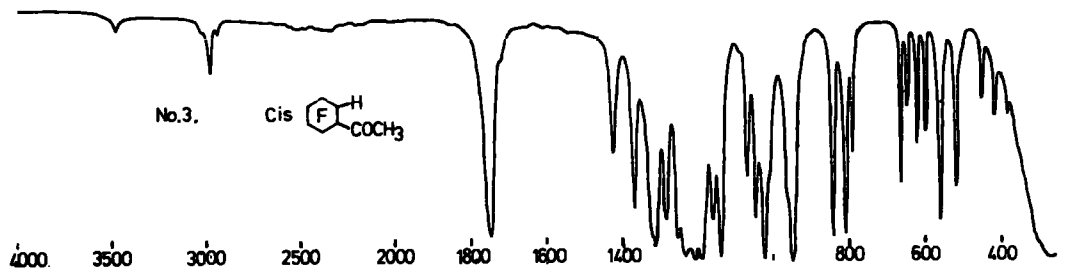
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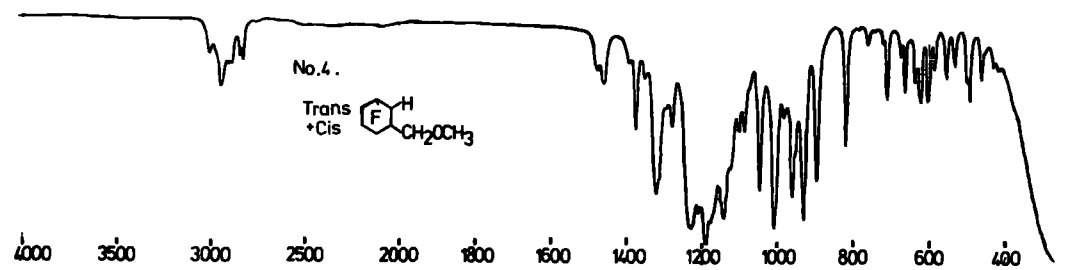
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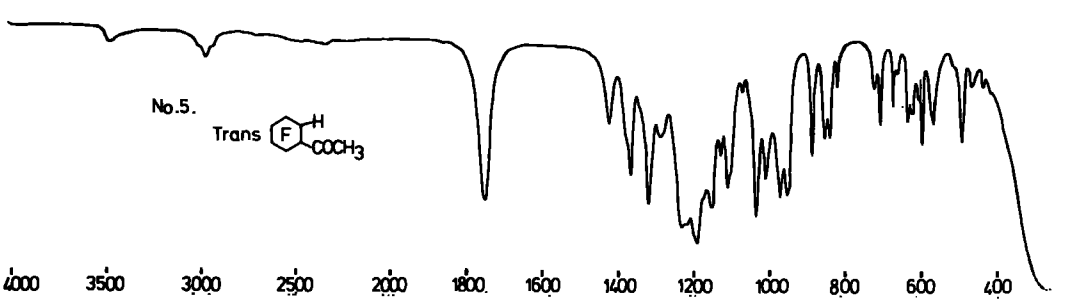
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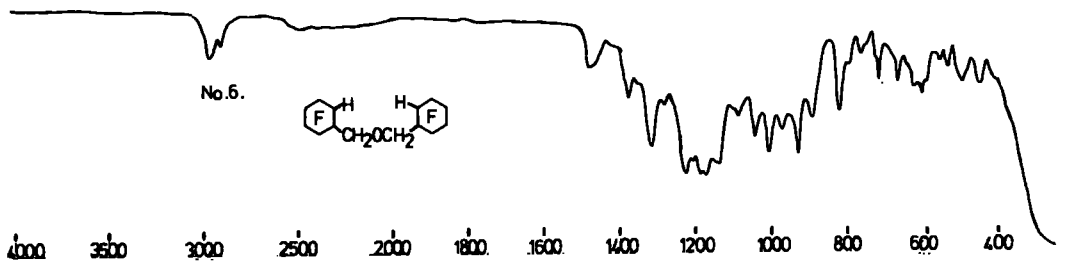
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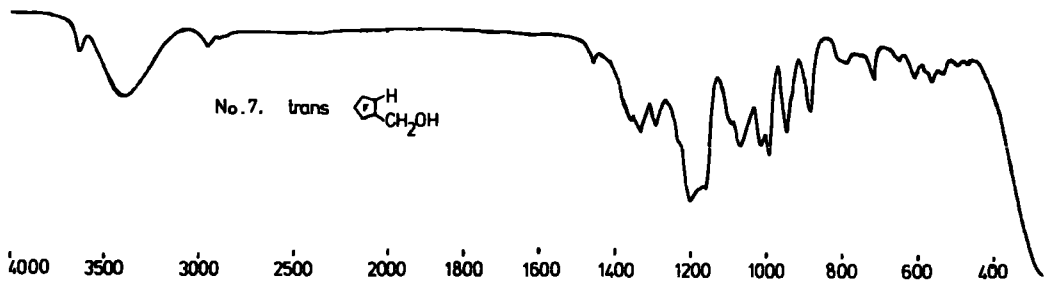
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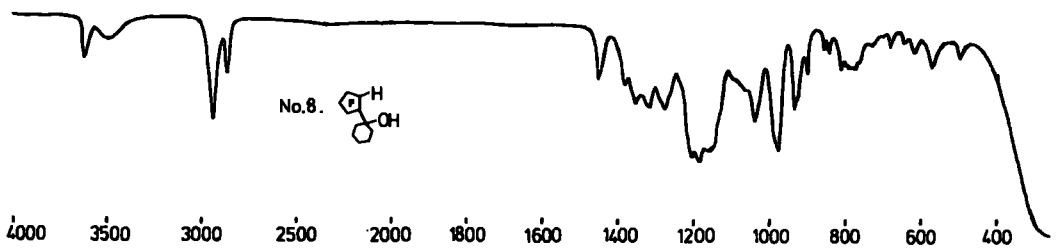
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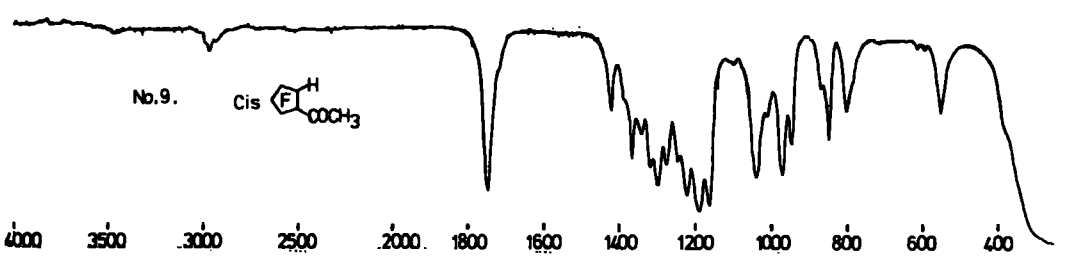
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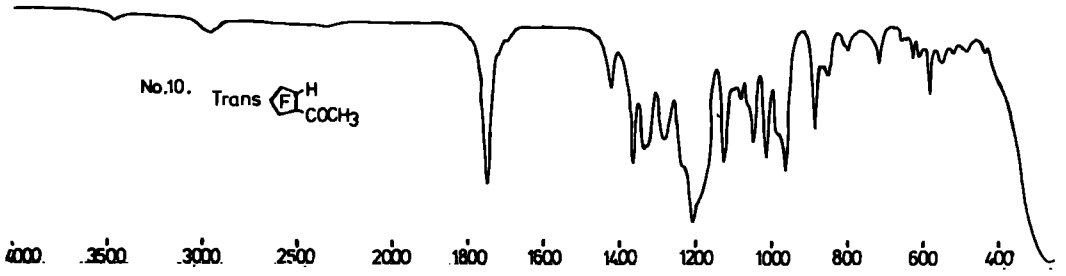
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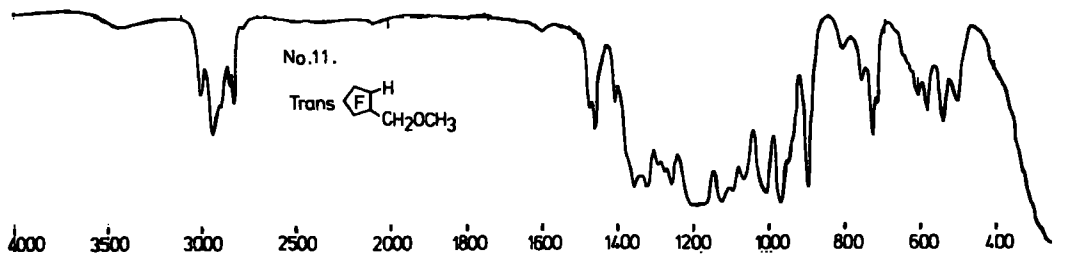
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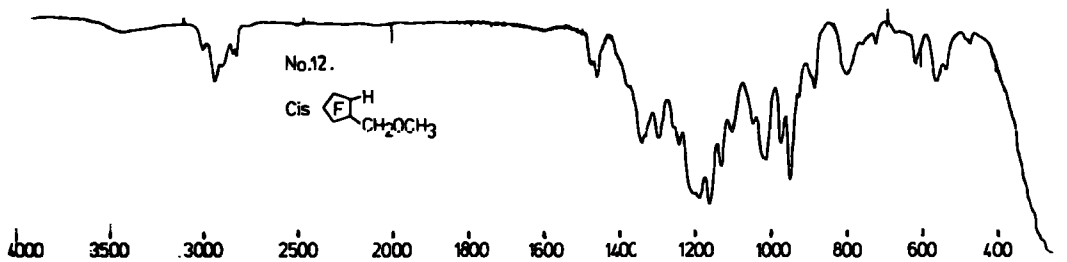
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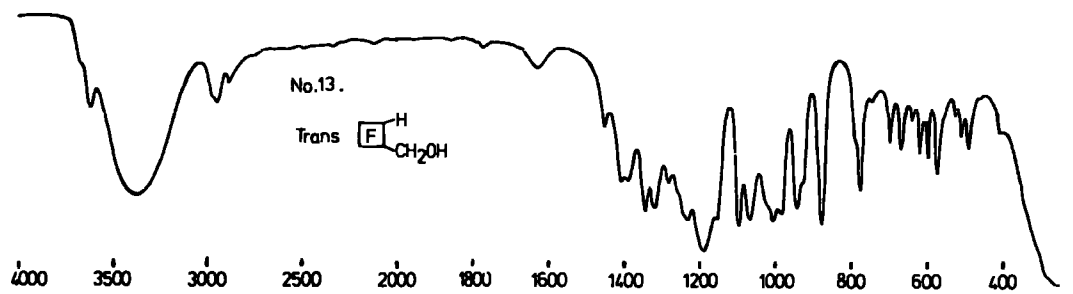
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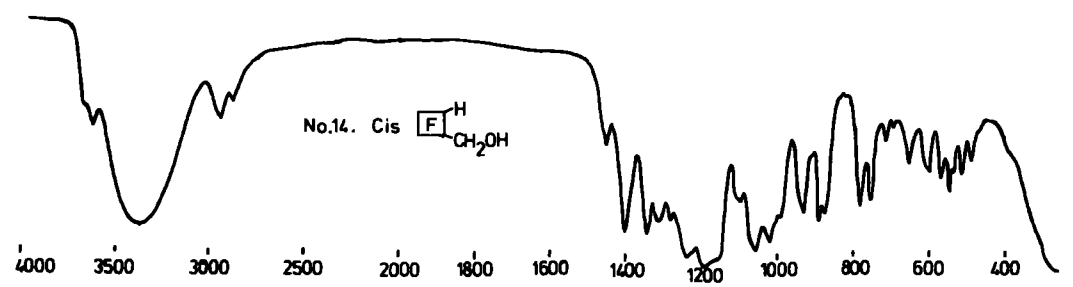
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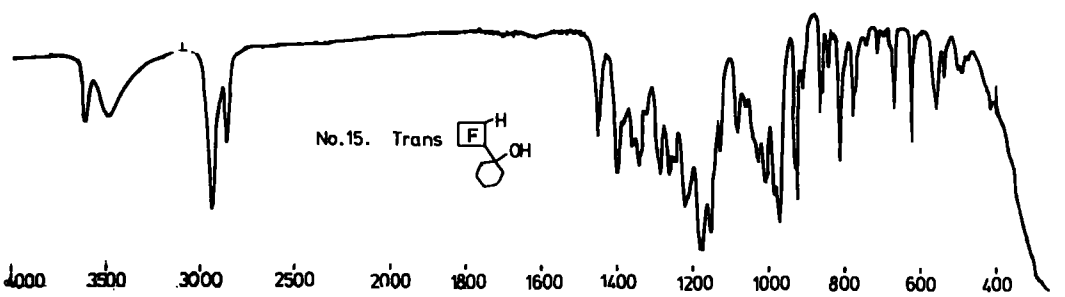
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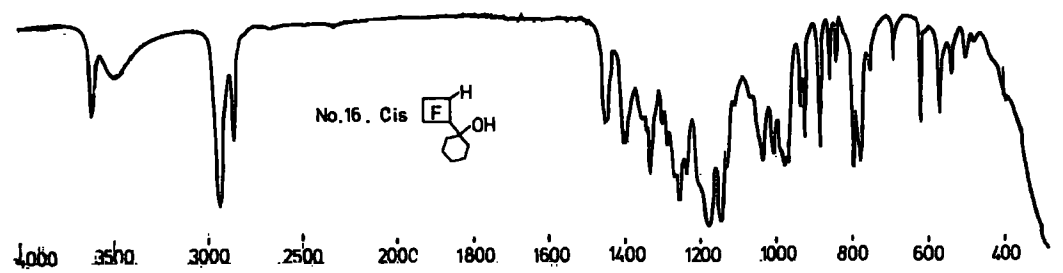
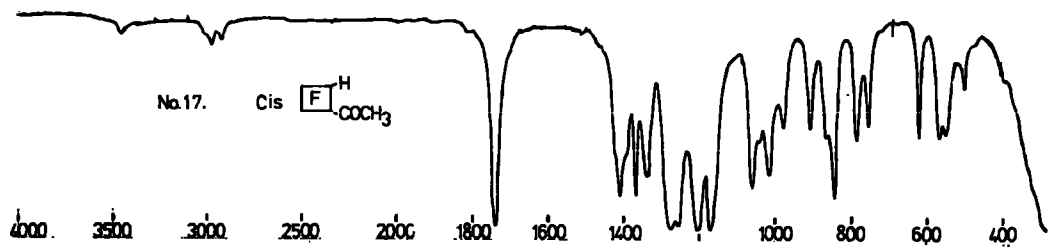
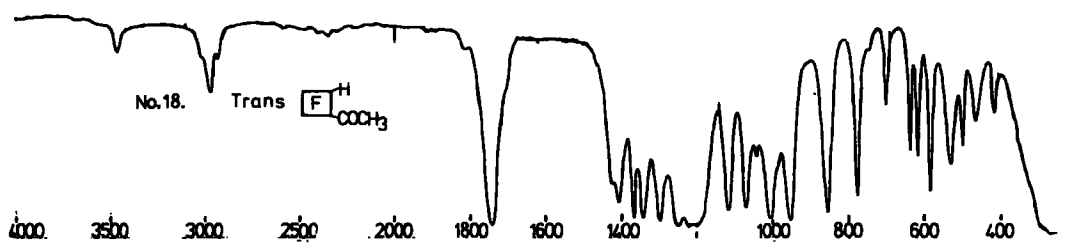
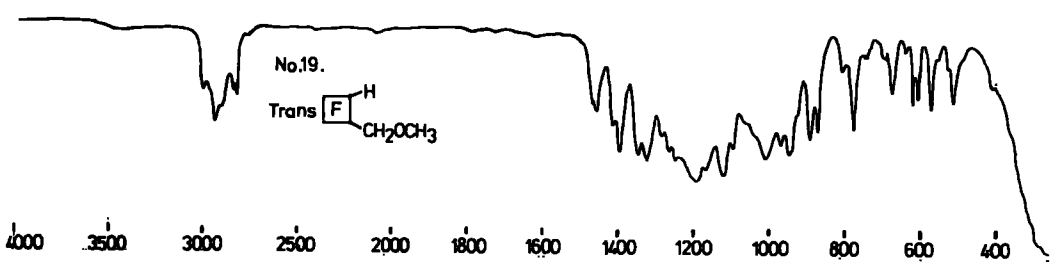
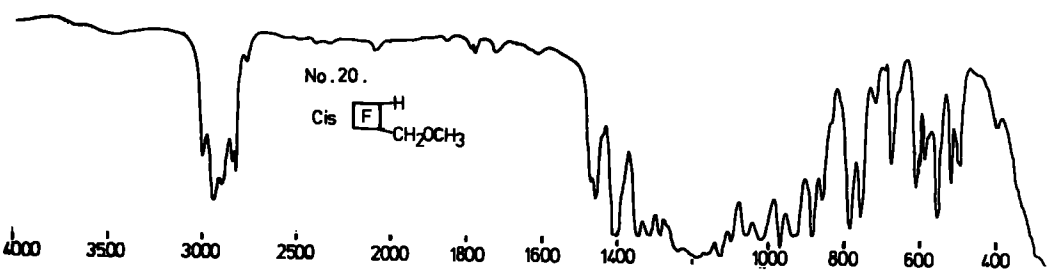
600
400

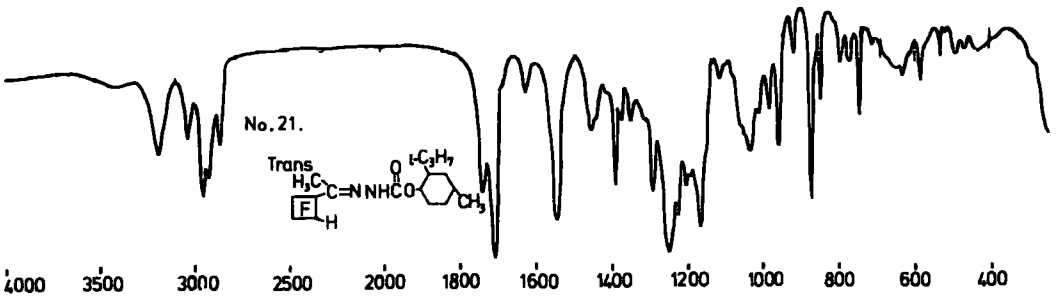

No.16. Cis
F
H
OH
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400

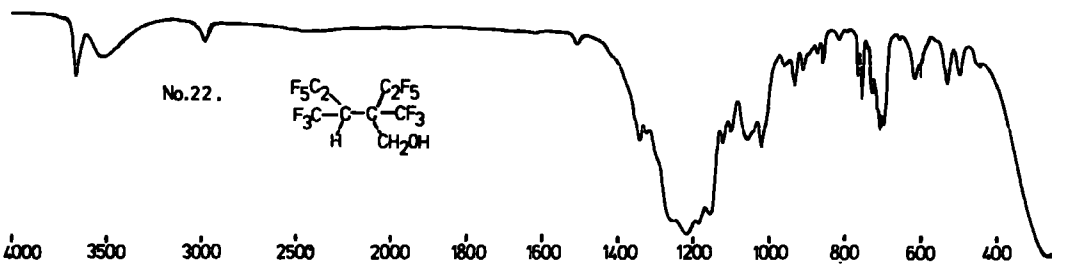

No.17.
Cis
F
H
COCH3
4000
3500
3000
2500
2000
1800
1600
1400
1000
800
600
400

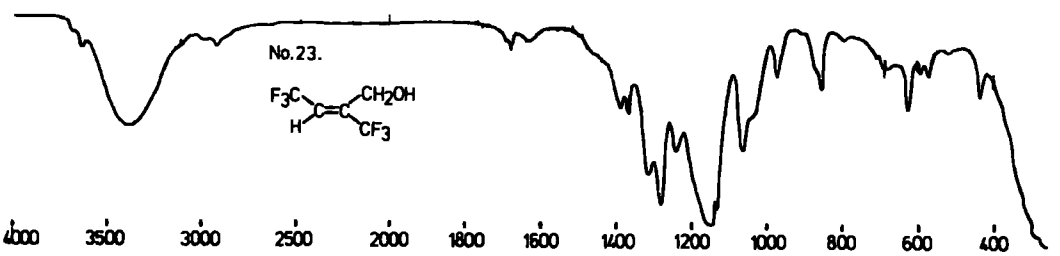

No.18.
Trans
F
H
COCH3
4000
3500
3000
2500
2000
1800
1600
1400
1000
800
600
400

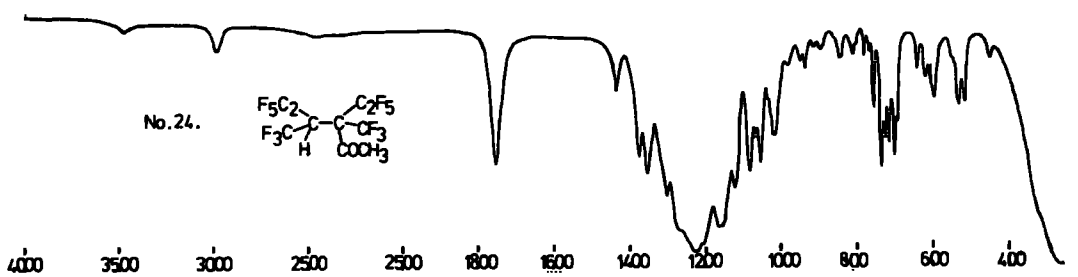

No.19.
Trans
F
H
CH2OCH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400

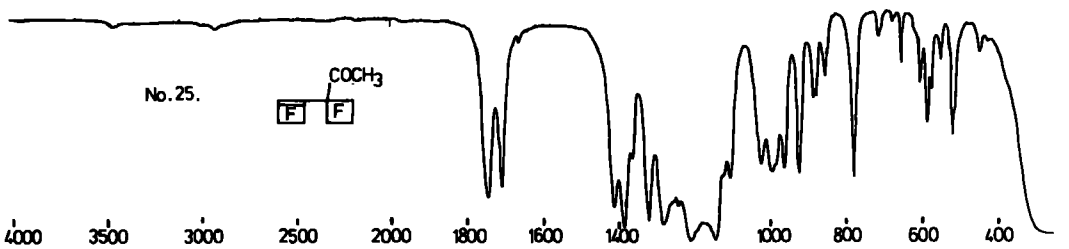

No.20.
Cis
F
H
CH2OCH3
4000
3500
3000
2500
2000
1800
1600
1400
1000
800
600
400

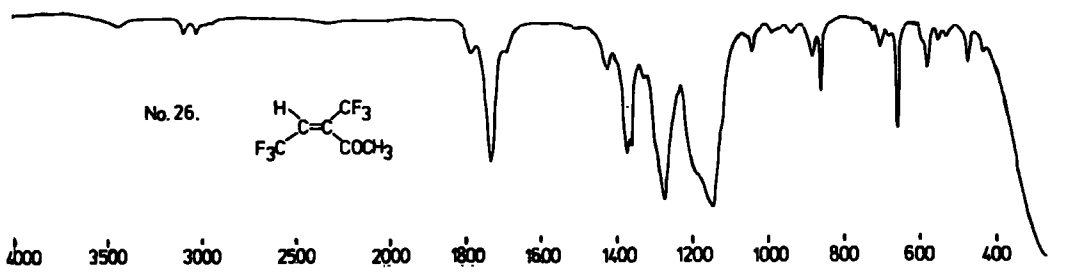

No.21.
Trans
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

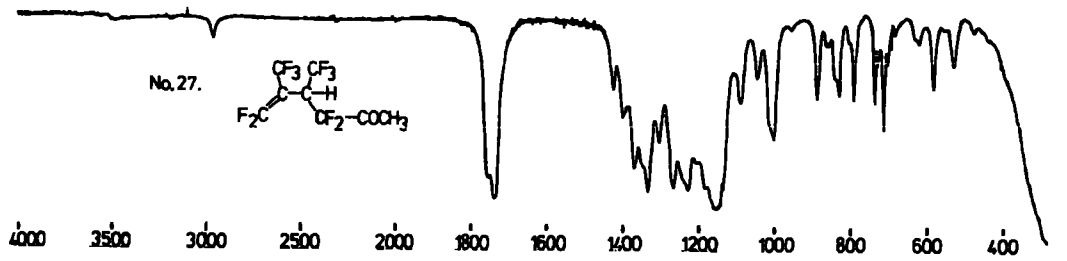

No.22.
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

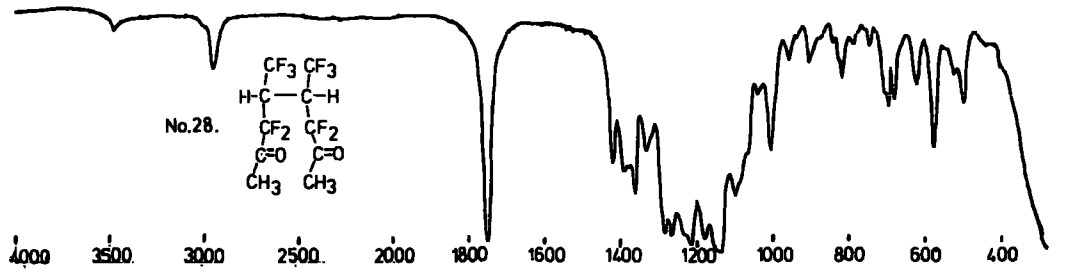

No.23.
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

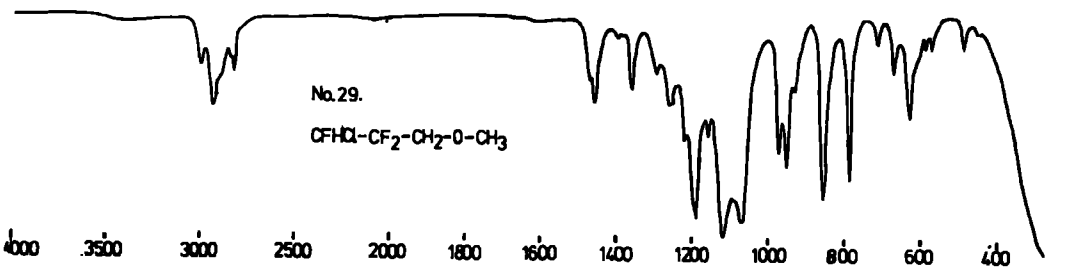

No.24.
4000 3500 3000 2500 2500 1800 1600 1400 1200 1000 800 600 400

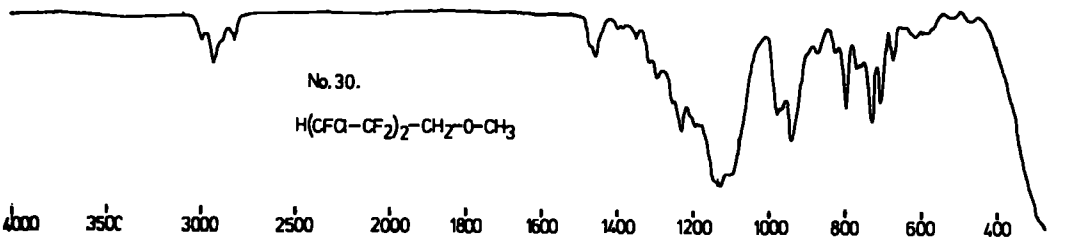

No.25.
4000 3500 3000 2500 2000 1800 1600 1400 1000 800 600 400

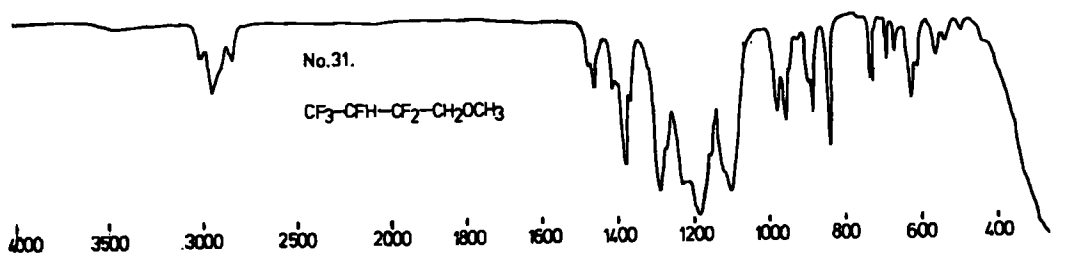

No. 26.
H
CF3
C=C
F3C
COCH3
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

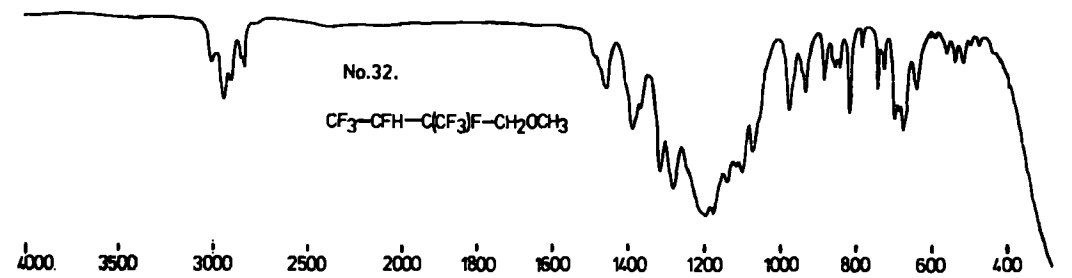

No. 27.
CF3 CF3
C—C—H
F2C
CF2—COCH3
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

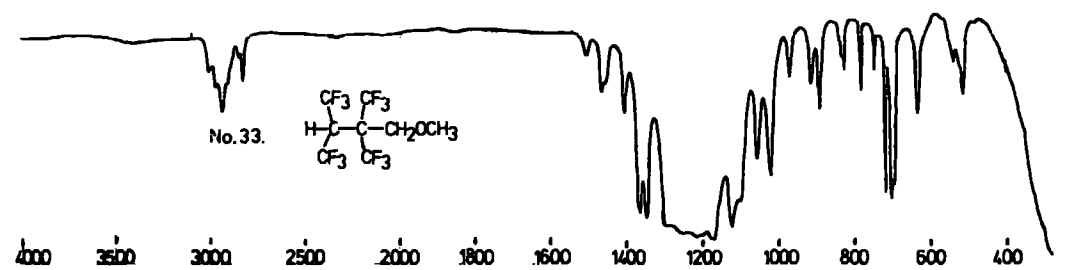

No. 28.
CF3 CF3
H-C—C-H
CF2 CF2
C=O C=O
CH3 CH3
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

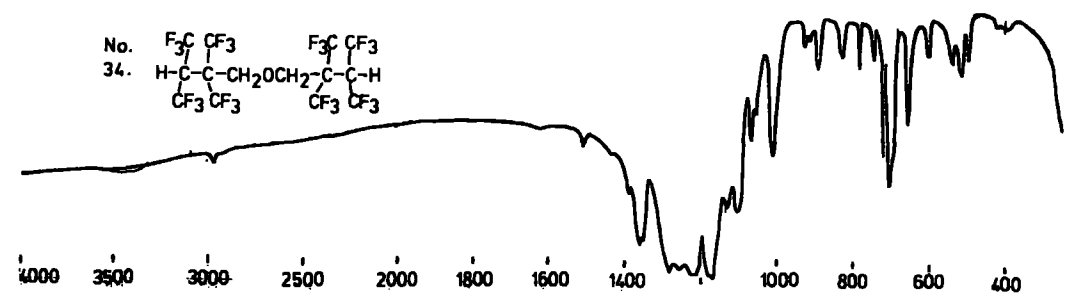

No. 29.
CFHCl-CF2-CH2-O-CH3
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

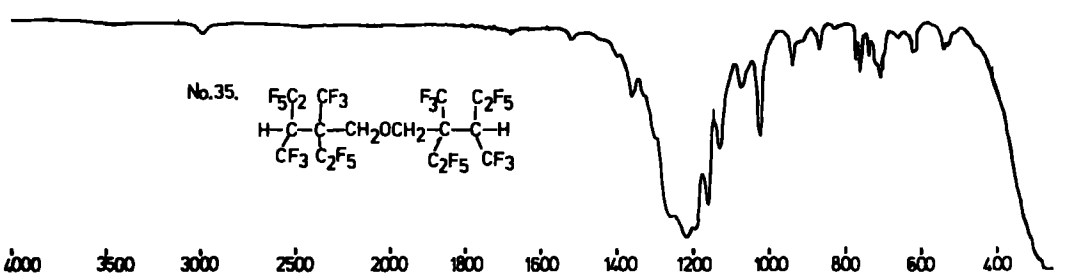

No. 30.
H(CFCl-CF2)2-CH2-O-CH3
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

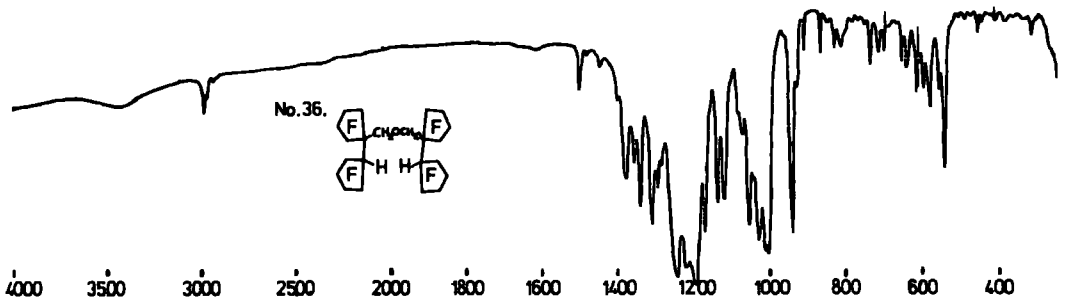

No.31.
CF3-CFH-CF2-CH2OCH3
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

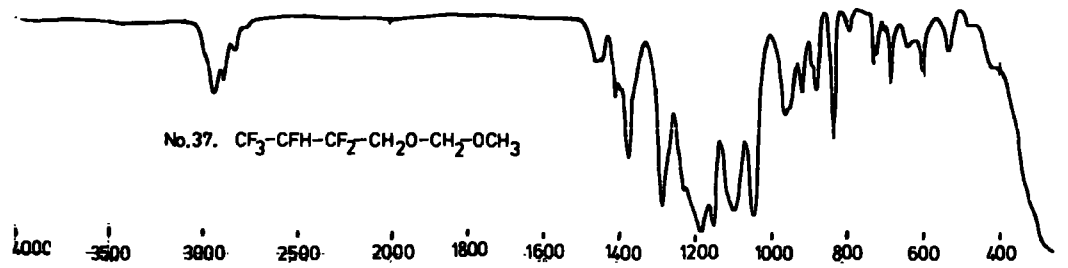

No.32.
CF3-CFH-C(CF3)F-CH2OCH3
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

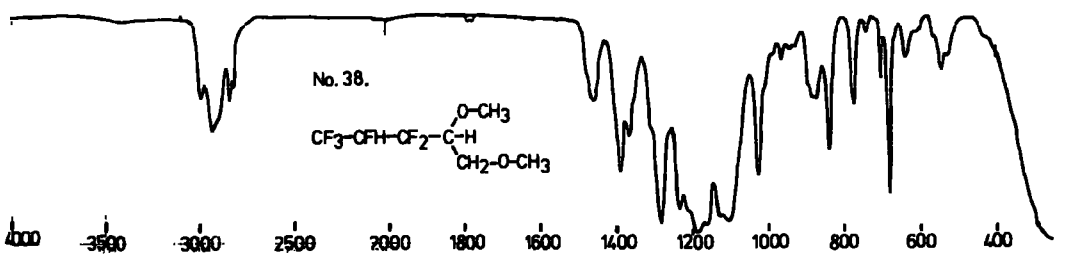

No.33.
CF3 CF3
H-C-C-CH2OCH3
CF3 CF3
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

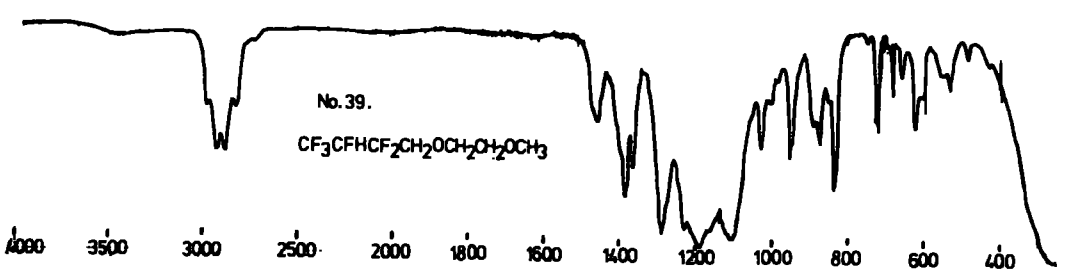

No. 34.
F3C CF3 F3C CF3
H-C-C-CH2OCH2-C-C-H
CF3 CF3 CF3 CF3
4000 3500 3000 2500 2000 1800 1600 1400 1000 800 600 400

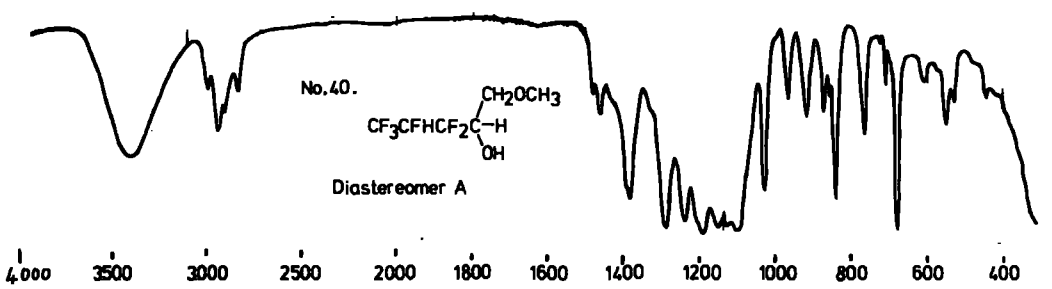

No.35.
F5C2 CF3 F3C C2F5
H-C-C-CH2OCH2-C-C-H
CF3 C2F5 C2F5 CF3
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

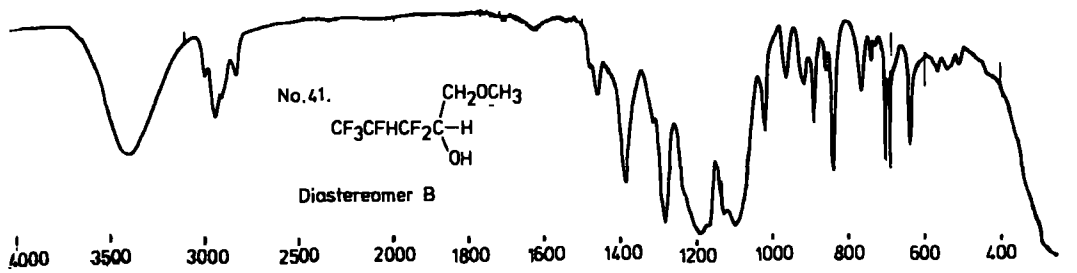

No.36.
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

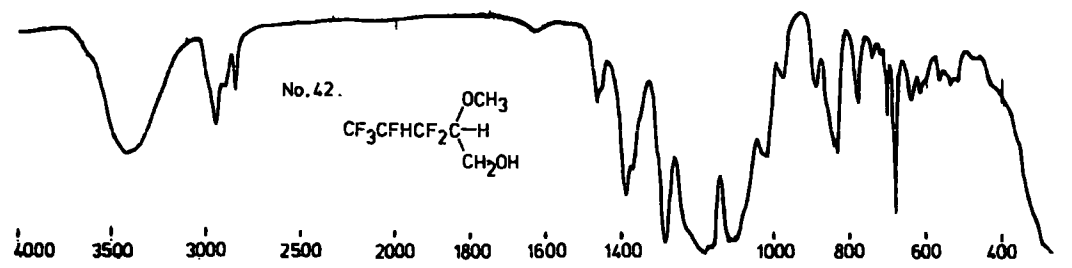

No.37. CF3-CFH-CF2-CH2O-CH2-OCH3
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

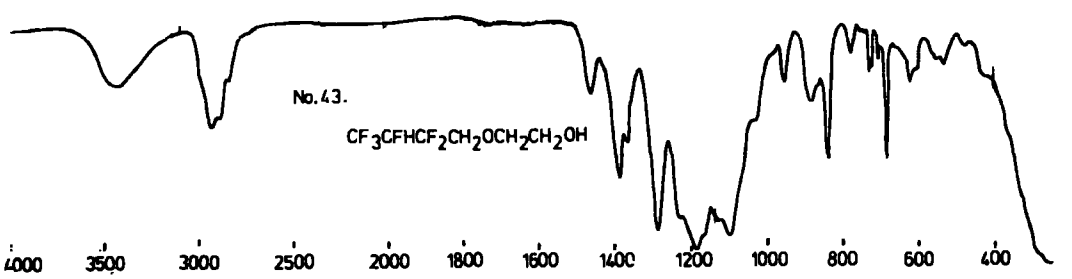

No.38.
CF3-CFH-CF2-C(O-CH3)(H)-CH2-O-CH3
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

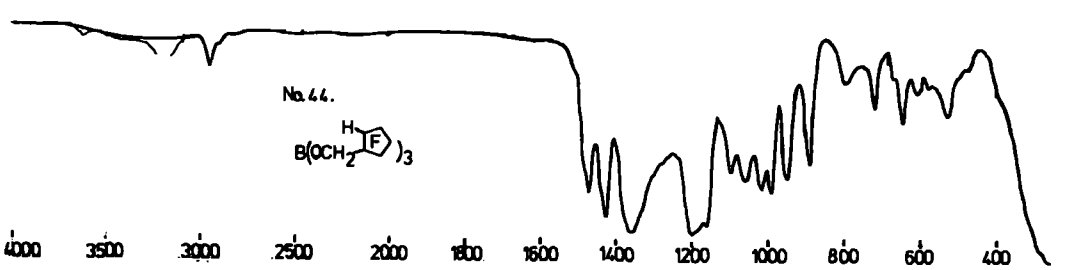

No.39.
CF3CFHCF2CH2OCH2CH2OCH3
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

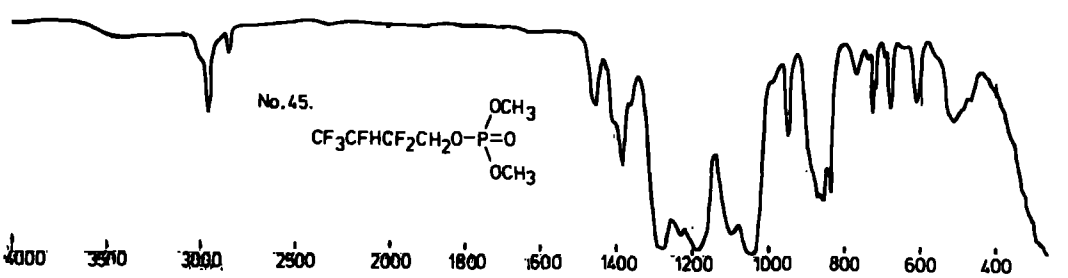

No.40.
CF3CFHCF2C(CH2OCH3)(H)-OH
Diastereomer A
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

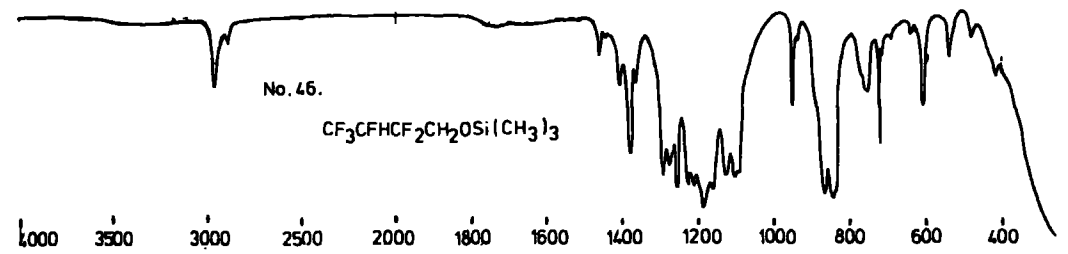

No.41.
CH2OCH3
CF3CFHCF2C—H
OH
Diastereomer B
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

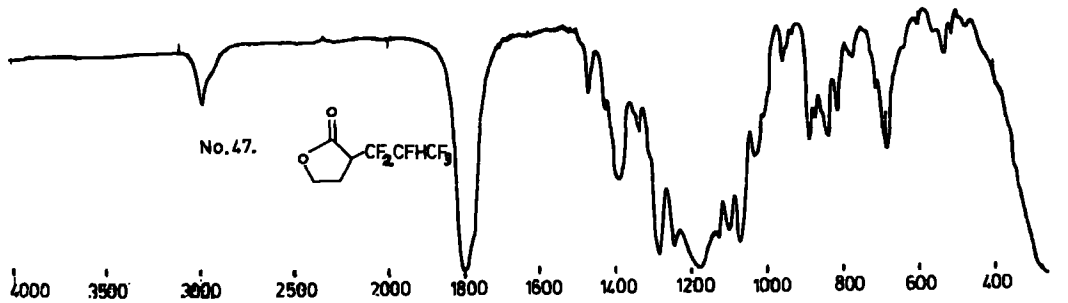

No.42.
OCH3
CF3CFHCF2C—H
CH2OH
4000 3500 3000 2500 2000 1800 1600 1400 1000 800 600 400

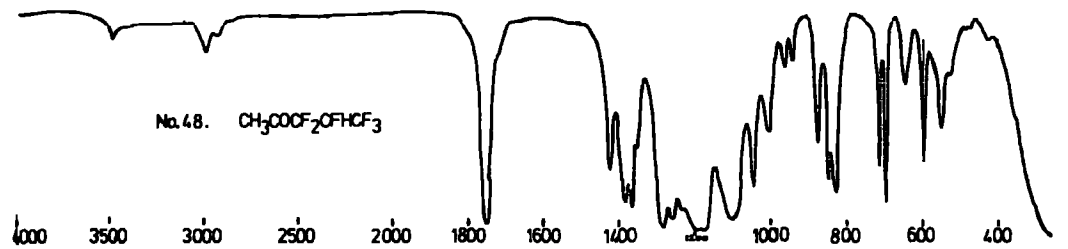

No.43.
CF3CFHCF2CH2OCH2CH2OH
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

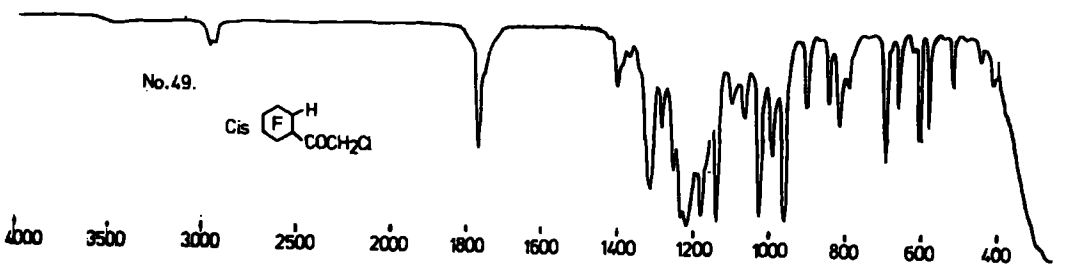

No.44.
H
B(OCH2
F
)3
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

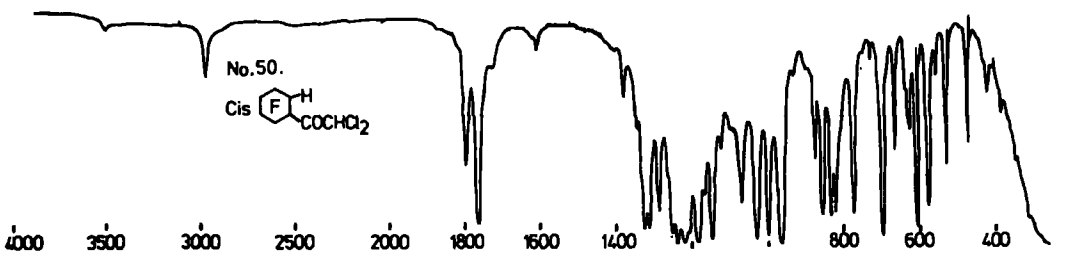

No.45.
OCH3
CF3CFHCF2CH2O—P=O
OCH3
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

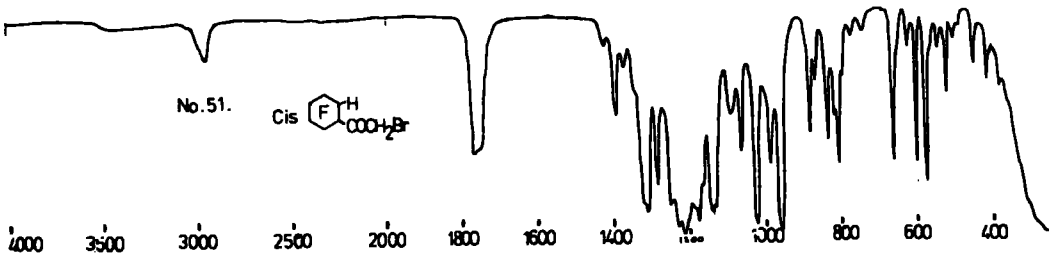

No.46.
$CF_3CFHCF_2CH_2OSi(CH_3)_3$
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

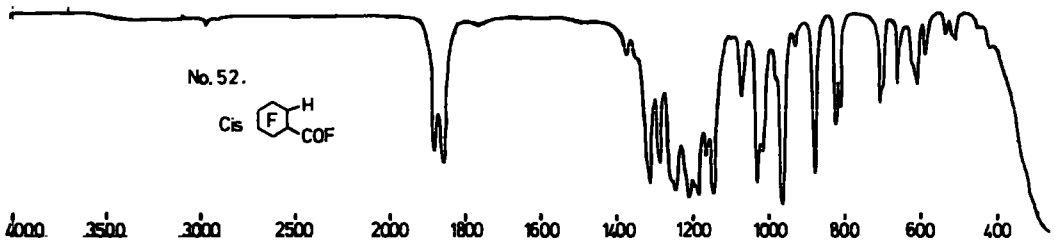

No.47.
CF_2CFHCF_3
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

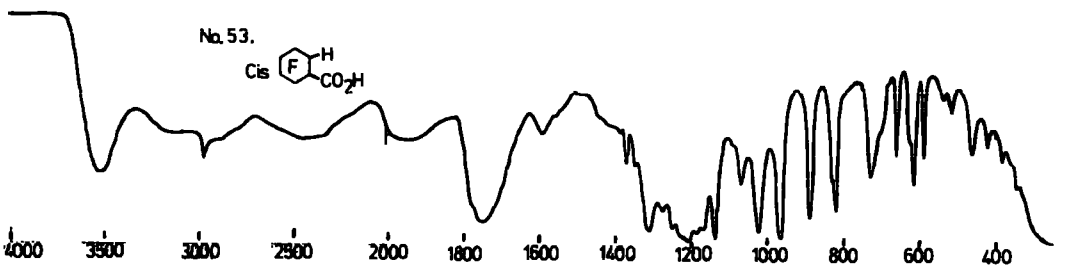

No.48. $CH_3COCF_2CFHCF_3$
4000 3500 3000 2500 2000 1800 1600 1400 1000 800 600 400

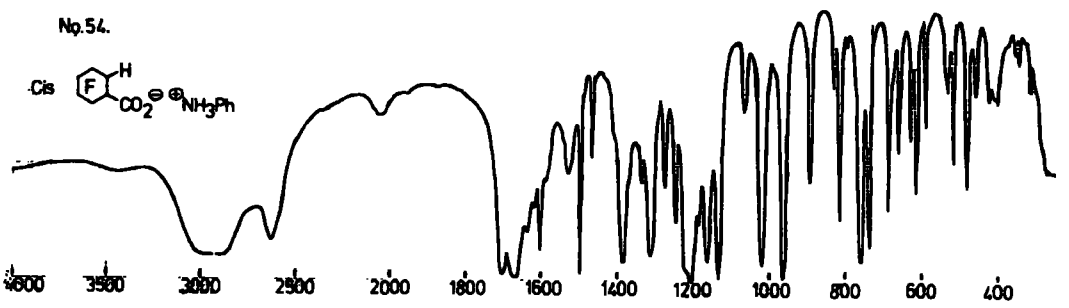

No.49.
Cis
F
H
$COCH_2Cl$
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

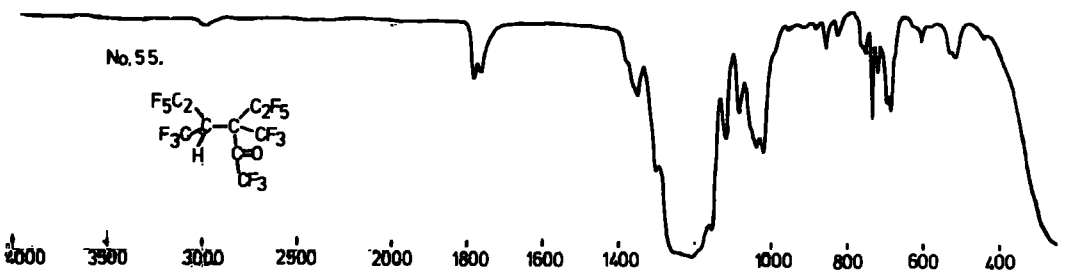

No.50.
Cis
F
H
$COCHCl_2$
4000 3500 3000 2500 2000 1800 1600 1400 800 600 400

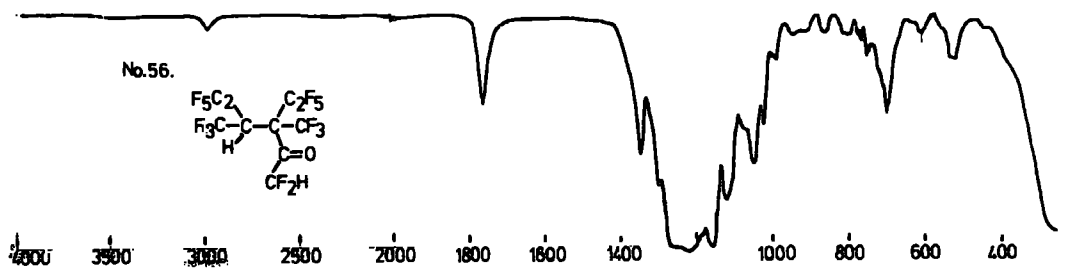

No.51.
Cis
4000 3500 3000 2500 2000 1800 1600 1400 800 600 400

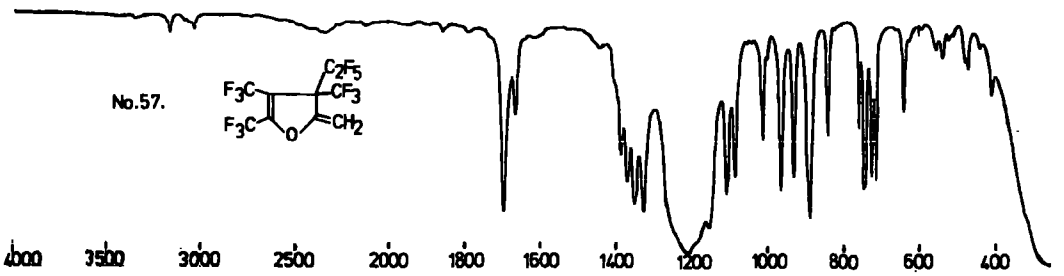

No.52.
Cis
COF
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400


No.53.
Cis
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400


No.54.
Cis
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400


No.55.
4000 3500 3000 2500 2000 1800 1600 1400 1000 800 600 400


No.56.
F_5C_2
C_2F_5
F_3C–C–C–CF_3
H
C=O
CF_2H
4000 3500 3000 2500 2000 1800 1600 1400 1000 800 600 400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CF_3
F_3C
O
CH_2
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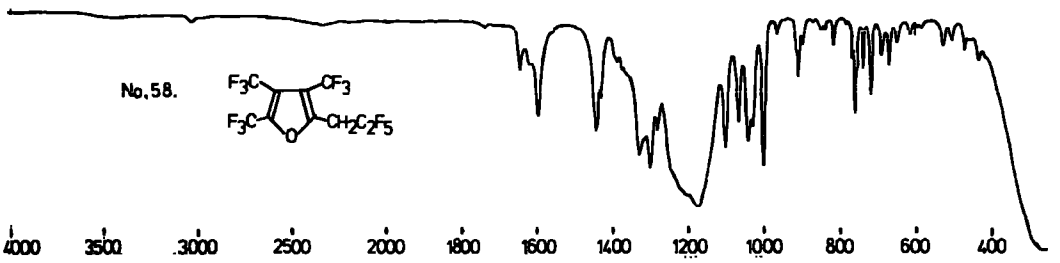
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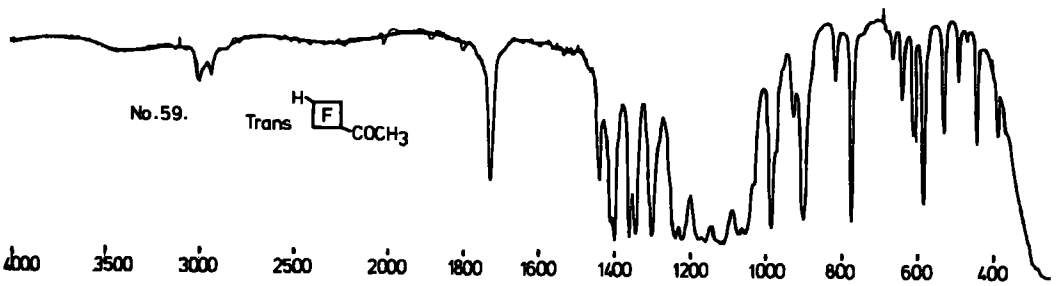
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Trans
F
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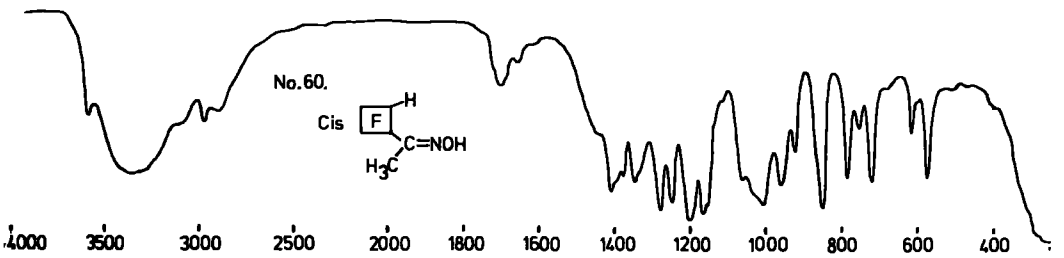
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H_3C
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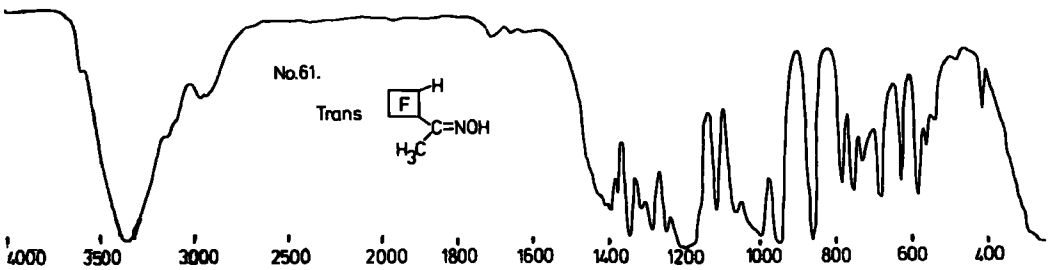
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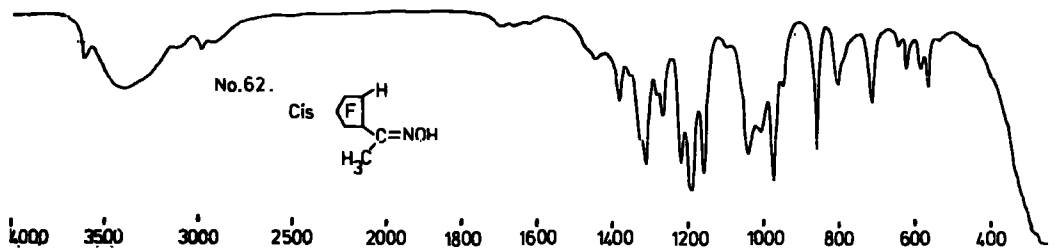
800
600
400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600
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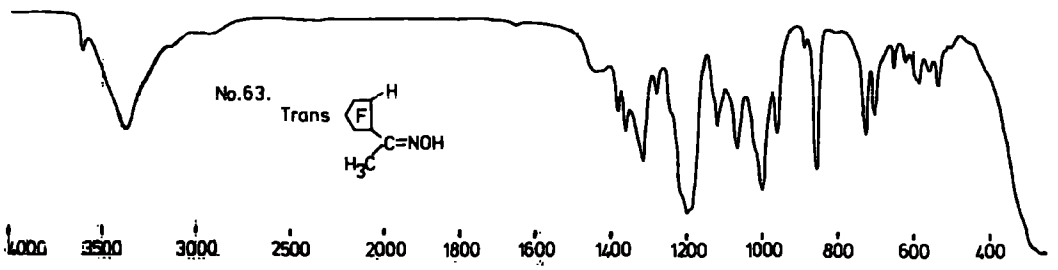
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600
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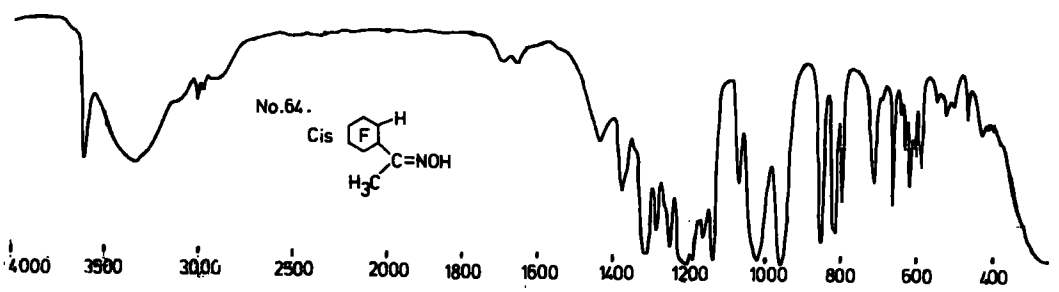
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C=NOH
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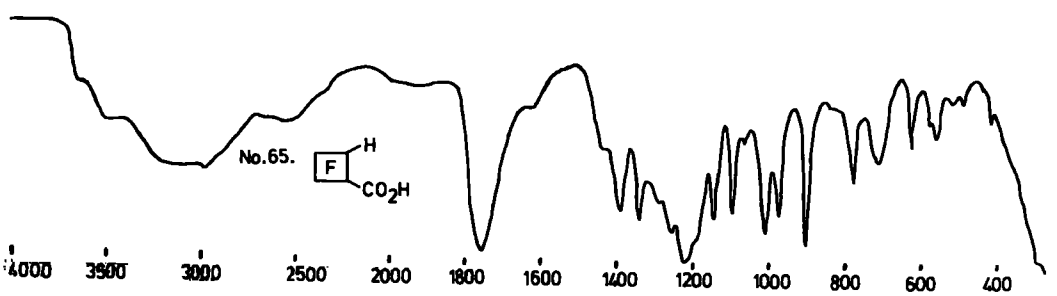
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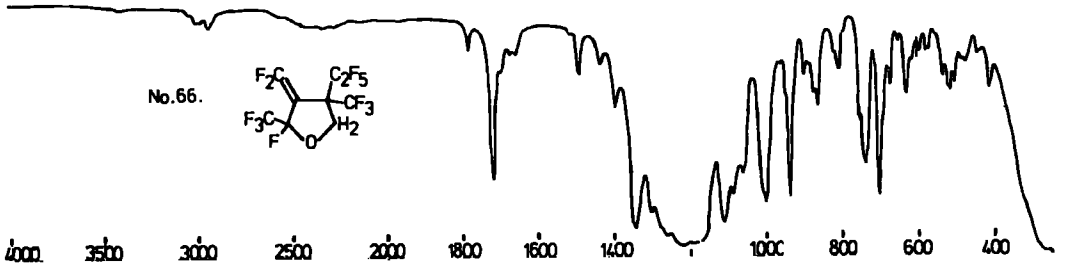
600
400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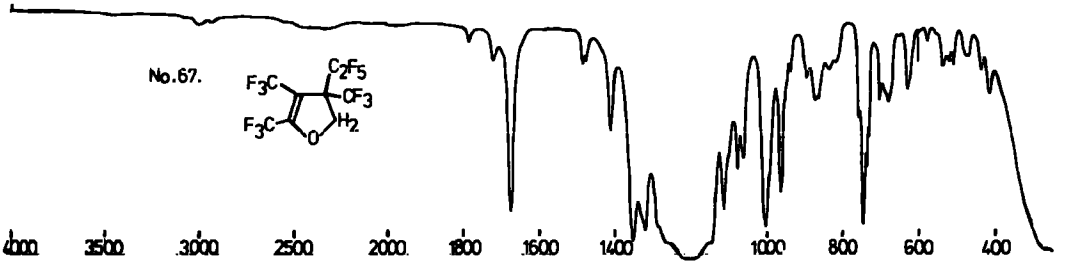
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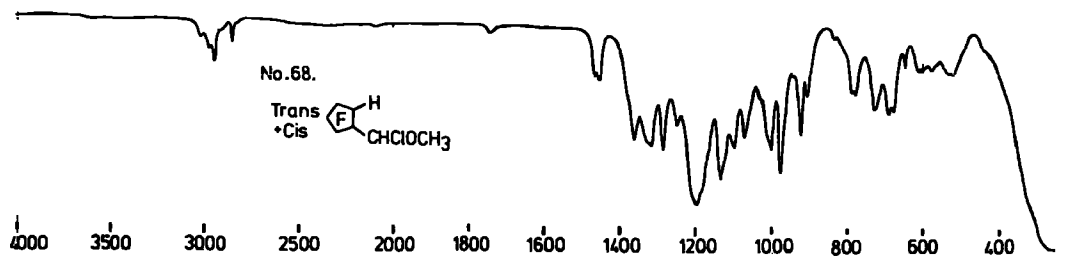
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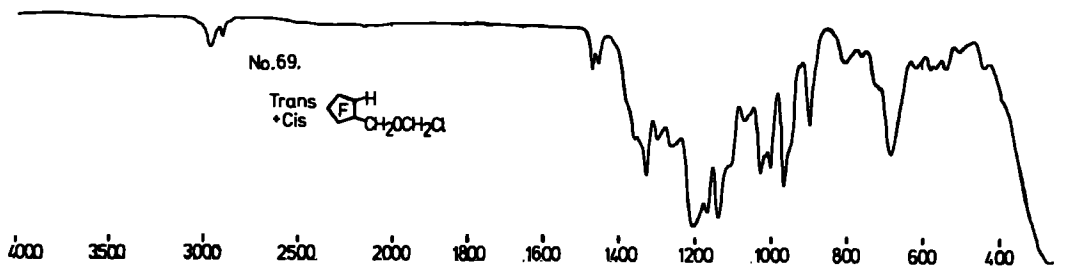
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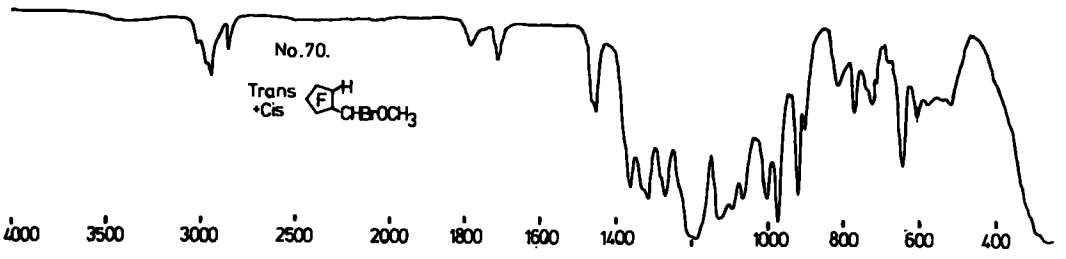
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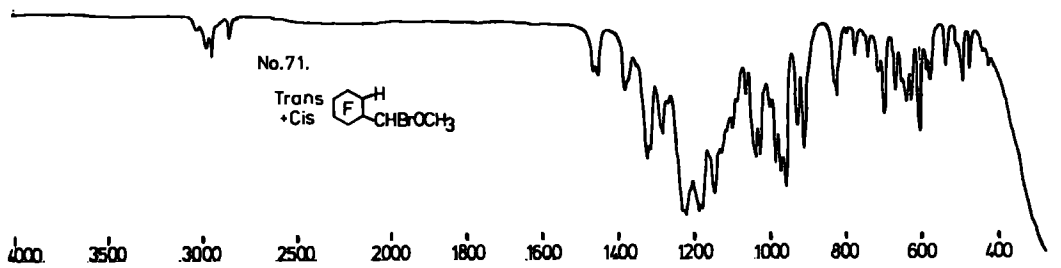
No.71.
Trans
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F
H
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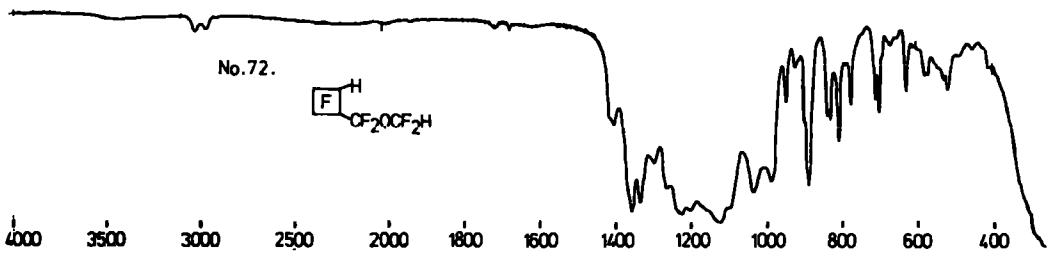
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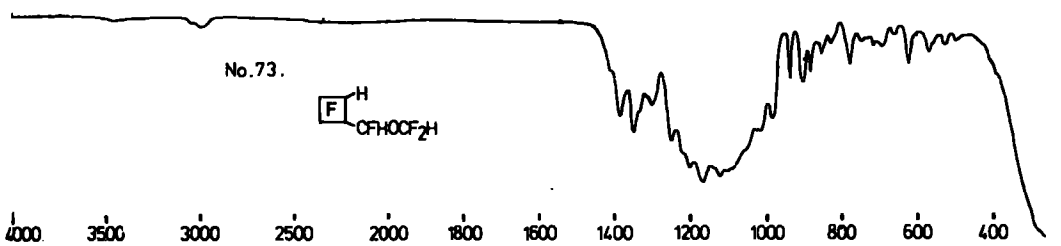
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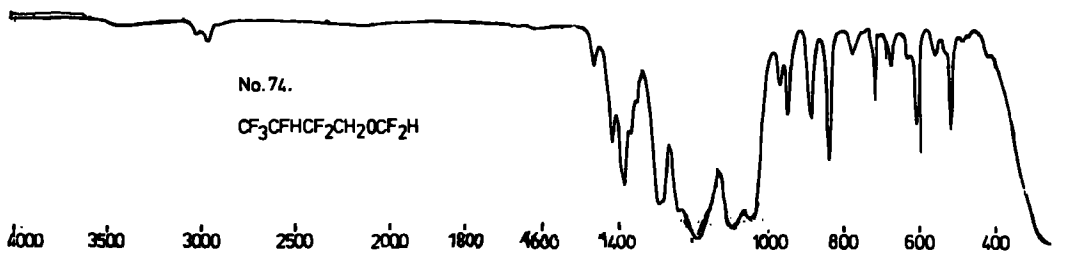
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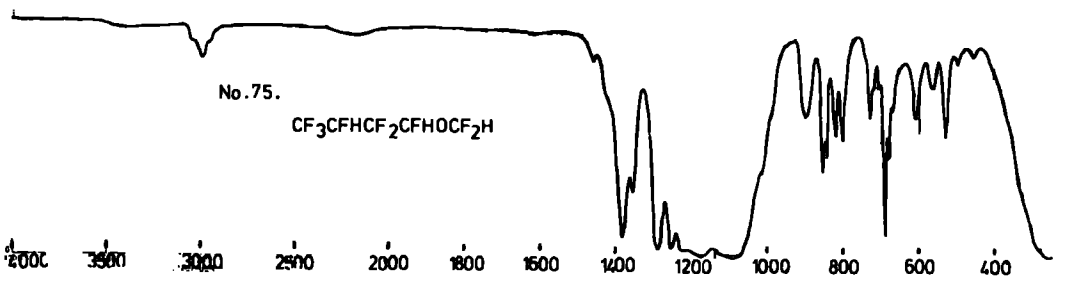
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1400
1200
1000
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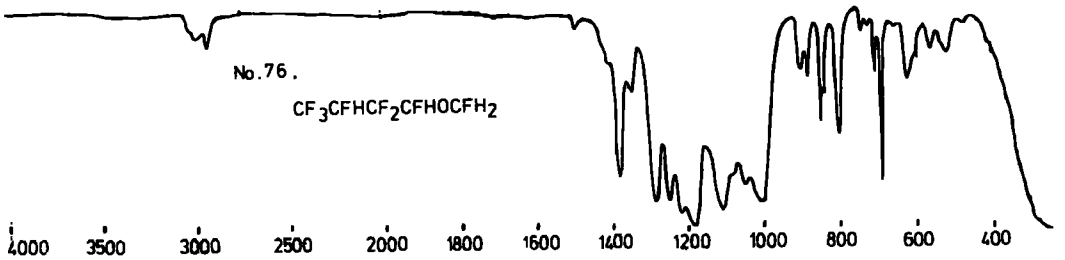
600
400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4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400

APPENDIX III

MASS SPECTRA

Index

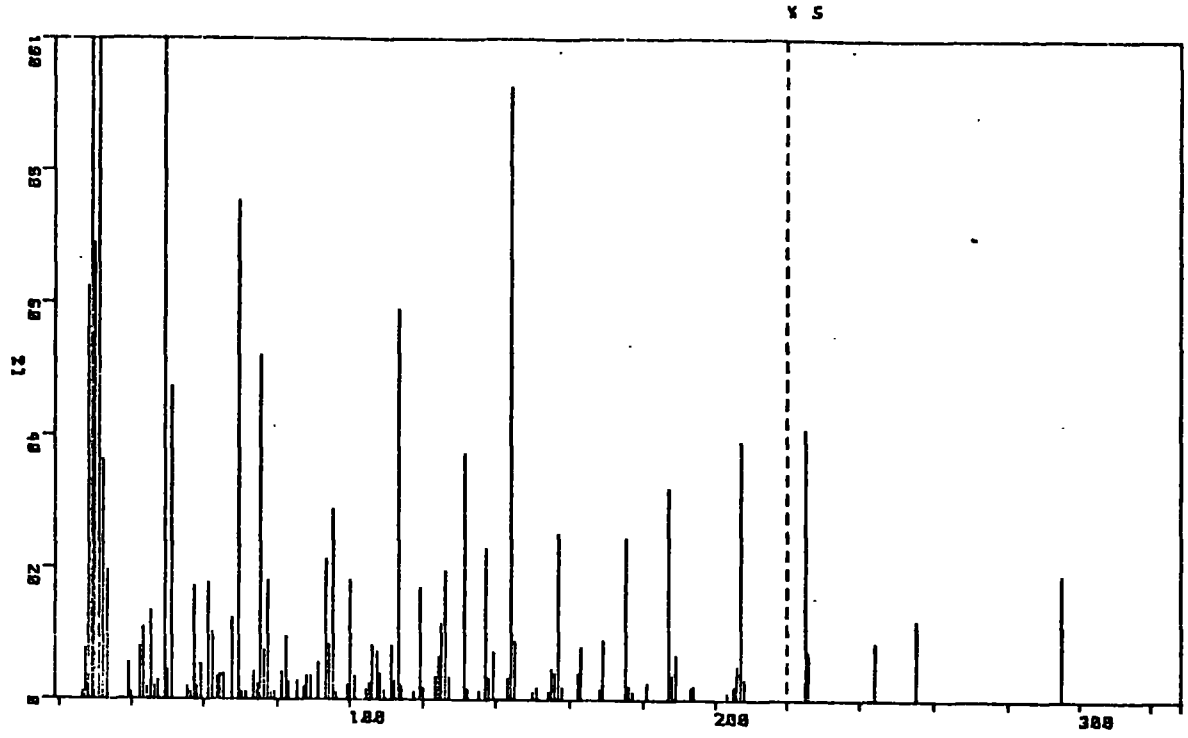
25. 4,5-bis(trifluoromethyl)-3,3,6,6-tetrafluorooctan-2,7-dione (101).
26. 2,2,3,3-tetrafluoropropyl methyl ether (102).
27. 2,2,3,3,4,4,5,5-octafluoropentyl methyl ether (102).
28. 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl methyl ether (102).
29. 3-chloro-2,2,3-trifluoropropyl methyl ether (103).
30. 3,5-dichloro-2,2,3,4,4,5-hexafluoropentyl methyl ether (104).
31. 2,2,3,4,4,4-hexafluorobutyl methyl ether (105).
32. 2,2,3-tris(trifluoromethyl)-4,4,4-trifluorobutyl methyl ether (107).
33. Bis-[2-pentafluoroethyl-2,3-bis(trifluoromethyl)-4,4,5,5,5-pentafluoropentyl] ether (109).
34. Bis-[1-spirooctafluorocyclopentyl-1-(2',2',3',3',4',4',5',5'-octafluorocyclopentyl)]-methyl ether (110).
35. 1,1,1,2,3,3-hexafluoro-5,7-dioxaoctane (118).
36. 1-methoxy di-2,2,3,4,4,4-hexafluorobutyl ether (119).
37. 2',2',3',4',4',4'-hexafluorobutoxymethyl 2,2,3,4,4,4-hexafluorobutyl ether (120).
38. 2-methoxy-3,3,4,5,5,5-hexafluoropentyl methyl ether (121).
39. 1,1,1,2,3,3-hexafluoro-5,8-dioxanonane (122).
40. 1-methoxymethyl di-2,2,3,4,4,4-hexafluorobutyl ether (123).
41. 2-methoxy-3,3,4,5,5,5-hexafluoropentyl 2,2,3,4,4,4-hexafluorobutyl ether (124).
42. 2-hydroxy-3,3,4,5,5,5-hexafluoropentyl methyl ether (Diastereomer A) (125).
43. 2-methoxy-3,3,4,5,5,5-hexafluoropentan-1-ol (126).
44. 4-(2'-hydroxyethoxy)-1,1,1,2,3,3-hexafluorobutane (127).
45. Tri-(2H-1,2,3,3,4,4,5,5-octafluorocyclopentyl)-methyl borate (131).
46. 2,2,3,4,4,4-hexafluorobutyl dimethyl phosphate (132).
47. Trimethyl 2,2,3,4,4,4-hexafluorobutoxy silane (133).
48. γ-[2-(1',1',2',3',3',3'-hexafluoropropyl)]-butyrolactone (134).
49. 1,1,1,2,3,3-hexafluoropentan-4-one (136).

50. Cis-2H-decafluorocyclohexyl chloromethyl ketone (137).
51. Cis-2H-decafluorocyclohexyl dichloromethyl ketone (138).
52. Cis-2H-decafluorocyclohexyl acyl fluoride (140).
53. Cis-2H-decafluorocyclohexyl carboxylic acid (141).
54. Anilinium cis-2H-decafluorocyclohexyl carboxylate (142).
55. 4H-perfluoro-3-ethyl-3,4-dimethyl-hexan-2-one (144).
56. 1,4-dihydro-F-3-ethyl-3,4-dimethyl-hexan-2-one (143).
57. 2-methylideno-F-3,4,5-trimethyl-3-ethyl-dihydrofuran (148).
58. 2,3,4-tris(trifluoromethyl)-5-(1',1'-dihydro-pentafluoropropyl) furan (149).
59. Trans-2H-hexafluorocyclobutyl methyl ketone oxime (154).
60. Cis-2H-octafluorocyclopentyl methyl ketone oxime (155).
61. Cis-2H-decafluorocyclohexyl methyl ketone oxime (156).
62. 5,5-dihydro-F-2,3,4-trimethyl-4-ethyl-dihydrofuran (162).
63. 2H-octafluorocyclopentyl methoxy chloromethane (164) isomer mixture.
64. 2H-octafluorocyclopentyl chloromethoxy methane (163) isomer mixture.
65. 2H-octafluorocyclopentyl methoxy bromomethane (165) isomer mixture.

Notes

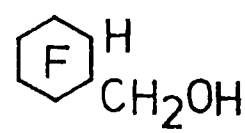
In most cases, an abbreviated list of peaks is recorded. A complete list of peaks is available in the mass spectrometry laboratory file of mass spectra for each compound.

NK2 4 M.Wt. 294 No.1.



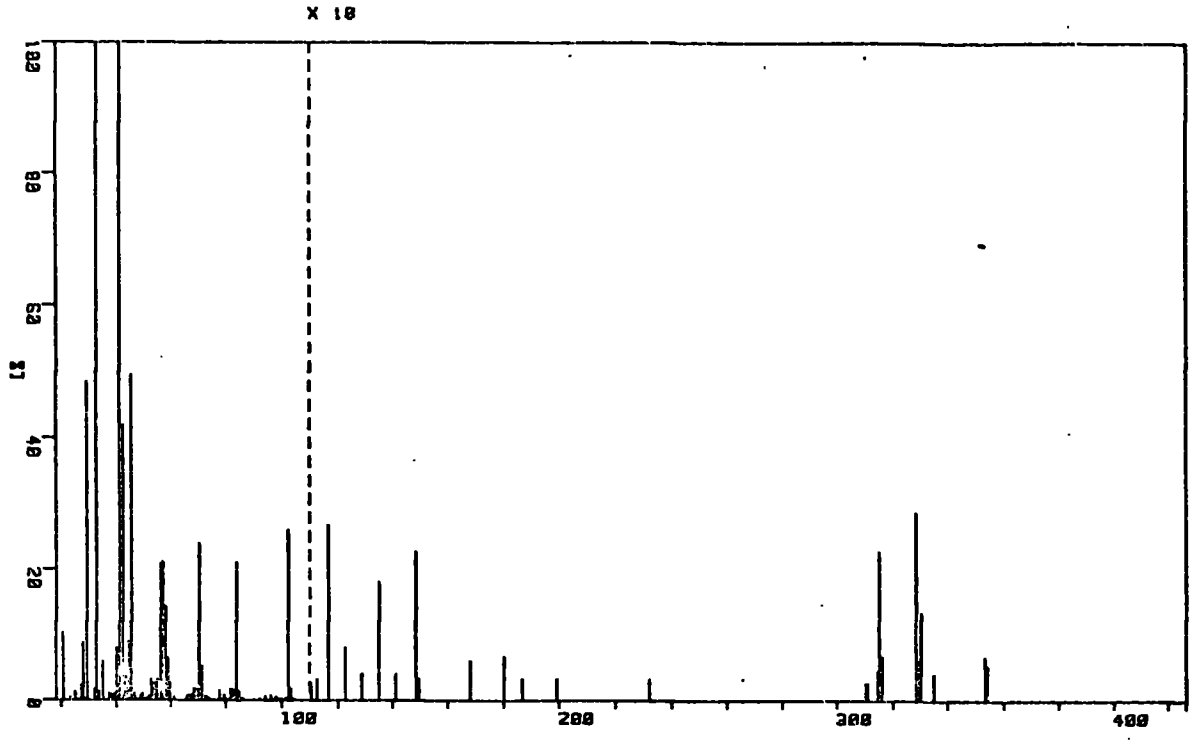
NK2 4

PEAK NO.	MASS	% INT BASE			
2	27.17	1.64	67	117.00	3.59
3	28.05	13.19	70	124.07	1.39
4	28.92	61.07	71	125.07	2.44
5	29.77	14.55	72	126.08	4.13
6	30.84	100.00	74	130.99	7.89
7	31.97	7.69	77	137.05	4.86
8	33.06	4.13	79	139.03	1.54
9	38.97	1.17	81	144.05	19.58
11	42.01	1.60	82	145.07	1.88
12	43.08	2.32	88	157.05	5.35
14	45.14	2.83	91	163.05	1.71
17	48.96	21.12	93	167.05	1.93
19	50.93	10.01	94	175.09	5.20
22	57.08	3.64	98	187.07	6.81
24	59.00	1.15	100	189.08	1.44
25	60.95	3.74	103	203.07	0.22
26	62.03	2.15	104	205.09	0.44
30	67.06	2.61	105	206.07	1.10
31	68.97	15.92	106	207.08	8.28
36	75.08	10.99	107	208.09	0.68
37	76.08	1.61	108	225.11	1.73
38	77.08	3.83	109	226.10	0.32
42	82.01	2.03	110	244.10	0.37
48	90.97	1.20			
49	93.04	4.52	111	255.12	0.51
50	94.06	1.78	112	295.09	0.81
51	95.06	6.11			
54	99.93	3.83			
58	106.05	1.76			
59	107.04	1.56			
62	110.99	1.76			
64	113.03	12.45			



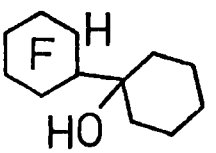
trans
+ cis

NK47 5 M.Wt. 362 No.2.



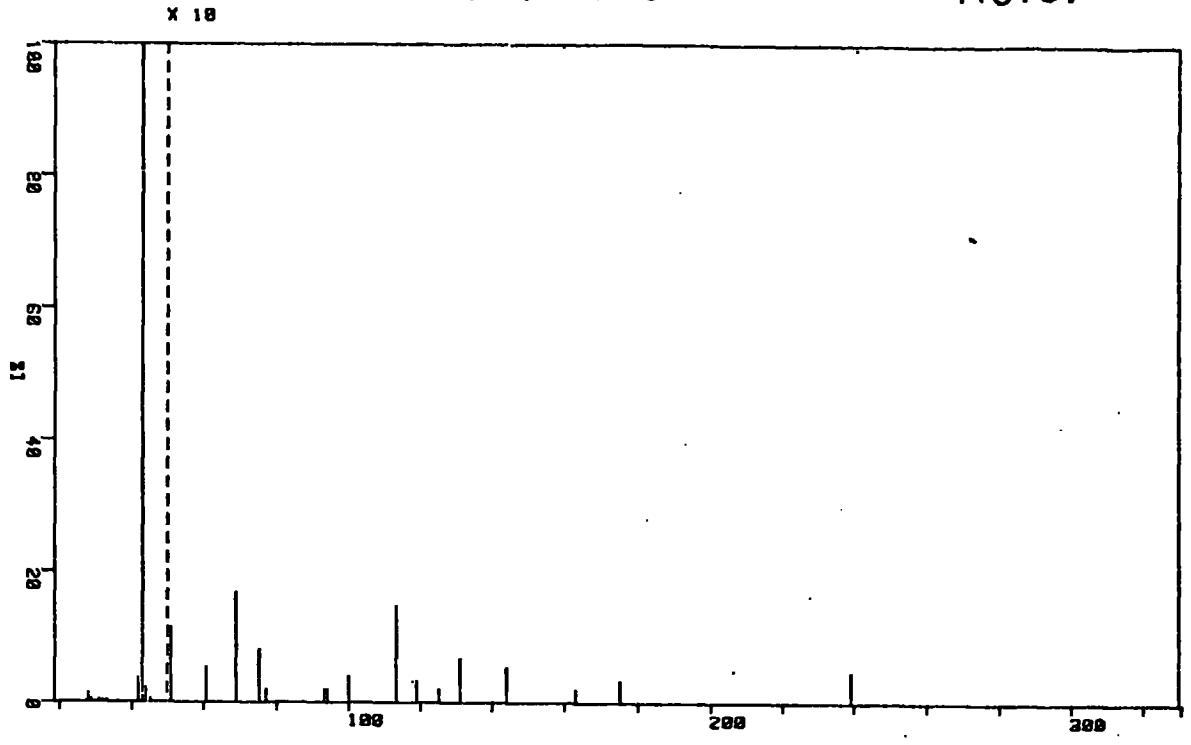
NK47 5 12-OCT-79

PEAK NO.	MASS	% INT BASE			
1	20.79	8.28			
3	27.07	1.88	43	67.24	0.78
4	27.99	7.06	44	68.22	1.59
7	24.95	1.10#	45	69.22	1.49
8	29.37	38.61#	46	70.20	19.05
9	31.95	1.39	48	71.23	4.22
11	32.94	100.00	53	77.42	1.25
14	34.12	1.12	57	81.55	1.47
15	35.18	4.81	58	82.61	1.37
16	37.20	0.81	59	83.66	16.73
17	38.21	0.81	60	84.72	1.15
18	39.16	0.81	70	102.21	20.68
19	40.12	6.47	71	103.21	1.49
20	41.19	79.61	75	116.52	2.15
21	42.38	33.36	78	135.08	1.44
22	43.47	5.35	80	148.44	1.83
23	44.54	7.23	86	231.92	0.32
24	45.54	39.39	87	310.18	0.22
25	46.60	0.81	88	311.23	0.24
28	49.58	0.93	89	314.35	0.42
31	52.77	2.61	90	315.20	1.86
32	53.85	2.22	91	316.29	0.56
33	54.91	2.61	92	328.40	2.32
34	55.92	16.48	93	329.51	0.49
36	56.94	16.80	94	330.51	1.10
37	57.94	11.50	95	334.77	0.34
38	58.91	5.15	96	353.24	0.54
39	59.86	2.20	97	354.27	0.44

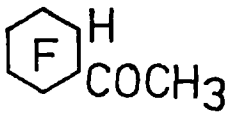


trans
+ cis

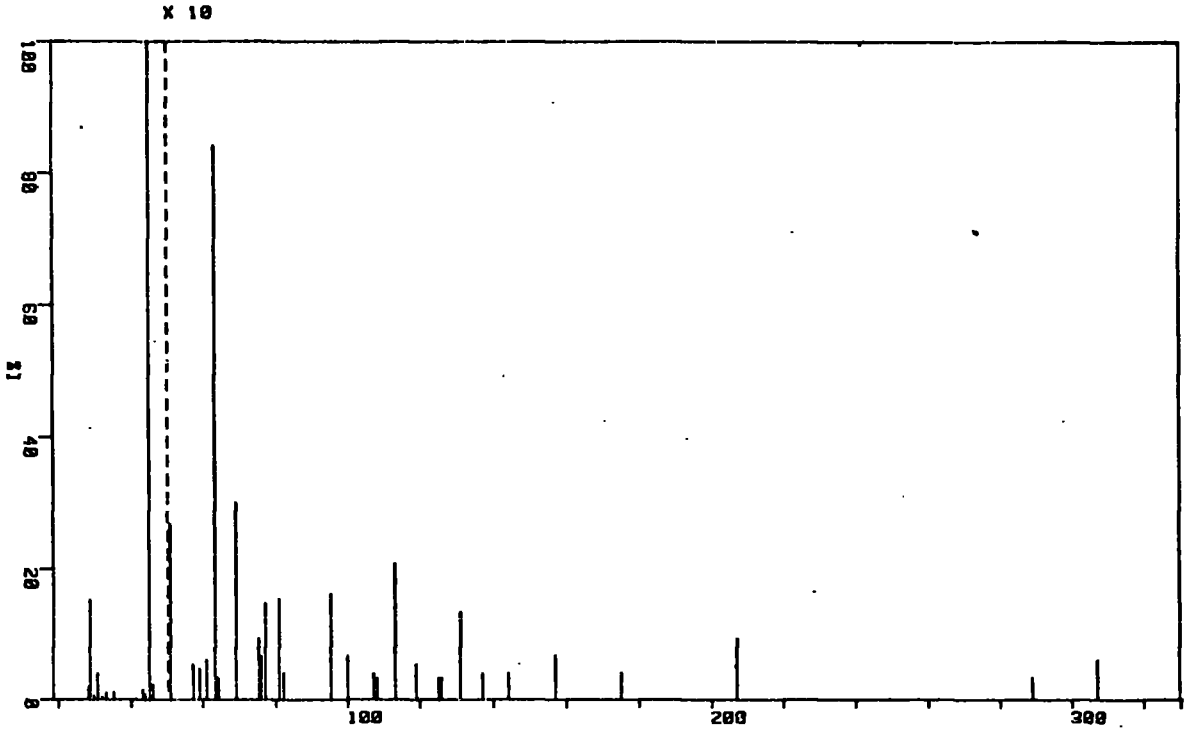
NK1 S M.Wt . 306 No.3.



NK1 S 02-OCT-79		
PEAK NO.	MASS	% INT BASE
1	27.17	0.32
2	28.05	1.47
3	28.94	0.49
4	30.84	0.51
5	31.94	0.37
6	33.06	0.37
7	40.92	0.24
8	42.01	3.69
9	43.08	100.00
10	44.13	2.37
11	45.14	0.56
12	50.94	1.15
13	60.95	0.59
14	68.97	1.68
15	75.08	0.83
16	77.08	0.22
17	93.01	0.24
18	94.04	0.22
19	99.92	0.42
20	113.02	1.51
21	118.96	0.37
22	125.03	0.22
23	130.97	0.68
24	144.03	0.54
25	162.98	0.22
26	175.03	0.34
27	238.98	0.51

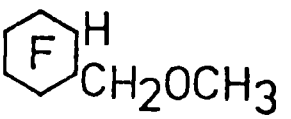
cis 

NK111 5 M.Wt. 308 No.4.



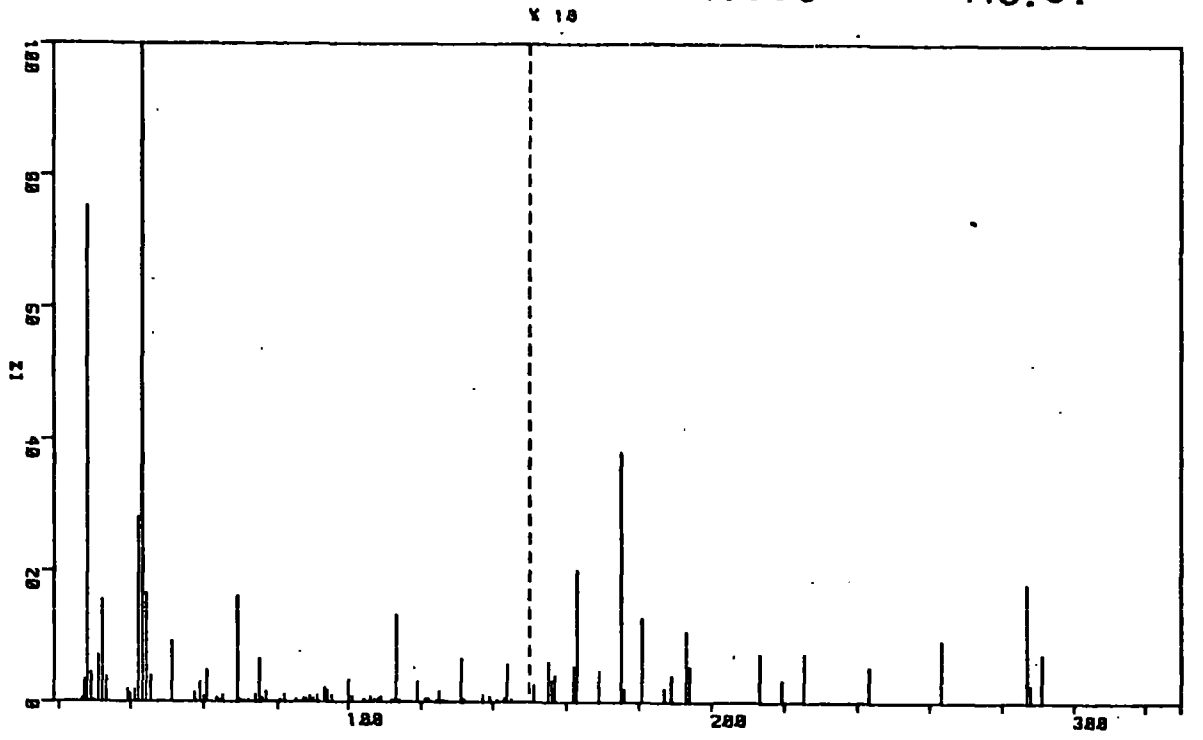
NK111 5 02-OCT-79

PEAK NO.	MASS	% INT BASE			
1	28.05	1.91	27	108.02	0.37
2	28.92	15.18	28	113.01	2.07
3	29.77	0.65	29	118.98	0.57
4	30.84	3.94	30	125.04	0.37
5	31.94	0.45	31	126.04	0.37
6	33.06	1.06	32	130.97	1.34
7	35.16	1.22	33	137.03	0.41
8	43.08	1.58	34	144.04	0.45
9	44.13	0.77	35	157.02	0.69
10	45.15	100.00	36	175.03	0.45
11	46.15	2.35	37	207.00	0.93
12	50.94	2.68	38	209.00	0.37
13	57.08	0.57	39	306.98	0.65
14	59.00	0.53			
15	60.95	0.61			
16	63.08	8.44			
17	64.10	0.37			
18	68.97	3.00			
19	75.08	0.93			
20	76.09	0.69			
21	77.07	1.50			
22	80.98	1.54			
23	82.01	0.45			
24	95.06	1.66			
25	99.93	0.69			
26	107.04	0.45			



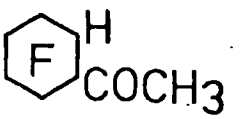
trans
+ cis

NK106T 2 M.Wt.306 No.5.



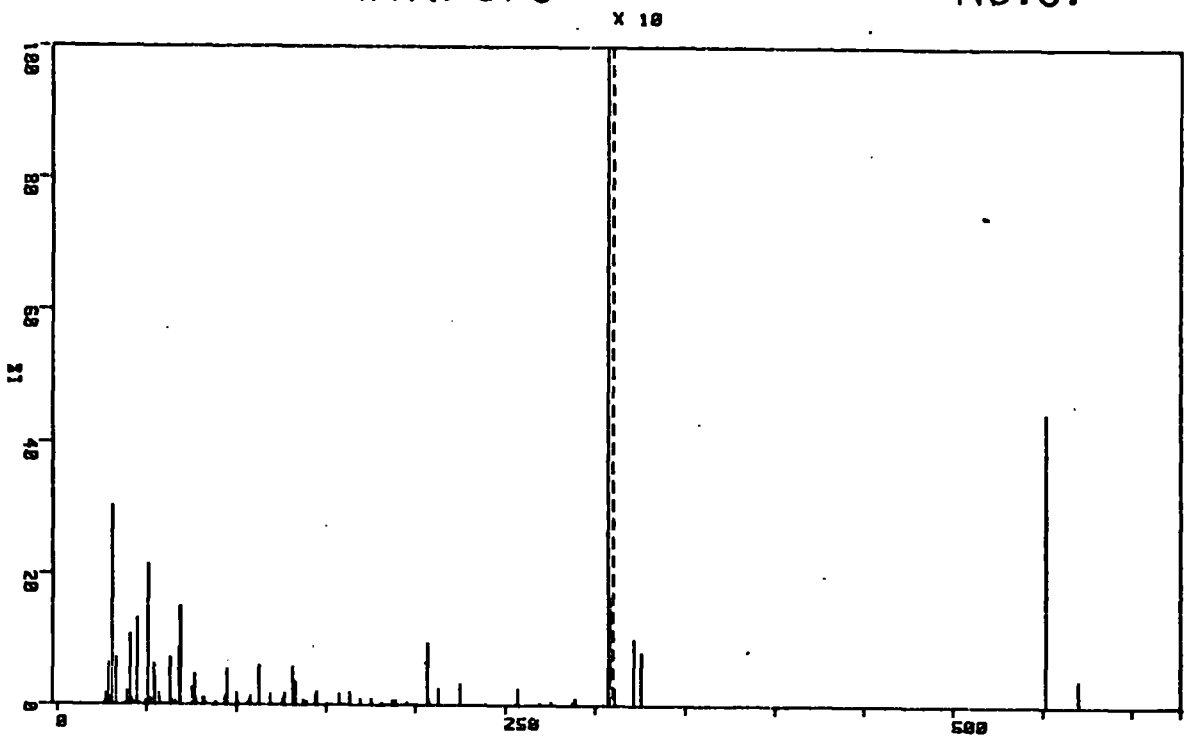
NK106T. 2 18-SEP-79

PEAK NO.	MASS	% INT BASE
2	27.17	3.44
3	28.05	75.16
4	28.94	4.42
6	30.84	7.11
7	31.94	15.51
8	33.06	3.76
9	38.97	1.88
10	39.80	1.25
11	40.93	1.93
12	42.01	28.21
13	43.08	100.00
14	44.13	16.48
15	45.15	3.98
17	50.93	9.21
18	57.08	1.42
20	59.00	2.98
22	60.96	4.79
25	65.11	1.07
26	68.98	16.02
31	74.13	1.17
32	75.08	6.57
34	77.07	1.56
36	82.01	1.15
40	88.99	0.98
42	90.96	1.00
43	93.02	2.22
44	94.05	1.81
45	95.06	1.00
46	99.92	3.44
55	113.02	13.26
57	118.98	3.25
61	125.06	1.68
64	130.97	6.62
66	137.03	1.05
70	144.03	5.79
77	163.04	2.03
79	175.05	3.83
81	180.99	1.29
84	193.03	1.12
86	213.04	0.76
87	219.04	0.34
88	225.05	0.76
89	243.02	0.56
90	263.03	0.95
91	287.06	1.81
92	288.06	0.29
93	291.01	0.76



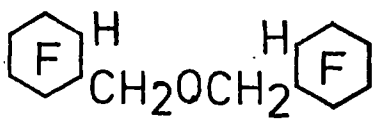
trans

NK195 4 M.Wt. 570 No.6.



NK195 4 12-OCT-79

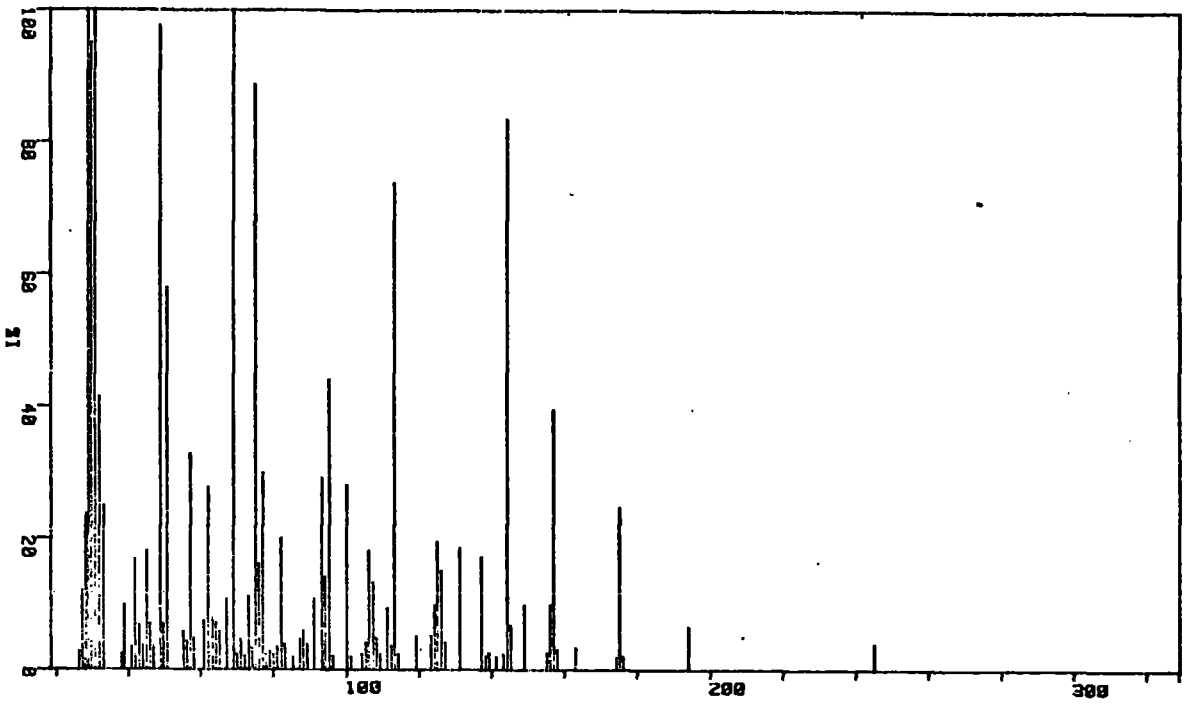
PEAK NO.	MASS	% INT BASE			
2	27.11	1.79			
3	27.99	1.63	52	119.08	1.63
4	28.85	6.41	55	127.15	1.92
7	30.72	30.27	56	131.08	5.75
8	32.91	7.26	57	133.15	3.62
10	38.87	2.23	61	144.18	1.63
12	40.84	10.69	62	145.16	2.26
16	45.07	13.23	64	157.20	1.73
19	50.96	21.50	66	163.21	2.01
22	54.12	6.22	73	207.14	9.53
23	55.14	4.18	76	213.18	2.55
24	57.09	1.82	77	225.19	3.30
27	63.08	7.20	80	257.27	2.58
31	68.09	8.74	86	304.33	0.28
32	68.99	15.06	87	307.26	100.00$
34	75.13	2.67	88	308.42	16.50$
36	77.09	4.68	89	310.89	0.28
44	94.17	1.54	90	321.49	1.04
45	95.16	5.50	91	325.53	0.82
46	100.03	1.82	92	551.90	4.50
51	113.11	6.07	93	570.15	0.41



NK10 18

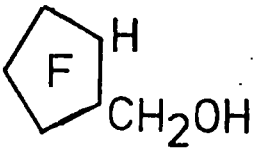
M.Wt. 244

No.7.



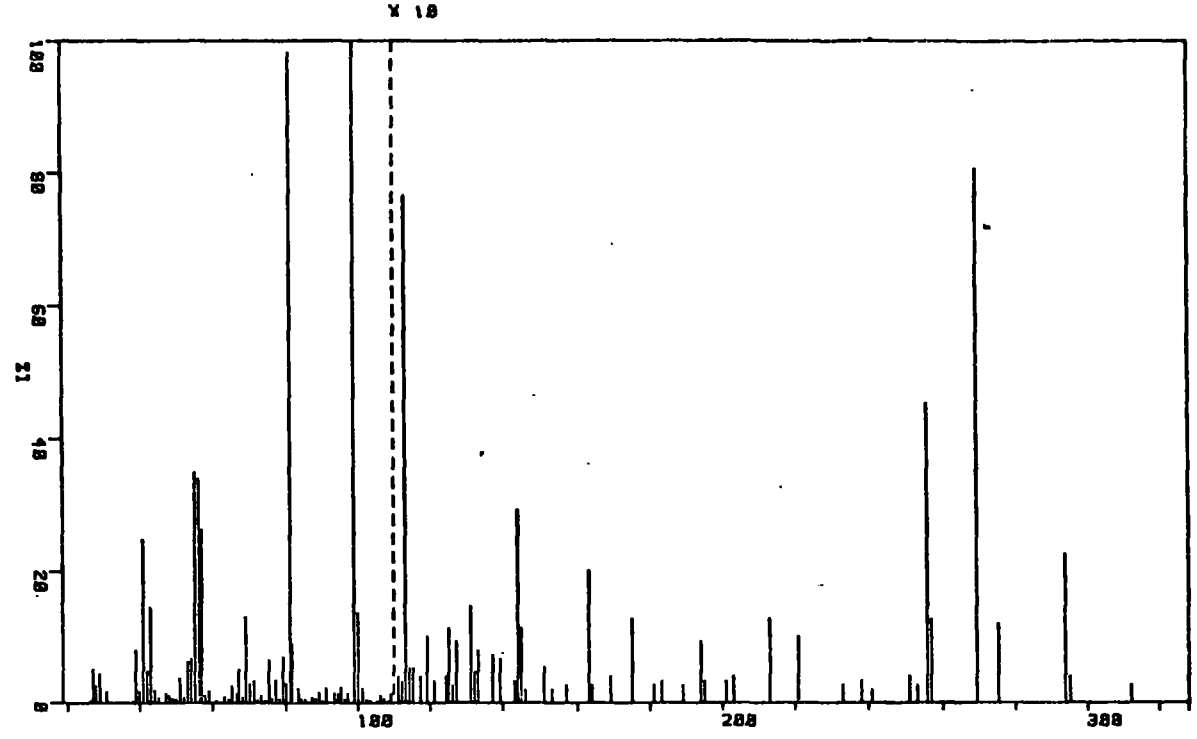
NK10 18 05-OCT-79

PEAK NO.	MASS	% INT BASE
1	26.22	0.32
2	27.17	1.34
3	28.05	2.66
4	28.93	44.76
5	29.77	10.62
6	30.67	100.00
7	31.97	4.64
8	33.06	2.78
9	38.05	0.27
10	38.97	1.10
11	40.96	0.39
12	42.02	1.88
13	43.11	0.76
14	44.12	0.42
15	45.14	2.03
16	46.14	0.78
17	47.09	0.46
18	48.97	10.92
19	49.88	0.70
20	50.95	6.47
21	55.14	0.66
22	56.13	0.49
23	57.10	3.66
24	58.05	0.54
25	60.97	0.83
26	62.04	3.10
27	63.07	0.88
28	64.10	0.81
29	65.12	0.66
30	67.08	1.20
31	68.98	11.18
32	69.97	0.27
33	71.03	0.51
34	72.03	0.24
35	73.08	1.25
36	74.10	0.37
37	75.10	9.91
38	76.10	1.81
39	77.09	3.35
40	78.07	0.27
41	78.99	0.32
42	79.94	0.27
43	80.98	0.39
44	82.03	2.25
45	83.09	0.44
46	85.17	0.22
47	87.06	0.51
48	88.04	0.66
49	89.00	0.44
50	90.98	1.20
51	93.05	3.27
52	94.06	1.59
53	95.08	4.93
54	96.07	0.24
55	99.94	3.15
56	101.01	0.22
57	104.08	0.27
58	105.09	0.46
59	106.07	2.03
60	107.06	1.49
61	108.04	0.54
62	109.00	0.27
63	111.00	1.05
64	112.04	0.42
65	113.05	8.25
66	114.07	0.27
67	119.00	0.56
68	123.06	0.59
69	124.07	1.10
70	125.07	2.17
71	126.08	1.68
72	127.07	0.46
73	130.99	2.08
74	137.05	1.93
75	138.06	0.24
76	139.04	0.29
77	141.05	0.22
78	143.05	0.27
79	144.05	9.33
80	145.07	0.76
81	149.04	1.10
82	155.07	0.29
83	156.06	1.10
84	157.05	4.42
85	158.05	0.34
86	163.07	0.37
87	174.10	0.22
88	175.06	2.76
89	176.08	0.24
90	194.05	0.73
91	245.07	0.44



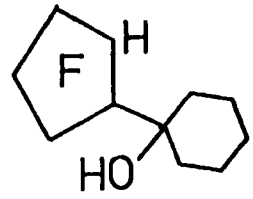
trans

NK45 4 M.Wt. 312 No.8.



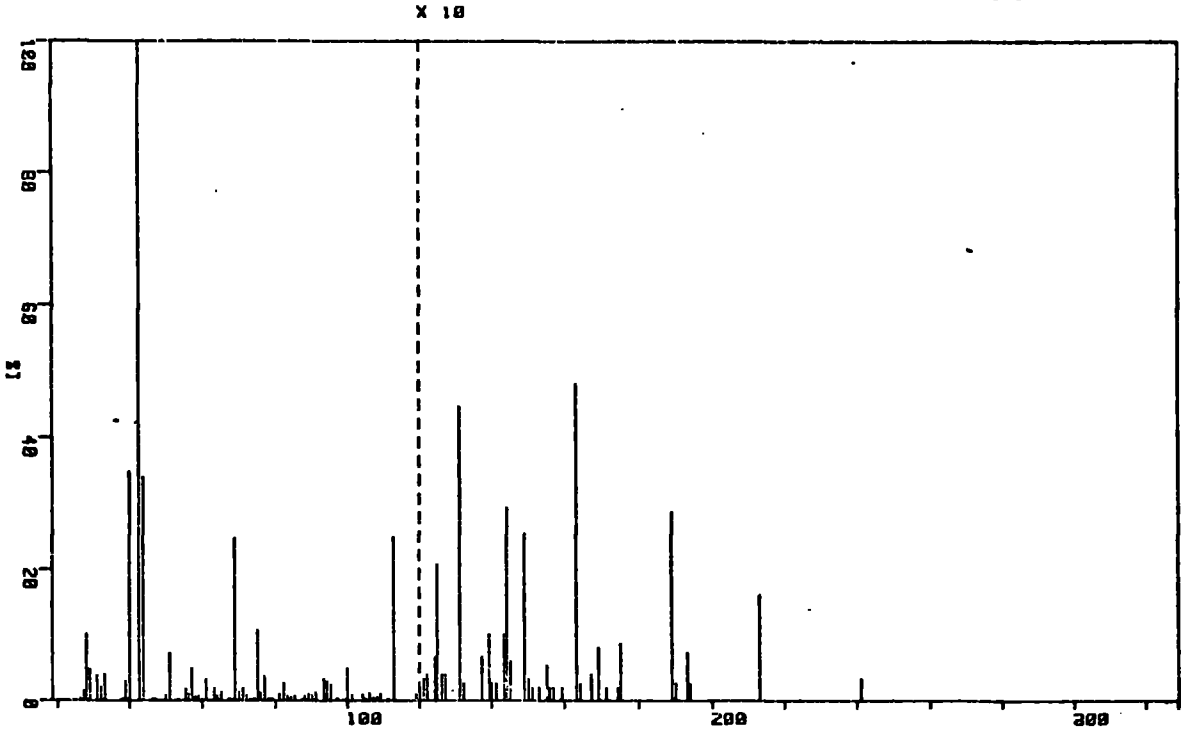
NK45 4 22-AUG-79

PEAK NO.	MASS	% INT BASE			
2	27.11	5.05	47	79.02	6.94
3	28.00	2.69	48	79.98	3.05
4	28.88	4.44	49	81.02	98.22#
5	30.73	1.76	50	81.83	8.91#
7	38.86	8.13	51	83.15	2.22
8	39.79	1.83	57	89.05	1.54
9	40.84	24.84	59	91.03	2.27
10	41.93	4.91	60	93.08	1.49
11	42.97	14.55#	62	95.12	2.44
12	43.04	14.24#	64	97.10	1.49
13	44.04	1.95	65	98.79	100.00#
19	50.95	3.69	66	99.89	13.60#
21	53.07	6.37	67	101.11	2.32
22	54.10	6.76	77	113.10	7.67
23	55.06	31.70#	87	131.07	1.51
24	55.15	35.02#	93	144.12	2.95
25	56.11	33.99	99	163.08	2.00
26	57.06	26.42	115	251.15	0.42
28	58.97	1.93	116	253.20	0.27
33	65.00	2.64	117	255.84	4.54
35	67.06	5.13	118	257.11	1.29
37	68.97	13.04	119	269.15	8.13
38	69.94	2.88	120	275.15	1.25
39	71.01	3.35	121	293.76	2.27
43	75.06	6.54	122	295.21	0.46
45	77.09	3.49	123	312.19	0.32



trans
+ cis

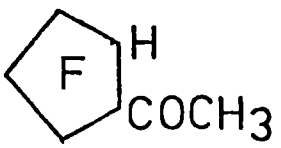
NK85 11 M.Wt. 256 No.9.



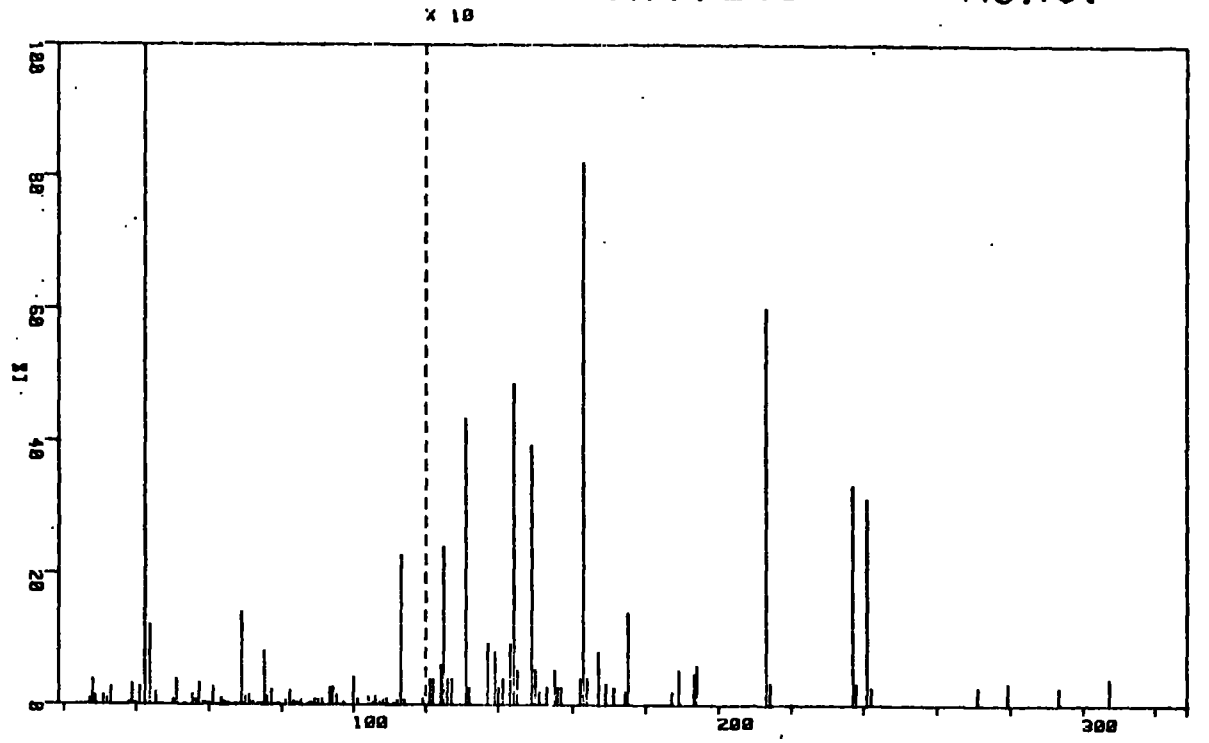
NK85 11 04-OCT-79

PEAK NO.	MASS	% INT BASE
3	28.05	10.01
4	28.93	4.84
5	30.83	3.93
6	31.95	2.32
7	33.06	4.03
10	38.90	3.03
15	40.00	34.80
16	42.53	100.00
17	43.77	33.92
22	50.95	7.25
26	57.12	4.93
30	60.97	3.32
39	68.99	24.74
41	71.04	1.98
45	75.10	10.70
48	77.07	3.79
52	82.01	2.71
61	93.02	3.49
62	94.05	3.08
63	95.06	2.56
68	99.92	4.91
78	112.76	24.91
86	125.10	2.12
89	131.03	4.49
96	144.11	2.95
98	149.01	2.54
106	162.96	4.01
113	189.02	2.91
117	213.04	1.61
118	241.03	0.34

cis



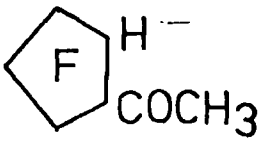
NK85 18 M.Wt. 256 No.10.



NK85 18 04-OCT-79

PEAK NO.	MASS	% INT BASE
3	28.05	3.86
7	33.06	2.71
9	38.97	3.25
11	40.94	2.81
12	42.20	13.75
13	42.52	100.00
14	43.65	12.16
15	45.15	1.98
19	50.95	3.83
23	57.12	3.39
27	60.98	2.69
33	69.00	14.11
39	75.10	8.21
41	77.07	2.47
45	82.02	2.25
54	93.03	2.76
55	94.05	2.83
60	99.93	4.40
70	113.03	22.78
76	125.06	2.47
79	130.99	4.37
86	144.06	4.93
88	149.02	3.98
96	163.03	8.21
107	213.03	6.06
108	214.05	0.39
109	237.06	3.35
110	238.05	0.34
111	241.00	3.17
112	242.01	0.27
113	271.08	0.32
114	279.19	0.37
115	293.20	0.32
116	307.23	0.46

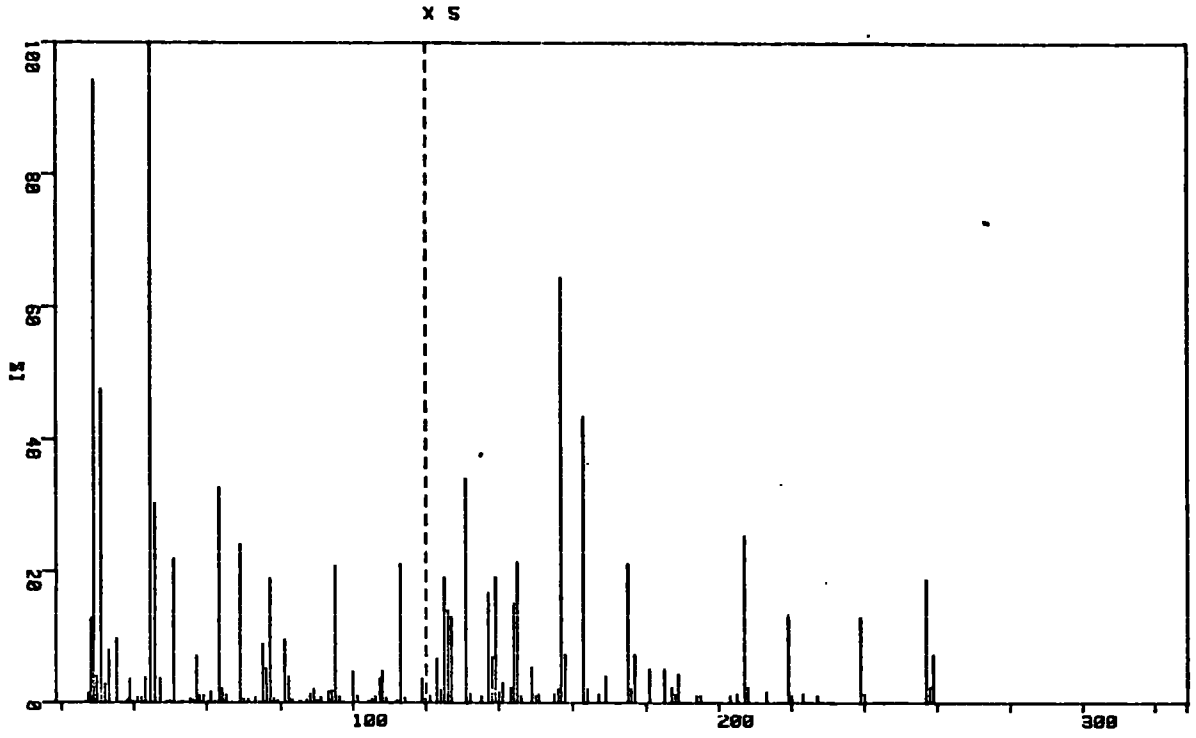
trans



NK112 26

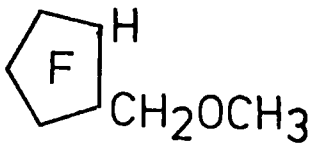
M.Wt. 258

No.11.



NK112 26 04-OCT-79

PEAK NO.	MASS	% INT BASE
3	28.05	12.77
4	28.72	94.14
5	29.77	4.13
6	30.84	47.50
7	31.95	2.91
8	33.06	7.89
9	35.15	9.69
11	38.96	3.54
16	43.08	3.81
17	44.47	100.00
18	45.71	30.33
19	47.11	3.71
22	50.93	21.81
27	57.08	7.16
33	63.06	32.63
34	64.09	2.20
36	68.97	24.08
41	75.07	8.91
42	76.09	5.15
43	77.06	18.93
46	80.95	9.52
47	81.99	3.96
52	88.97	2.05
57	95.04	20.78
60	99.91	4.71
65	107.03	3.69
66	108.00	4.06
70	113.00	21.03
72	118.96	3.69
77	125.02	3.81
78	126.03	2.81
79	127.03	2.66
80	130.94	6.84
83	137.00	3.39
85	138.96	3.83
89	144.00	3.00
90	145.00	4.30
97	156.97	12.87
99	162.96	8.67
103	174.99	4.22
113	202.93	0.24
114	204.97	0.29
115	206.93	5.13
116	207.94	0.51
117	212.93	0.37
118	218.96	2.71
119	219.98	0.22
120	222.93	0.32
121	226.96	0.22
122	238.92	2.61
123	239.92	0.32
124	256.92	3.79
125	257.91	0.49
126	258.91	1.49

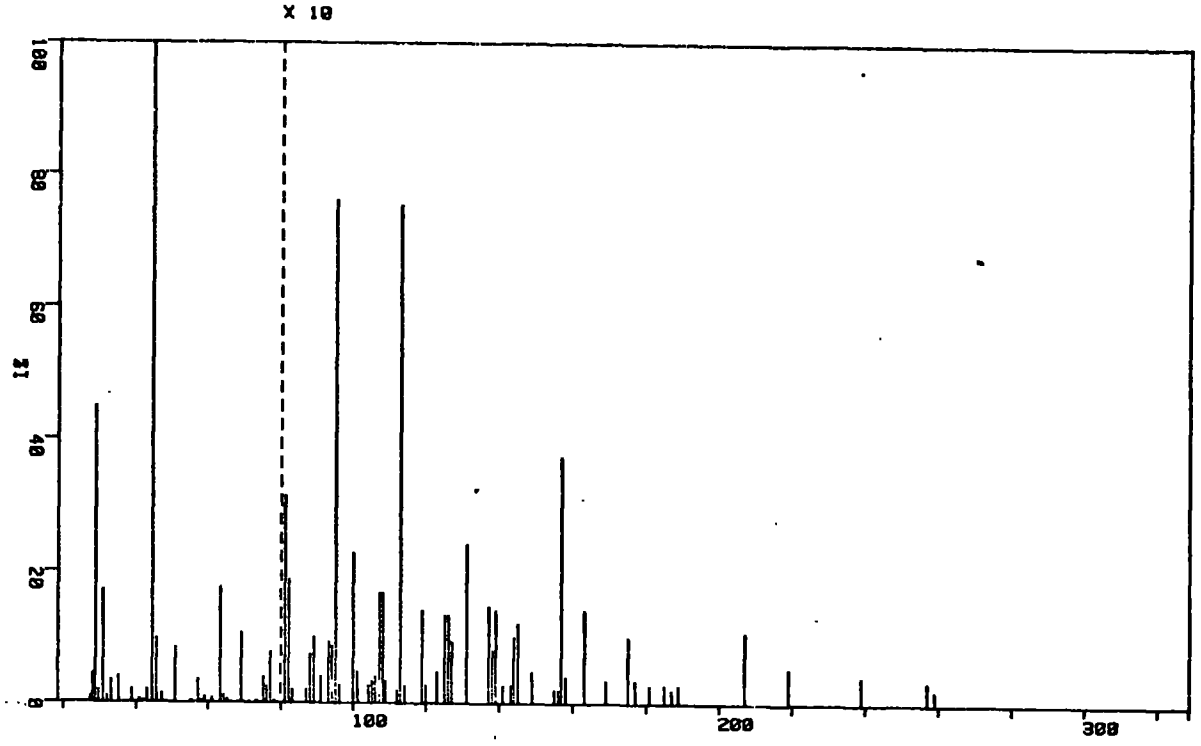


trans

M.Wt. 258

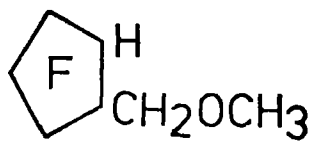
NK112 34

No.12.



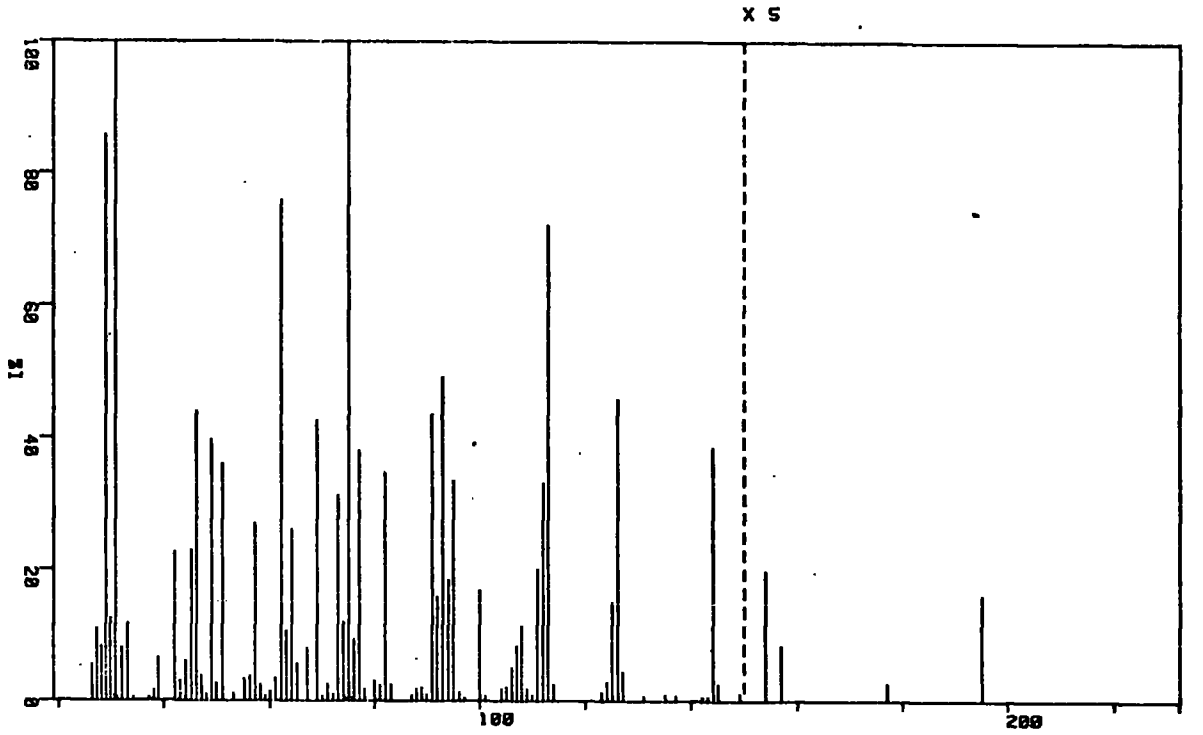
NK112 34 04-OCT-79

PEAK NO.	MASS	% INT BASE			
2	28.05	4.42	49	99.91	2.27
3	28.92	44.93	54	107.03	1.68
5	29.77	1.93	55	108.02	1.48
6	30.84	17.12	58	113.00	7.57
7	31.95	1.07	60	118.97	1.47
8	33.06	3.39	63	125.03	1.37
9	35.15	4.10	64	126.04	1.37
11	38.96	2.05	65	127.03	0.98
14	43.09	1.95	66	130.95	2.42
15	44.46	100.00	67	137.01	1.51
16	45.71	9.65	69	138.98	1.47
17	47.11	1.34	72	144.01	1.05
19	50.93	0.38	73	145.01	1.25
22	57.08	3.57	77	156.97	3.79
26	63.07	17.63	79	162.97	1.44
27	64.10	1.03	81	175.00	1.05
29	68.97	10.60	83	180.92	0.27
33	75.00	3.91	84	184.98	0.29
34	76.09	2.54	85	186.97	0.22
35	77.07	7.72	86	188.95	0.27
38	80.97	3.17	87	206.95	1.10
39	82.00	1.93	88	218.96	0.54
43	86.98	1.03	89	230.92	0.42
45	93.01	0.98	90	256.94	0.39
47	95.04	7.64	91	258.95	0.22



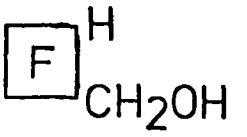
cis

NK8 24 M.Wt. 194 No.13.

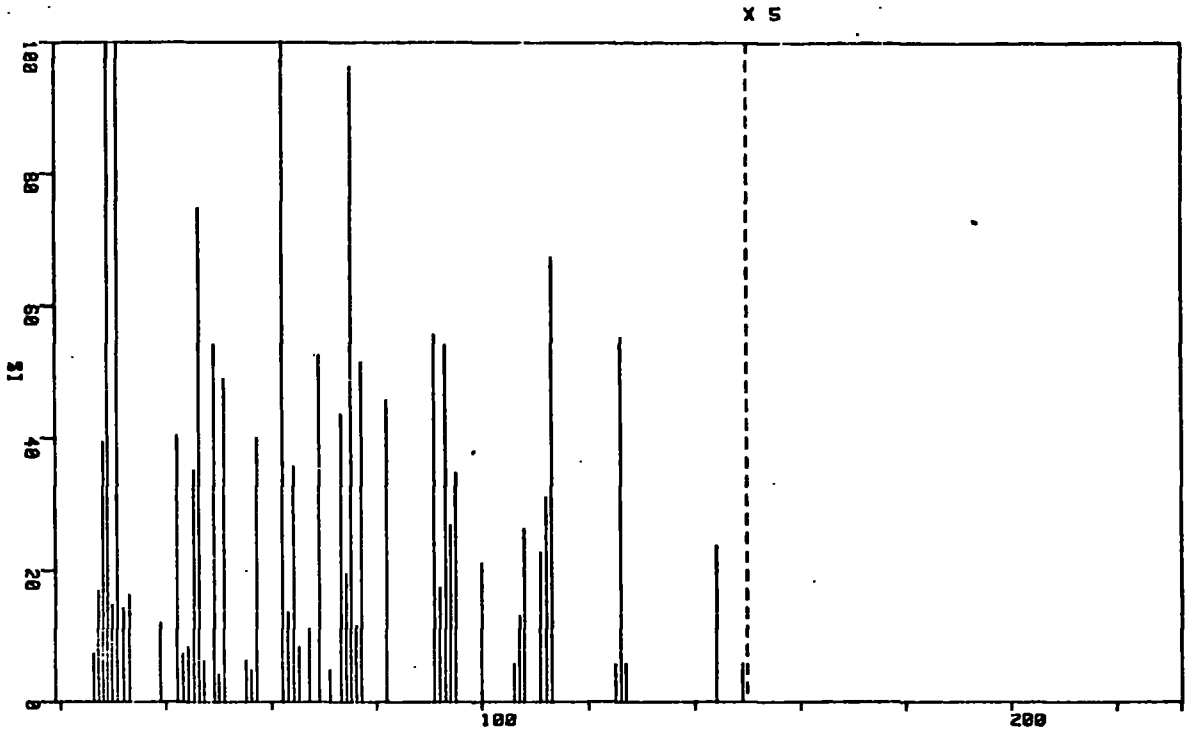


NK8 24 05-OCT-79

PEAK NO.	MASS	% INT BASE			
1	26.22	2.20	58	90.93	17.07
2	27.17	4.37	59	91.98	6.23
3	28.05	3.27	60	93.02	19.32
4	28.93	33.63	61	94.03	7.20
5	29.77	4.91	62	95.04	13.16
7	30.85	100.00	65	99.91	6.62
9	31.97	3.15	69	106.04	2.00
10	33.06	4.62	70	107.03	3.27
14	38.97	2.54	71	108.01	4.47
15	42.02	8.89	74	110.96	7.89
16	43.10	1.25	75	111.98	12.97#
17	44.13	2.42	76	112.96	28.30#
18	45.14	8.99	80	125.04	5.86
19	46.14	17.24	81	126.04	17.97
20	47.10	1.51	82	127.05	1.73
22	48.98	15.56	83	130.98	0.27
24	50.95	14.19	84	135.07	0.37
26	55.13	1.29	85	137.03	0.29
27	56.11	1.49	86	142.04	0.24
28	57.09	10.62	87	143.06	0.27
32	60.97	1.34	88	144.04	15.12
33	62.04	29.74			
34	63.08	4.18	89	145.05	1.00
35	64.11	10.26	90	149.02	0.46
36	65.10	2.22	91	154.04	1.56
37	67.03	3.15	92	157.02	0.66
38	68.94	16.73	93	177.08	0.22
42	73.03	12.26	94	195.07	1.27
43	74.06	4.71			
45	75.06	39.27			
47	76.05	3.71			
48	77.04	14.92			
50	79.89	1.22			
52	81.98	13.60			

trans 

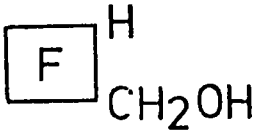
NK8 34 M.Wt. 194 No. 14.



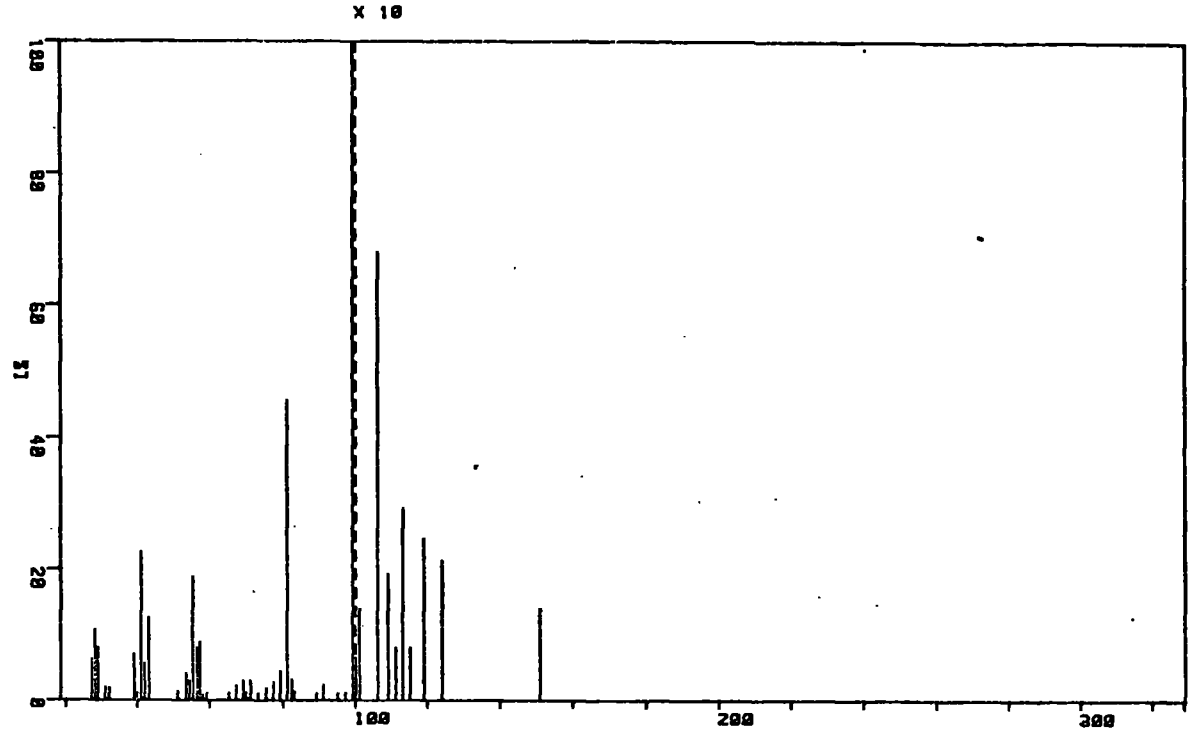
NK8 34 05-OCT-79

PEAK NO.	MASS	% INT BASE			
1	26.22	1.75	26	67.07	2.63
2	27.17	4.01	27	68.98	12.52
3	28.05	9.39	28	70.97	1.13
4	28.92	28.16	29	73.07	10.39
5	29.77	3.50	30	74.10	4.63
6	30.85	100.00	31	75.10	22.90
7	31.96	3.38	32	76.09	2.75
8	33.06	3.88	33	77.08	12.27
9	38.97	2.88	34	82.01	10.89
10	42.01	9.64	35	90.96	13.27
11	43.10	1.75	36	92.01	4.13
12	44.12	2.00	37	93.05	12.89
13	45.14	8.39	38	94.07	6.38
14	46.14	17.77	39	95.07	8.26
15	47.09	1.50	40	99.93	5.01
16	48.97	12.89	41	106.07	1.38
17	49.87	1.00	42	107.06	3.13
18	50.94	11.64	43	108.04	6.26
19	55.13	1.50	44	110.99	5.38
20	56.11	1.13	45	112.03	7.38
21	57.08	9.51	46	113.04	16.02
22	62.03	23.78	47	125.06	1.38
23	63.07	3.25	48	126.07	13.14
24	64.10	8.51	49	127.08	1.38
25	65.11	2.00	50	144.06	5.63
			51	149.03	1.38

cis

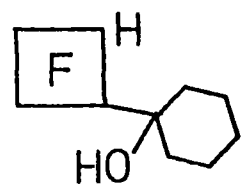


NK461 5 M.Wt. 262 No.15.



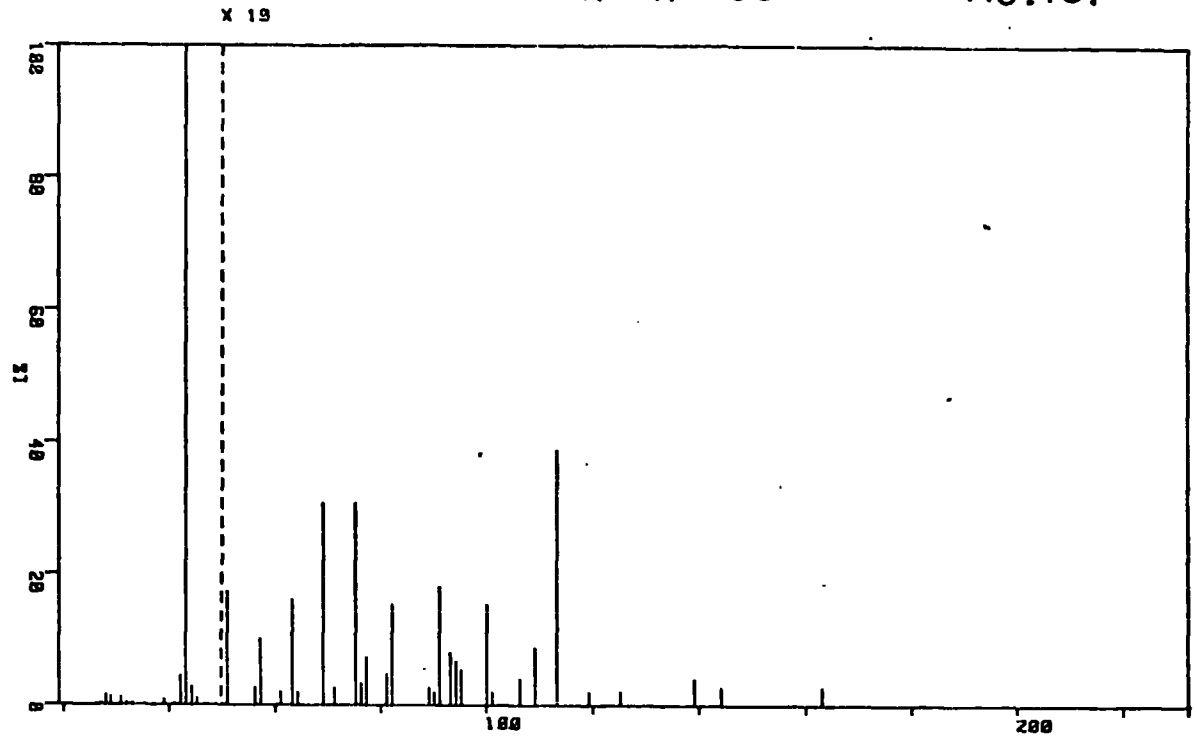
NK461 5 12-OCT-79

PEAK NO.	MASS	% INT BASE
1	27.16	6.46
2	28.05	10.77
3	28.95	8.05
4	30.84	2.06
5	31.93	1.97
6	38.96	7.12
7	39.86	1.31
8	40.94	22.66
9	42.03	5.71
10	43.09	12.64
11	50.93	1.40
12	53.08	4.31
13	54.12	3.18
14	55.12	10.82
15	56.13	7.96
16	57.08	8.90
17	58.02	0.94
18	58.97	1.22
19	65.10	1.22
20	67.09	2.34
21	68.99	3.00
22	69.93	1.31
23	70.99	3.09
24	73.06	1.03
25	75.06	1.87
26	77.05	2.81
27	78.99	4.49
28	81.00	45.69
29	82.04	3.28
30	83.04	1.40
31	88.95	1.22
32	90.93	2.53
33	95.04	1.22
34	97.04	1.31
35	99.01	100.00
36	99.96	6.65
37	100.95	1.40
38	106.02	6.84
39	108.96	1.97
41	112.99	3.00
43	118.96	2.53
44	123.99	2.15
45	150.92	1.40



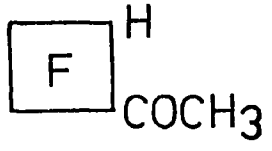
trans

NK9 18 M.Wt. 206 No.16.



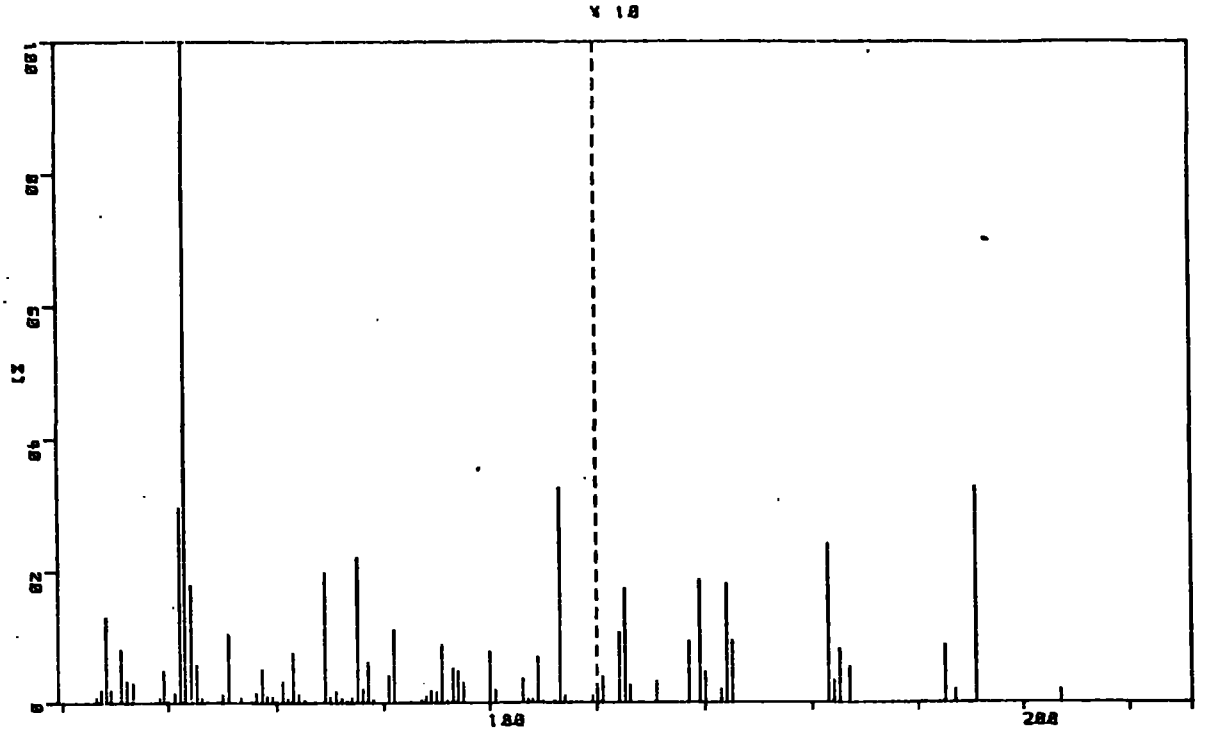
NK9. 18 04-OCT-79

PEAK NO.	MASS	% INT BASE
1	26.22	0.27
2	27.17	0.44
3	28.05	1.54
4	28.92	1.27
5	30.83	1.25
6	31.95	0.44
7	33.06	0.39
8	38.97	0.83
9	40.93	0.27
10	42.01	4.49
11	43.00	100.00
12	44.13	2.81
13	45.14	1.15
14	49.87	0.29
15	50.94	1.78
16	56.11	0.27
17	57.08	1.05
18	60.96	0.24
19	63.05	1.64
20	64.10	0.24
21	68.97	3.10
22	70.99	0.27
23	75.08	3.08
24	76.08	0.37
25	77.07	0.76
26	80.95	0.51
27	82.00	1.59
28	88.99	0.27
29	89.92	0.22
30	90.95	1.86
31	93.01	0.81
32	94.05	0.73
33	95.06	0.59
34	99.91	1.54
35	100.97	0.22
36	106.05	0.44
37	108.96	0.93
38	113.01	3.93
39	119.00	0.22
40	125.04	0.22
41	138.97	0.46
42	144.01	0.27
43	162.98	0.32

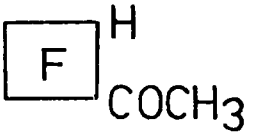


cis

NK92 3 M.Wt. 206 No.17.

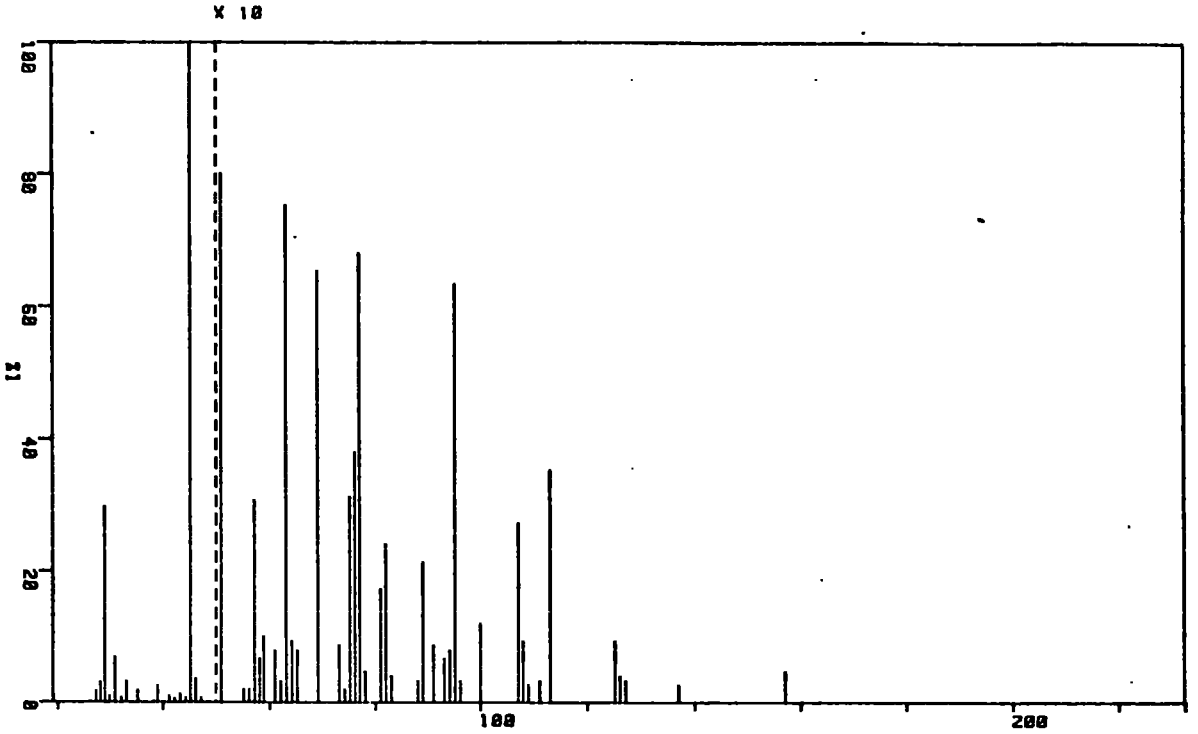


PEAK NO.	MASS	% INT BASE			
2	27.17	2.03	45	76.09	2.22
3	28.05	13.04	46	77.08	6.20
4	28.93	2.08	48	80.96	4.22
5	30.83	8.16	49	82.02	11.04
6	31.95	3.39	53	88.04	1.03
7	33.06	3.13	54	89.01	1.81
9	38.97	4.91	55	89.94	1.71
12	40.92	1.56	56	90.97	8.82
13	42.01	29.77	58	93.04	5.32
16	43.07	100.00	59	94.07	4.93
18	44.13	17.30	60	95.07	3.15
19	45.14	5.84	61	99.93	7.84
23	49.87	1.37	62	101.00	2.00
24	50.94	10.48	64	106.07	3.69
27	56.11	1.54	67	108.97	7.08
28	57.08	5.23	70	113.04	32.72
29	58.04	1.15	71	114.06	1.20
30	58.99	1.05	75	119.01	1.20
32	60.96	3.35	78	124.07	1.07
34	63.06	7.64	79	125.08	1.76
35	64.09	1.34	83	139.03	1.93
38	68.98	19.80	86	144.07	1.81
40	70.99	1.83	88	163.07	2.42
44	75.10	22.03	94	190.97	3.30
			95	207.05	0.24



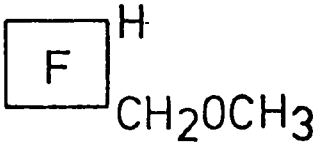
trans

NK113 21 M.Wt. 208 No.18.

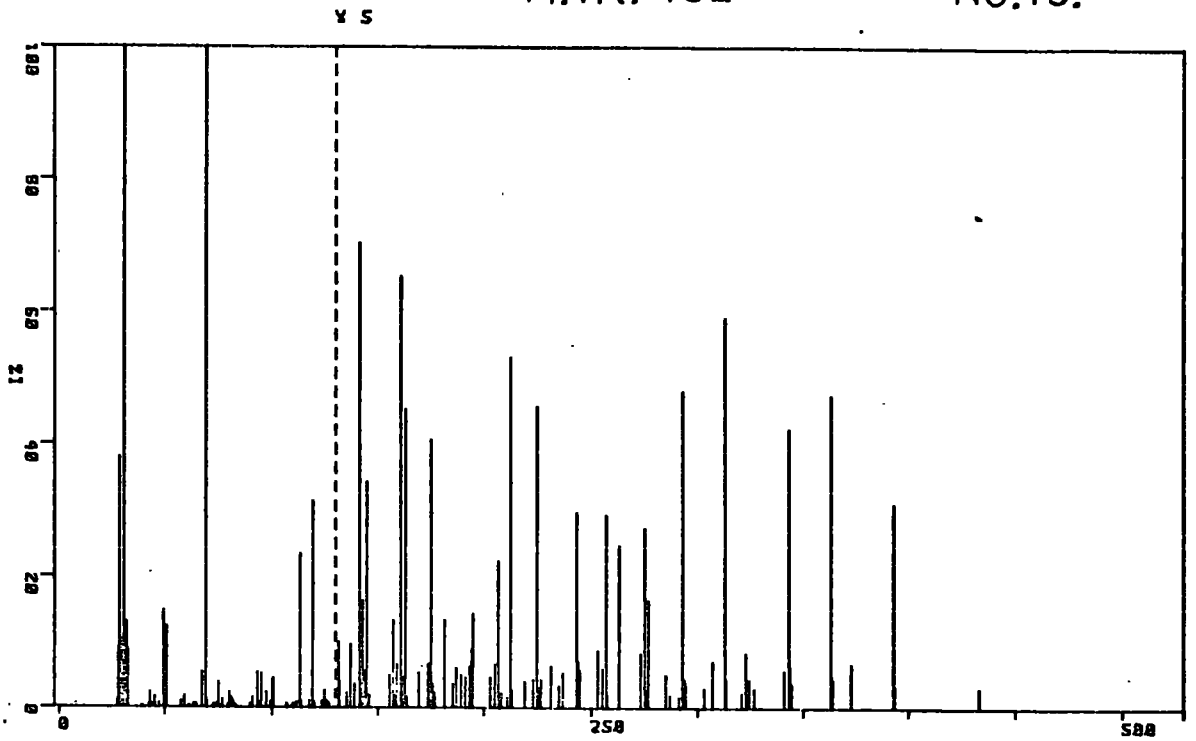


NK113 21 04-OCT-79

PEAK NO.	MASS	% INT BASE
3	20.05	3.20
4	28.92	29.77
6	30.83	6.98
8	33.05	3.30
11	38.96	2.54
17	45.14	100.00
19	46.13	3.66
22	50.93	8.03
25	57.07	3.08
30	63.05	7.57
33	68.96	6.59
36	75.06	3.17
37	76.08	3.81
38	77.05	6.86
41	81.98	2.42
44	88.97	2.17
48	95.02	6.37
51	107.02	2.76
55	112.98	3.57

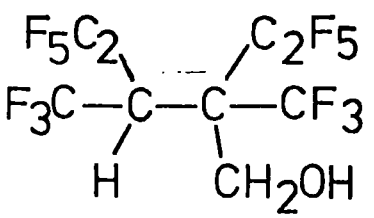
trans 

NK3 12 M.Wt. 432 No.19.

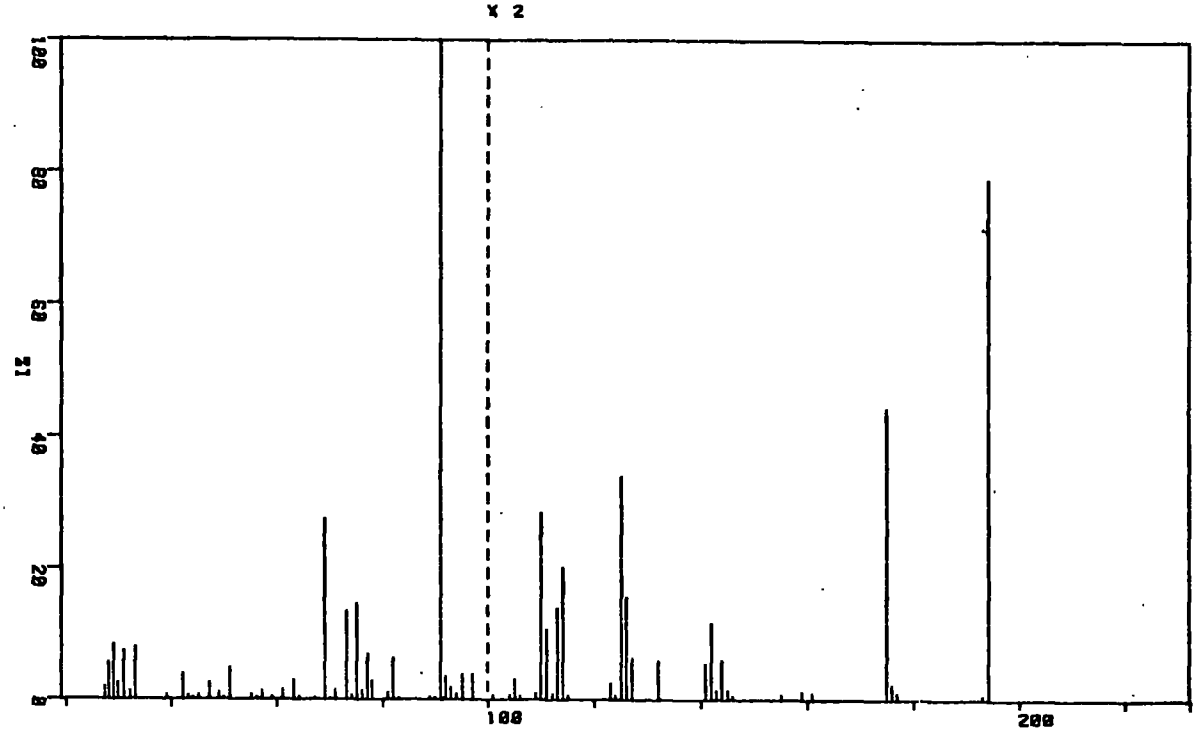


NK3 12 26-SEP-79

PEAK NO.	MASS	% INT BASE
2	28.05	5.13
3	28.93	21.20
4	29.78	5.81
5	30.85	100.00
6	31.98	7.28
7	33.06	4.96
10	43.10	1.34
14	48.97	0.25
16	50.95	6.94
23	67.08	3.05
24	68.99	55.70
29	75.11	2.22
33	79.92	1.34
39	93.05	3.03
41	95.08	2.95
42	97.04	1.34
44	99.93	2.34
45	100.90	2.56
52	113.04	13.06
55	119.00	17.56
59	125.08	1.49
62	131.02	1.15
65	137.07	1.10
67	141.02	7.86
69	143.07	1.83
71	145.09	3.83
74	157.09	1.49
77	161.04	7.30
79	163.09	5.08
83	175.09	4.57
86	181.03	1.49
93	195.08	1.61
96	207.09	2.52
100	213.09	5.93
104	225.09	5.10
110	243.06	3.35
115	257.07	3.30
117	263.08	2.76
119	275.12	3.05
121	277.10	1.83
125	293.08	5.37
130	313.08	6.62
138	343.08	4.74
141	363.07	5.30
144	393.13	3.49
146	433.14	0.37

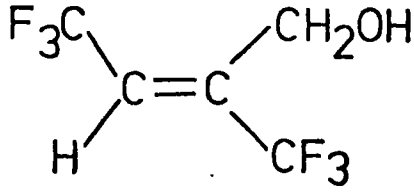


NK571 S M.Wt.194 No.20.

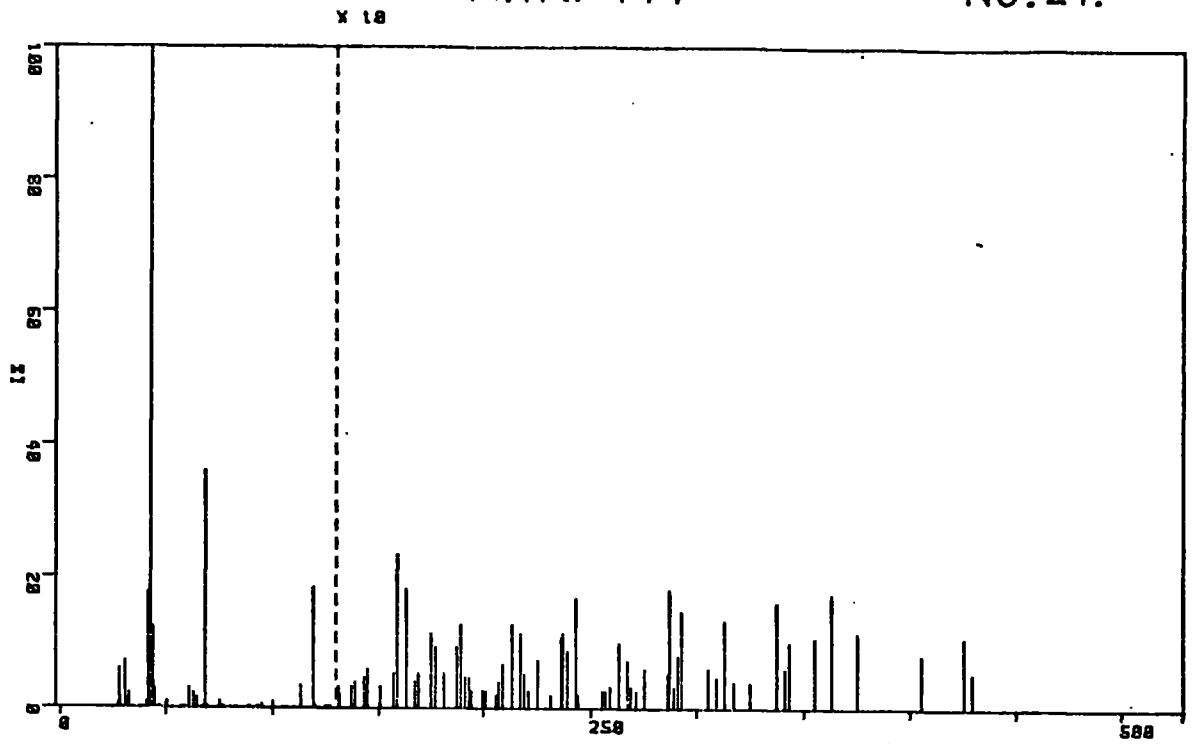


NK571 5 24-OCT-79

PEAK NO.	MASS	% INT BASE			
1	27.24	2.02	44	95.05	3.87
2	28.12	5.72	45	97.01	3.91
3	28.99	8.40	48	105.04	1.65
4	29.83	2.72	51	109.90	14.24
5	30.92	7.45	52	110.96	5.35
7	33.12	7.90	54	113.09	6.96
9	42.05	3.91	55	114.02	10.09
13	47.12	2.55	59	125.04	16.96
16	50.95	4.82	60	126.02	7.82
21	60.99	1.56	61	127.01	3.21
22	63.09	2.96	62	131.98	2.96
25	68.99	27.50	63	140.94	2.76
27	70.98	1.56	64	141.97	5.93
28	73.08	13.50	66	144.01	3.09
30	75.11	14.62	69	154.95	0.41
31	76.07	1.48	70	158.95	0.70
32	77.08	6.86	71	160.91	0.54
33	78.00	2.92	72	175.00	22.19
35	82.00	6.50	73	176.01	1.24
39	90.95	100.00	74	176.96	0.54
41	91.98	3.58	75	192.91	0.37
42	93.01	1.98	76	194.05	39.48

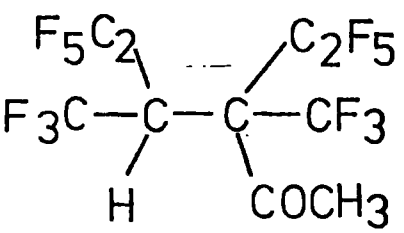


NK4 11 M.Wt. 444 No.21.

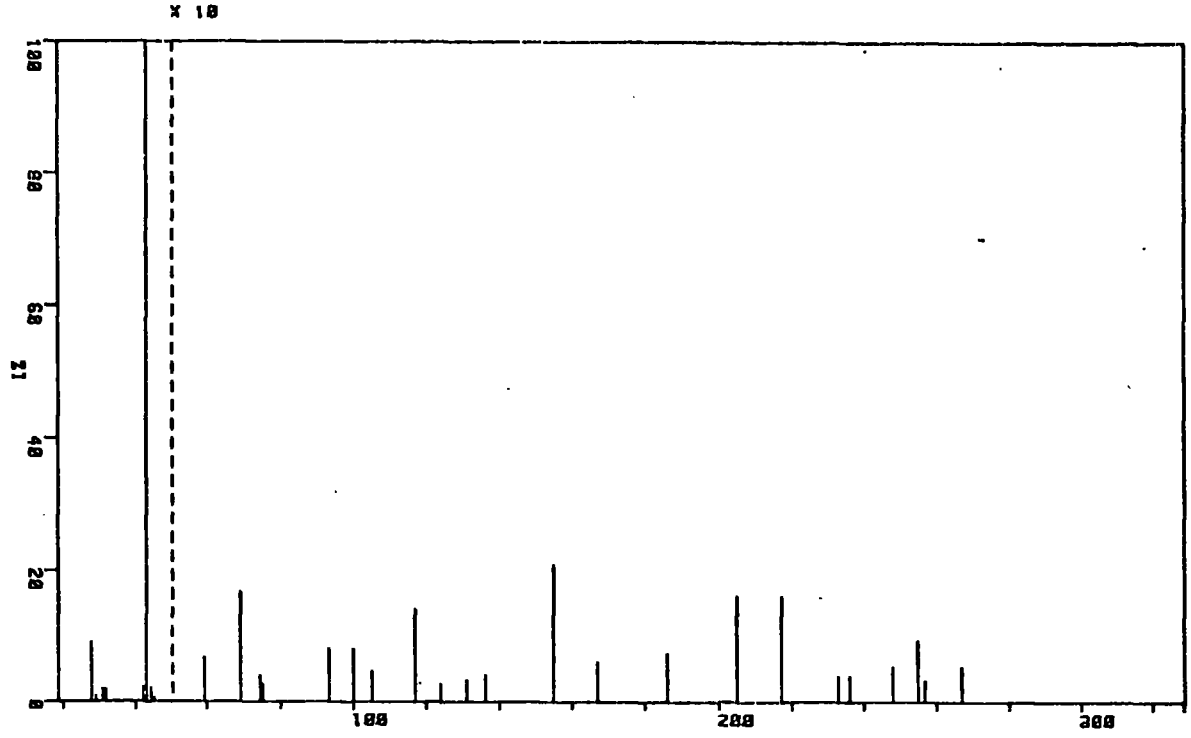


NK4 11 26-SEP-79

PEAK NO.	MASS	% INT BASE			
2	28.05	5.98	64	213.08	1.29
3	28.94	1.59	65	217.11	1.15
4	30.84	7.03	70	236.08	1.12
5	31.95	1.29	71	237.08	1.20
6	33.06	2.34	73	243.08	1.71
9	42.01	17.73	78	263.10	1.05
10	43.09	100.00	84	287.11	1.81
11	44.13	12.38	87	293.04	1.49
12	45.15	3.05	88	305.11	0.61
15	50.94	1.17	89	309.08	0.49
18	60.97	3.20	90	313.07	1.39
19	63.08	2.37	91	317.10	0.42
21	65.12	1.68	92	325.10	0.46
23	68.99	36.02	93	337.13	1.66
25	75.10	1.05	94	341.06	0.66
32	113.06	3.49	95	343.06	1.05
33	119.01	18.36	96	355.07	1.07
47	159.03	2.37	97	363.05	1.73
48	163.09	1.86	98	375.14	1.15
51	175.11	1.15	99	405.14	0.81
54	187.08	0.98	100	425.11	1.10
55	189.05	1.29	101	429.09	0.56

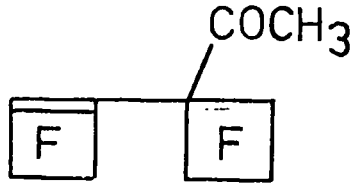


NK65R1 6 M.Wt. 348 No. 22.

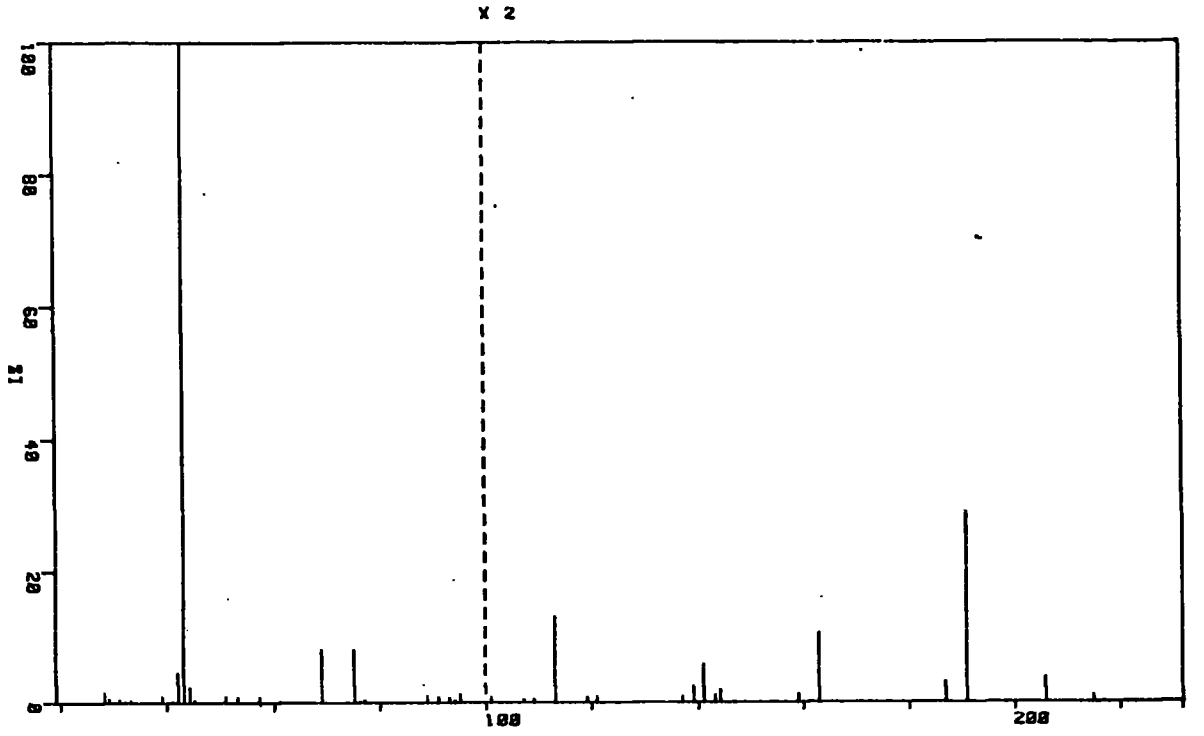


NK65R1. 6 24-OCT-79

PEAK NO.	MASS	% INT BASE
1	27.23	0.30
2	27.25	0.27
3	28.12	8.97
4	29.00	0.91
5	30.92	2.00
6	38.01	1.92
7	42.05	2.29
8	43.12	100.00
9	44.16	2.32
10	45.17	0.71
11	59.03	0.71
12	68.99	1.68
13	74.14	0.44
14	75.09	0.30
15	93.02	0.84
16	99.93	0.81
17	105.03	0.50
18	117.01	1.45
19	123.97	0.27
20	130.93	0.34
21	136.01	0.44
22	154.99	2.08
23	166.98	0.64
24	185.96	0.77
25	204.96	1.65
26	216.96	1.61
27	232.91	0.44
28	235.88	0.40
29	247.89	0.57
30	254.87	0.94
31	256.93	0.37
32	266.91	0.57

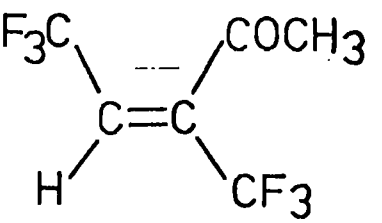


NK691 S M.Wt. 206 No.23.

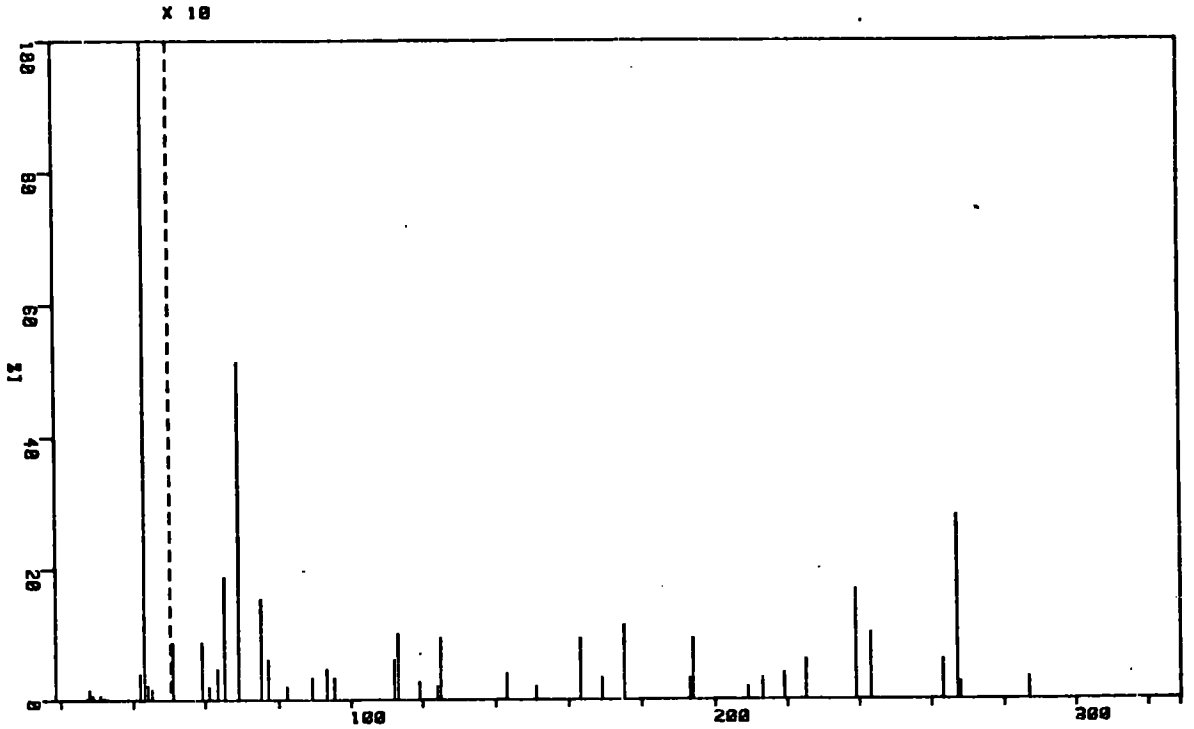


NK691 S 24-OCT-79

PEAK NO.	MASS	% INT BASE
1	27.23	0.32
2	28.12	1.65
3	28.99	0.70
4	30.91	0.56
5	32.01	0.32
6	33.12	0.46
7	39.01	1.09
8	40.96	0.39
9	42.05	4.59
10	43.12	100.00
11	44.16	2.46
12	45.17	0.49
13	50.96	1.09
14	53.08	0.98
15	57.10	0.95
16	59.01	0.32
17	60.98	0.35
18	68.99	7.96
19	75.11	8.03
20	76.06	0.39
21	77.06	0.49
22	87.98	0.32
23	88.99	1.16
24	90.95	0.88
25	93.02	0.81
26	94.03	0.46
27	95.05	1.37
28	100.96	0.53
29	107.01	0.28
30	108.97	0.39
31	113.01	6.56
32	118.96	0.46
33	120.95	0.53
34	137.02	0.53
35	138.99	1.23
36	140.96	2.91
37	142.97	0.67
38	144.02	0.95
39	158.97	0.70
40	162.99	5.30
41	187.01	1.61
42	191.00	14.42
43	205.99	1.09
44	214.97	0.56

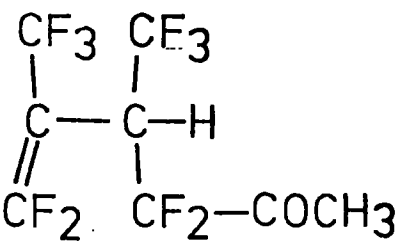


NK701 S M.Wt. 306 No.24.

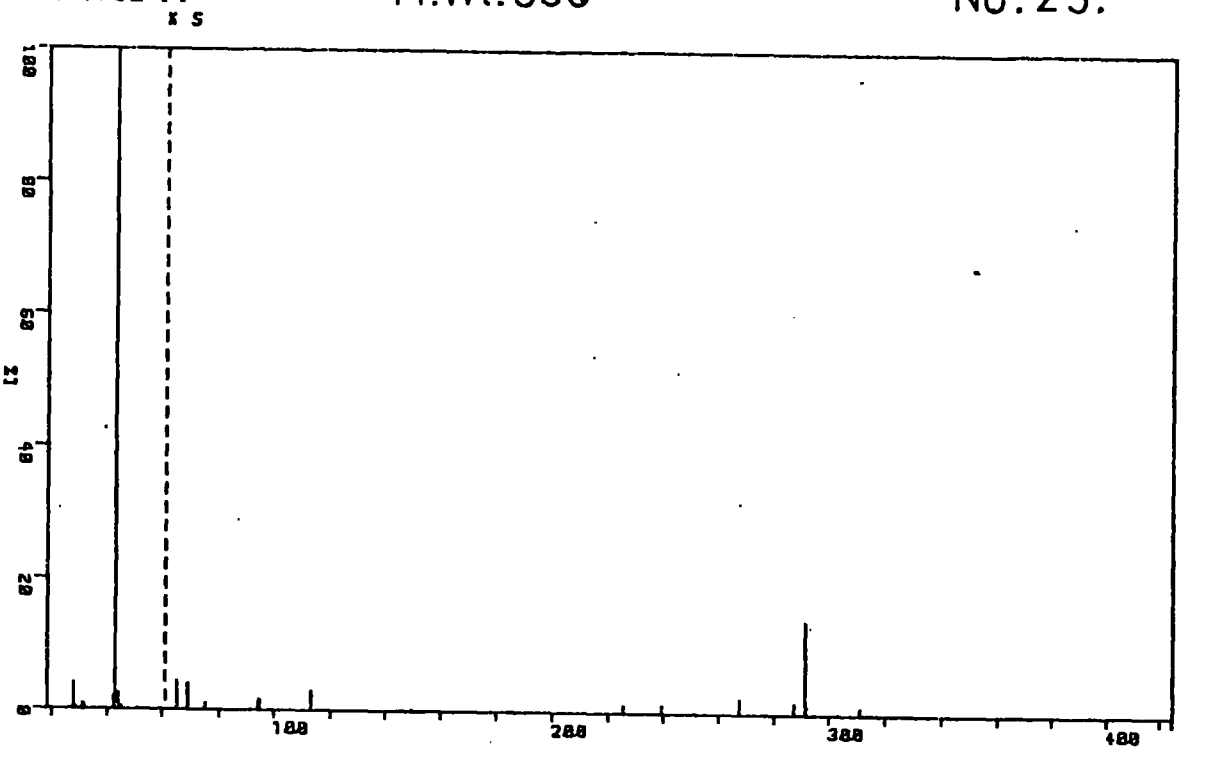


NK701 S 03-OCT-79

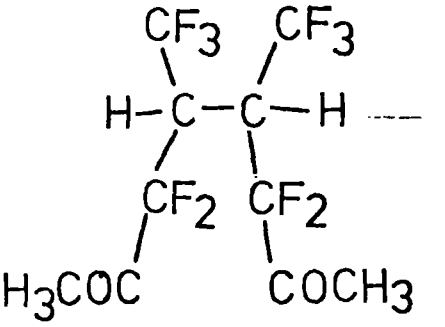
PEAK NO.	MASS	% INT BASE			
1	27.17	0.34	23	95.07	0.34
2	28.05	1.56	24	112.01	0.66
3	28.93	0.69	25	113.03	1.01
4	30.84	0.72	26	118.99	0.32
5	31.94	0.34	27	124.05	0.24
6	33.06	0.24	28	125.07	0.95
7	40.92	0.24	29	143.04	0.42
8	42.01	4.03	30	151.03	0.24
9	43.08	100.00	31	163.02	0.98
10	44.13	2.31	32	169.04	0.34
11	45.15	1.62	33	175.06	1.14
12	50.94	0.93	34	193.02	0.34
13	59.01	0.93	35	194.03	0.98
14	60.96	0.24	36	209.04	0.24
15	63.07	0.50	37	213.04	0.40
16	65.10	1.88	38	219.03	0.45
17	68.98	5.17	39	225.05	0.64
18	75.09	1.56	40	239.02	1.72
19	77.08	0.61	41	243.02	1.03
20	82.01	0.24	42	263.04	0.61
21	89.01	0.34	43	267.06	2.81
22	93.03	0.53	44	268.04	0.29
			45	287.06	0.37



NK702 11 M.Wt.350 No.25.



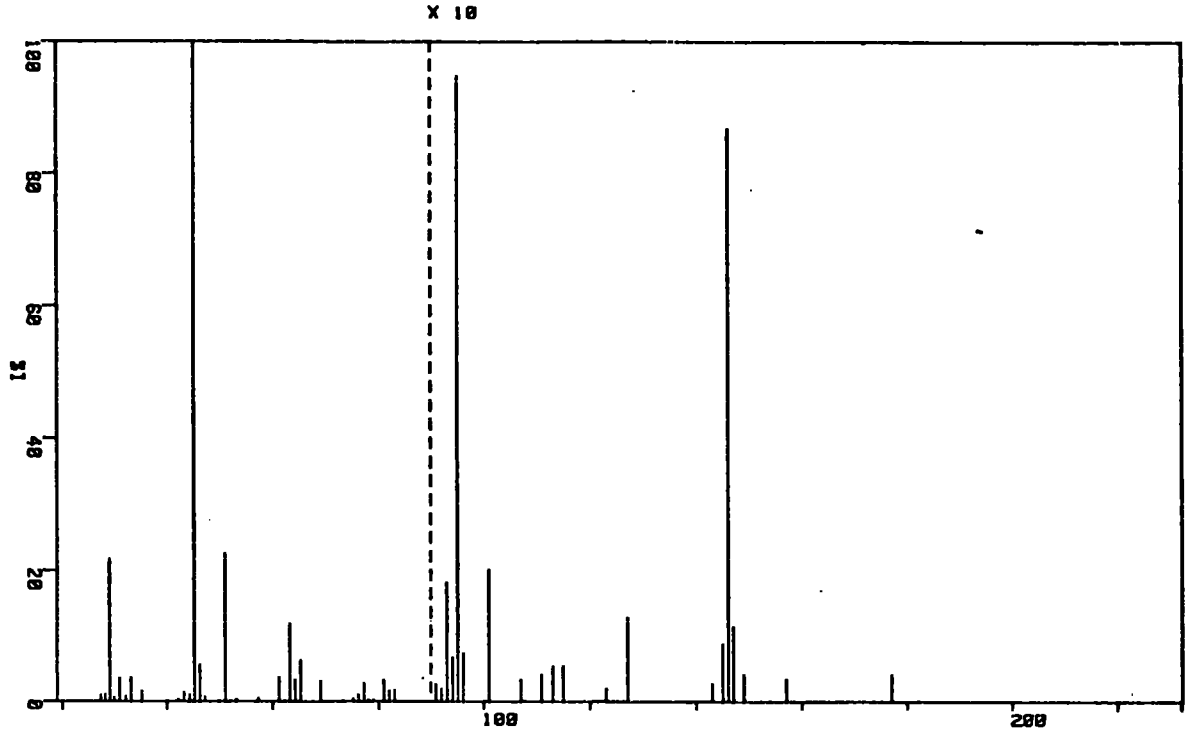
NK702	11	26-SEP-79
PEAK NO.	MASS	% INT BASE
1	27.17	0.34
2	28.05	4.03
3	28.95	0.44
4	30.84	0.98
5	31.94	0.68
6	42.01	2.10
7	43.08	100.00
8	44.13	2.59
9	45.15	0.56
10	50.94	0.27
11	59.01	0.27
12	65.12	0.90
13	68.98	0.83
14	75.10	0.22
15	94.09	0.32
16	95.08	0.34
17	113.05	0.66
18	225.17	0.27
19	239.13	0.27
20	267.19	0.51
21	287.16	0.37
22	291.13	2.81
23	292.14	0.29
24	311.15	0.22



NK1971 6

M.Wt. 146

No.26.



NK1971. 6 24-OCT-79

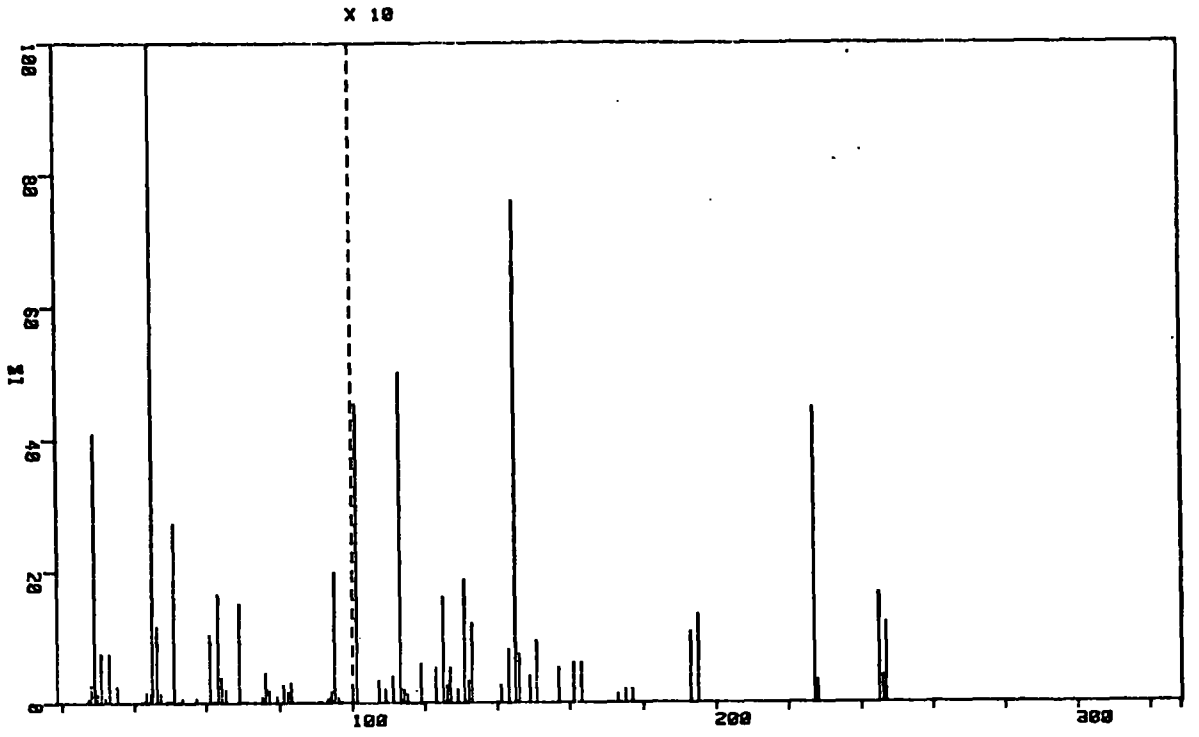
PEAK NO.	MASS	% INT BASE			
1	27.24	1.12	30	76.08	1.20
2	28.12	1.20	31	77.06	2.81
3	28.99	21.66	32	78.00	0.46
4	29.83	0.68	33	78.94	0.44
5	30.92	3.54	34	80.95	3.32
6	32.02	0.78	35	82.00	1.68
7	33.12	3.57	36	83.02	1.73
8	35.21	1.61	37	90.92	0.27
9	42.05	0.46	38	91.97	0.22
10	43.12	1.44	39	93.01	1.81
11	44.16	1.00	40	94.04	0.71
12	45.19	100.00	41	95.05	9.50
13	46.17	5.59	42	96.04	0.78
14	47.14	0.78	43	100.94	2.03
15	49.88	0.24	44	107.04	0.39
16	50.96	22.44	45	110.95	0.46
17	52.03	0.32	46	113.01	0.59
18	53.09	0.42	47	115.03	0.59
19	57.12	0.54	48	123.01	0.24
20	59.02	0.24	49	127.03	1.27
21	60.99	3.74	50	143.00	0.27
22	62.05	0.27	51	145.03	0.90
23	63.11	11.84	52	146.04	8.67
24	64.09	3.35	53	147.03	1.15
25	65.11	6.32	54	148.97	0.46
26	68.94	3.17	55	157.01	0.37
27	71.01	0.22			
28	73.04	0.32	56	177.03	0.42
29	75.07	0.56			

$HCF_2CF_2CH_2OCH_3$

NK1971 8

M.Wt. 246

No.27.



NK1971. 0 24-OCT-79

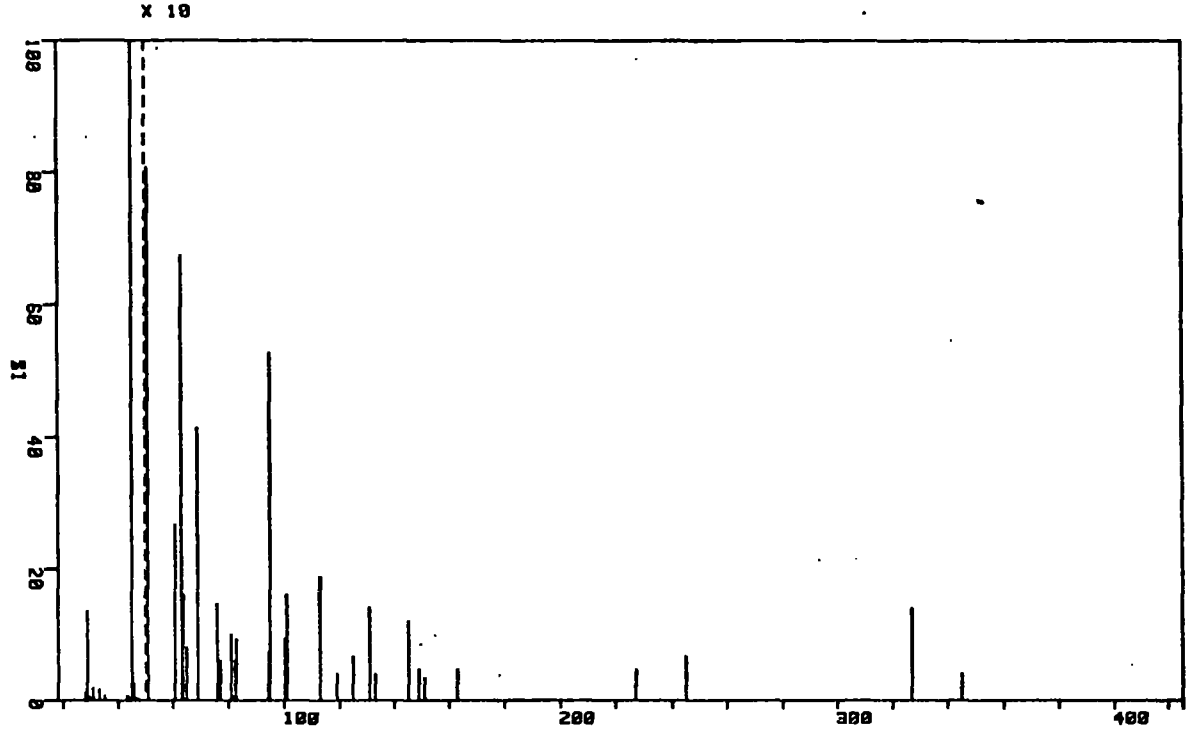
PEAK NO.	MASS	% INT BASE			
2	28.12	2.78			
3	28.98	40.93			
4	29.02	1.34	41	95.03	19.76
5	30.92	7.50	44	99.88	2.32
7	33.12	7.45	45	100.97	4.54
8	35.21	2.49	49	113.01	5.03
10	43.11	1.66	54	125.03	1.61
11	44.16	1.44	58	130.95	1.93
12	44.95	100.00	60	132.99	1.22
13	46.16	11.55	63	144.99	7.62
14	47.13	1.47	66	150.93	0.98
17	50.95	27.33	67	157.00	0.54
21	60.97	10.38	68	160.93	0.61
23	63.09	16.53	69	162.96	0.66
24	64.11	3.93	70	172.93	0.20
25	65.09	2.03	71	174.99	0.22
26	68.94	15.02	72	176.98	0.22
31	76.08	4.54	73	192.94	1.12
32	77.04	1.88	74	194.98	1.34
33	78.95	1.10	75	226.96	4.49
34	80.95	2.76	76	227.93	0.37
35	81.99	1.66	77	244.91	1.68
36	83.03	2.98	78	245.92	0.42
40	94.03	1.81	79	246.90	1.22

$H(CF_2CF_2)_2CH_2OCH_3$

NK1971 12

M.Wt. 346

No.28.

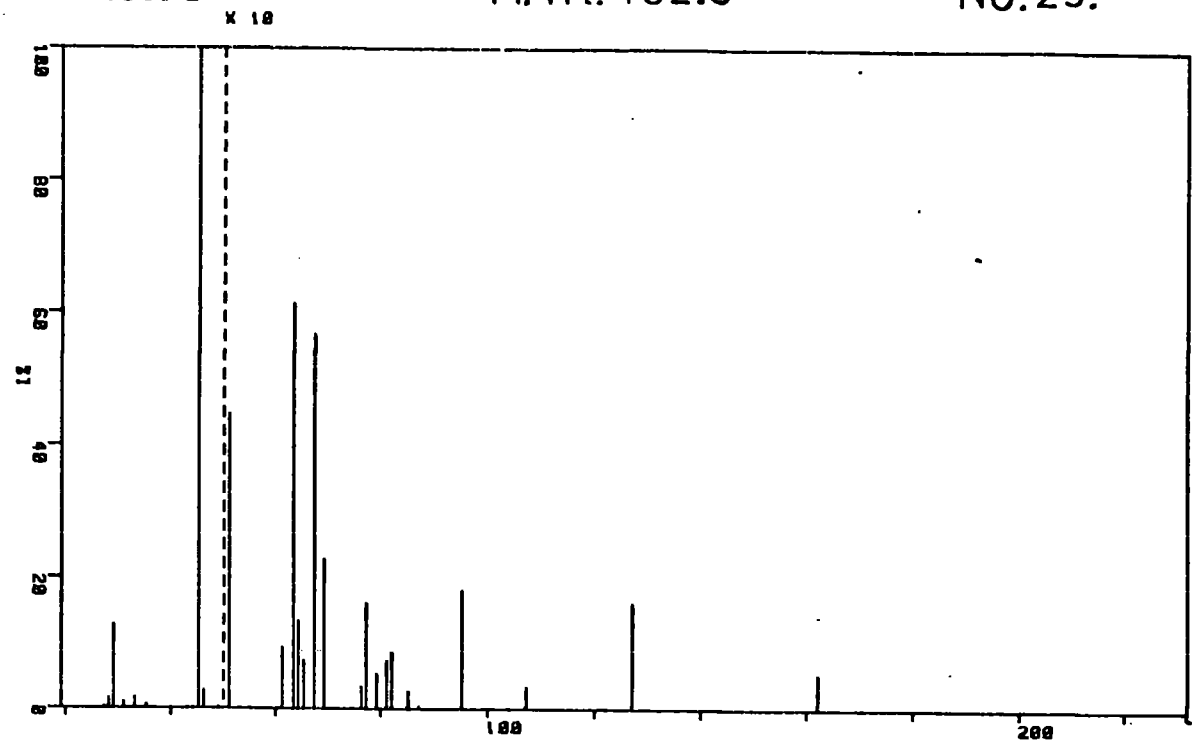


NK1971. 12 24-OCT-79

PEAK NO.	MASS	% INT BASE
1	28.12	1.25
2	28.99	13.55
3	29.83	0.51
4	30.92	1.94
5	33.12	1.76
6	35.21	0.74
7	43.13	0.69
8	44.16	0.51
9	45.19	100.00
10	46.17	2.50
11	47.13	0.37
12	50.96	8.09
13	60.98	2.73
14	63.10	6.80
15	64.10	1.62
16	65.11	0.83
17	68.97	4.16
18	76.10	1.53
19	77.08	0.60
20	80.97	1.06
21	82.01	0.60
22	83.05	0.97
23	94.05	0.79
24	95.06	5.32
25	99.90	0.97
26	100.96	1.62
27	113.02	1.90
28	118.95	0.46
29	125.03	0.69
30	130.95	1.43
31	133.00	0.46
32	145.02	1.20
33	148.96	0.51
34	150.90	0.37
35	162.98	0.51
36	227.00	0.51
37	244.98	0.69
38	326.94	1.43
39	344.86	0.42

$H(CF_2CF_2)_3CH_2OCH_3$

NK1981 5 M. Wt. 162.5 No. 29.

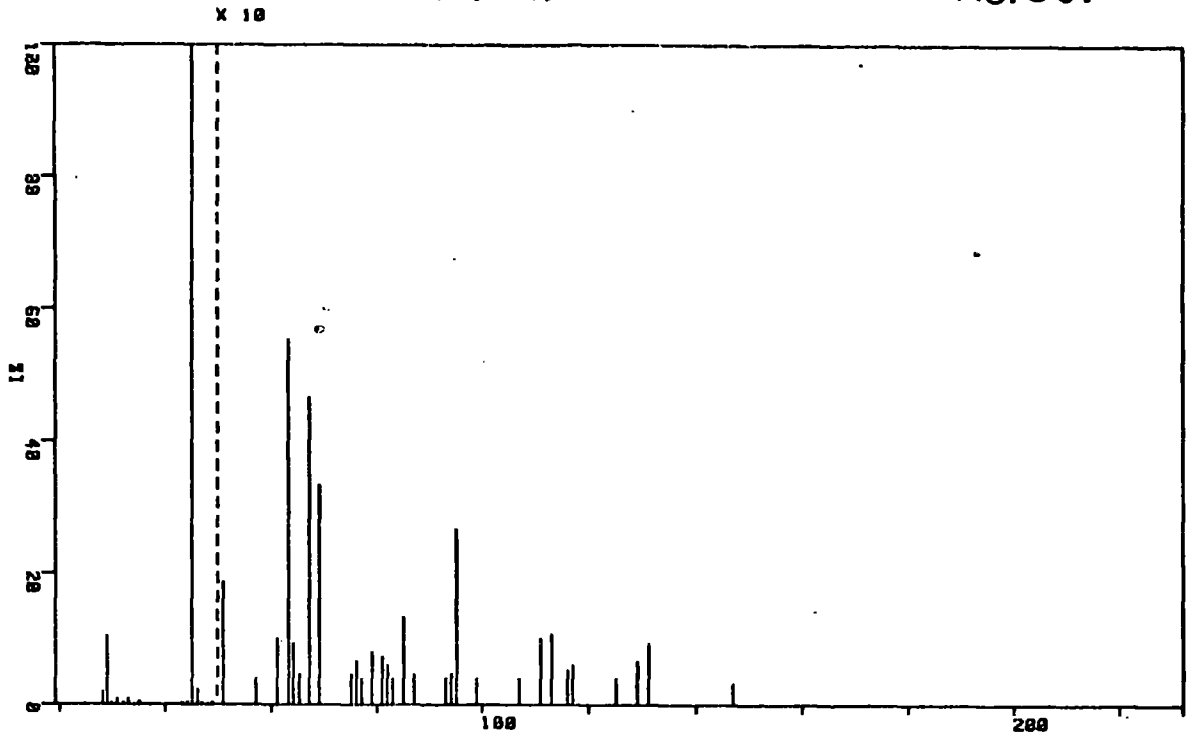


NK1981. 5 24-OCT-79

PEAK NO.	MASS	% INT BASE
1	27.24	0.43
2	28.12	1.63
3	28.98	12.75
4	30.91	1.20
5	32.02	0.37
6	33.13	1.68
7	35.21	0.74
8	43.11	0.31
9	44.15	0.37
10	45.19	100.00
11	46.18	2.88
12	48.96	0.43
13	50.96	4.51
14	60.99	1.00
15	63.11	6.19
16	64.10	1.34
17	65.11	0.77
18	67.04	5.73
19	68.95	2.31
20	76.10	0.34
21	77.07	1.65
22	78.97	0.54
23	80.98	0.77
24	82.02	0.88
25	85.03	0.31
26	95.07	1.85
27	107.06	0.34
28	127.07	1.63
29	162.04	0.54

$HCFClCF_2CH_2OCH_3$

NK198 5 M.Wt. 279 No. 30.

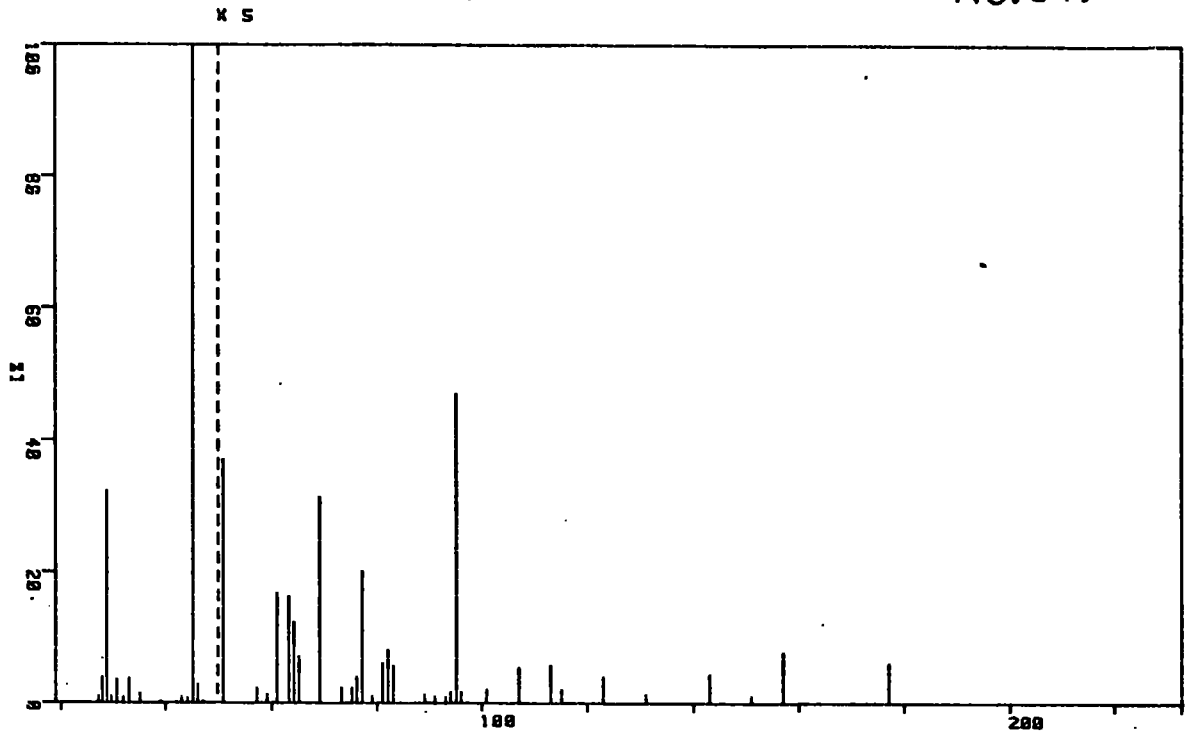


NK193 5 24-OCT-79

PEAK NO.	MASS	% INT BASE			
1	28.12	2.07			
2	28.98	10.52	23	76.09	0.73
3	29.82	0.41	24	77.08	0.45
4	30.91	0.93	25	78.97	0.85
5	32.01	0.53	26	80.97	0.77
6	33.12	0.93	27	82.01	0.65
7	35.21	0.57	28	83.02	0.41
8	43.11	0.45	29	85.02	1.34
9	44.16	0.49	30	87.00	0.53
10	45.19	100.00	31	93.02	0.41
11	46.18	2.52	32	94.06	0.49
12	47.12	0.45	33	95.07	2.72
13	48.96	0.49	34	98.93	0.41
14	50.95	1.91	35	107.05	0.45
15	57.11	0.41	36	110.95	1.06
16	60.99	1.06	37	113.01	1.10
17	63.11	5.56	38	115.99	0.57
18	64.09	0.93	39	116.99	0.61
19	65.11	0.53	40	125.04	0.45
20	67.04	4.67	41	128.96	0.69
21	68.96	3.37	42	130.95	0.93
22	75.09	0.53	43	146.95	0.37

$H(CFClCF_2)_2CH_2OCH_3$

NK186 6 M.Wt. 196 No.31.

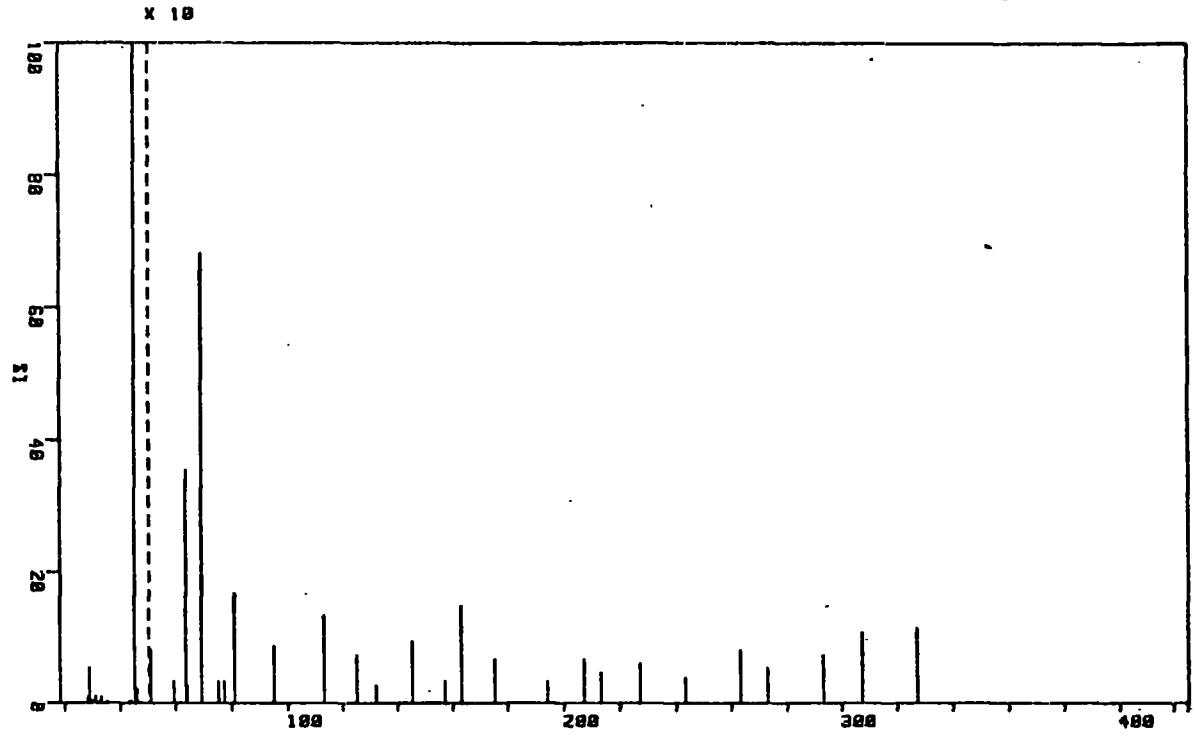


NK186 6 02-OCT-79

PEAK NO.	MASS	% INT BASE			
1	27.17	1.11	24	73.06	0.49
2	28.05	3.07	25	75.08	0.52
3	38.92	32.23	26	76.09	0.80
4	29.77	1.03	27	77.06	4.00
5	30.84	3.56	28	78.96	0.23
6	31.95	0.98	29	80.95	1.26
7	33.06	3.77	30	81.99	1.63
8	35.15	1.47	31	83.03	1.16
9	38.96	0.34	32	88.97	0.28
10	42.00	0.23	33	90.95	0.26
11	43.08	0.98	34	93.01	0.21
12	44.12	0.83	35	94.05	0.39
13	45.15	100.00	36	95.04	9.45
14	46.14	2.81	37	96.06	0.36
15	47.10	0.39	38	100.96	0.41
16	50.93	7.41	39	107.03	1.08
17	57.07	0.52	40	113.01	1.19
18	58.99	0.31	41	115.04	0.46
19	60.94	3.38	42	123.00	0.85
20	63.06	3.33	43	130.95	0.29
21	64.09	2.53	44	143.00	0.80
22	65.10	1.42	45	150.97	0.26
23	68.97	6.27	46	157.01	1.57
			47	177.01	1.26

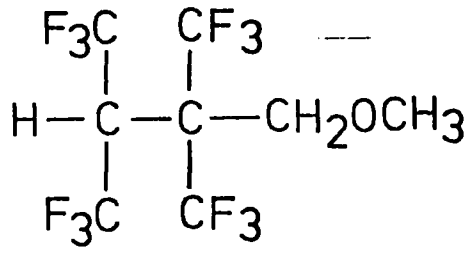
$CF_3CFHCF_2CH_2OCH_3$

NK1891 4 M.Wt. 346 No.32.

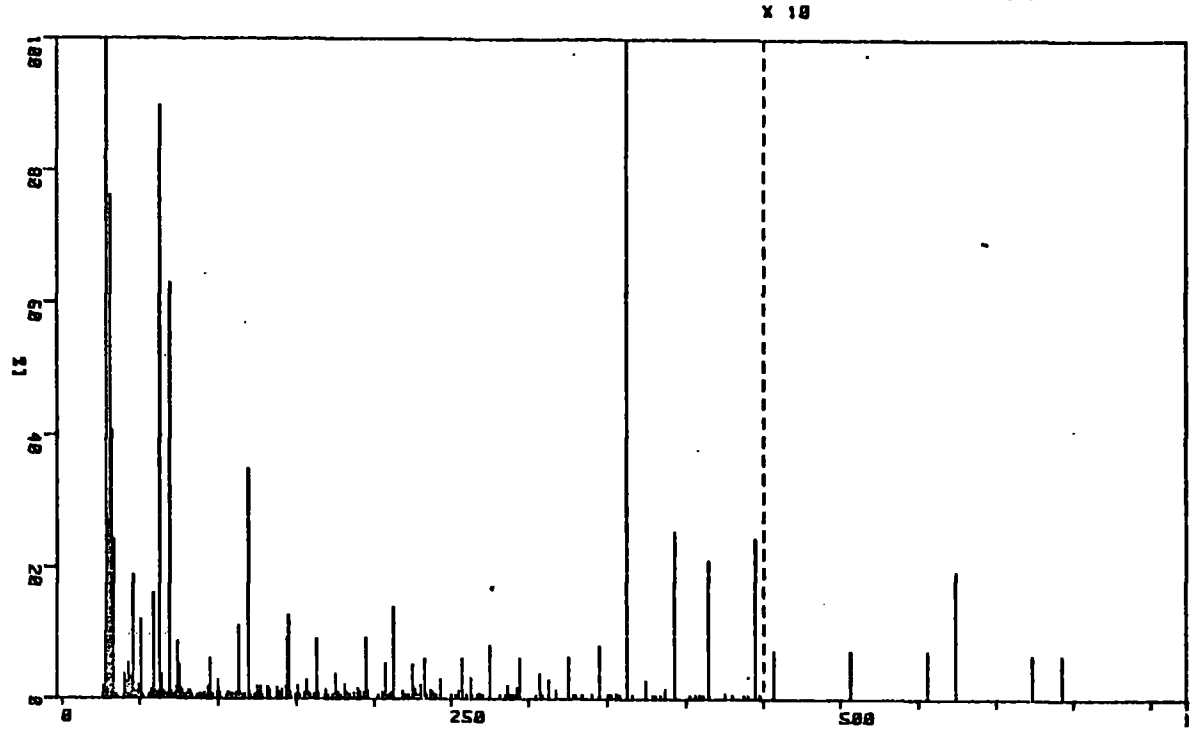


NK1891. 4 24-OCT-79

PEAK NO.	MASS	% INT BASE
1	28.12	1.01
2	38.99	5.46
3	29.82	0.58
4	30.92	1.31
5	32.00	0.27
6	33.12	1.19
7	35.21	0.40
8	43.11	0.46
9	44.14	0.52
10	45.18	100.00
11	46.17	2.32
12	47.10	0.27
13	50.95	0.82
14	59.01	0.37
15	63.11	3.54
16	64.08	0.27
17	68.97	6.80
18	75.08	0.37
19	77.07	0.37
20	80.98	1.68
21	95.06	0.88
22	113.02	1.37
23	125.06	0.76
24	132.00	0.27
25	145.05	0.95
26	157.02	0.40
27	163.02	1.49
28	175.03	0.67
29	194.02	0.37
30	207.03	0.70
31	213.01	0.52
32	227.00	0.64
33	242.99	0.43
34	263.01	0.82
35	273.00	0.58
36	293.94	0.79
37	307.04	1.13
38	327.04	1.16

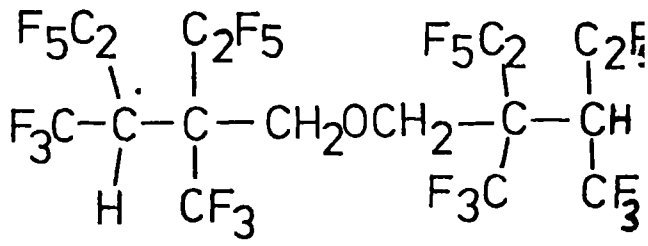


NK115 S M. Wt. 846 No.33.

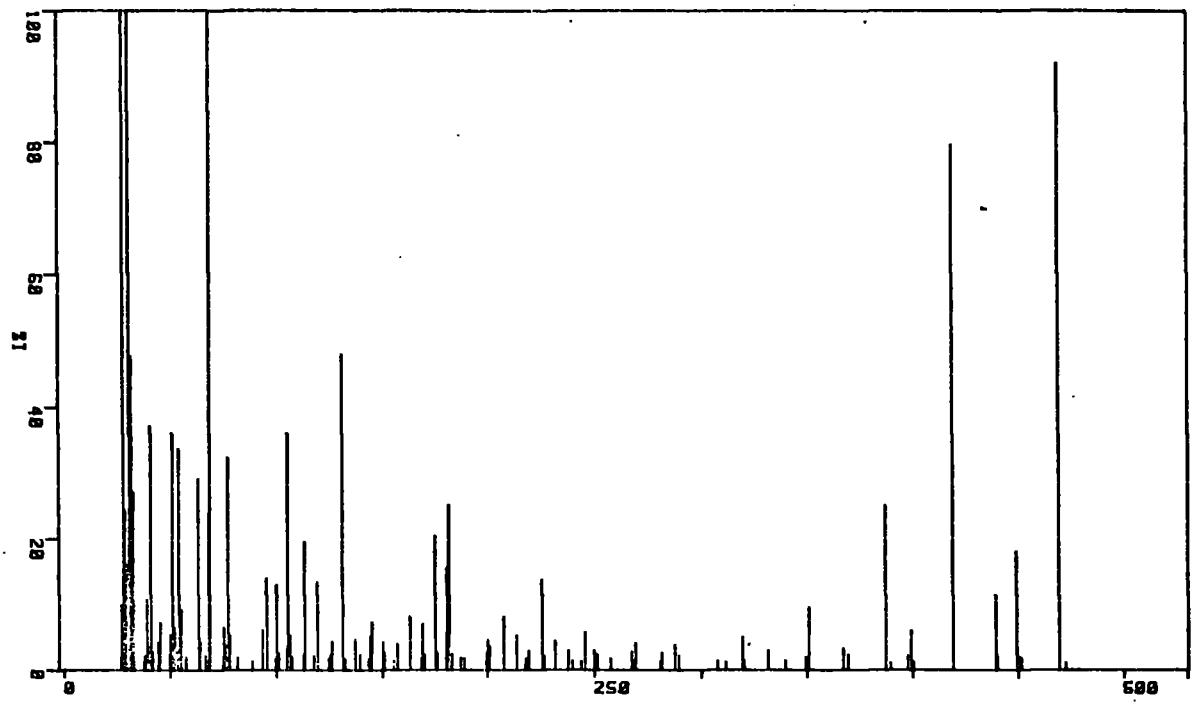


NK115 S 24-OCT-77

PEAK NO.	MASS	% INT BASE			
3	27.24	5.47			
6	28.12	100.00	173	194.83	5.10
15	29.01	15.21	179	207.37	2.99
16	29.53	3.58	183	213.03	7.63
19	30.93	41.54	191	225.15	2.90
20	32.01	22.26	198	233.04	3.35
21	33.12	13.24	207	243.74	1.70
25	39.84	2.16	211	257.47	3.40
28	43.12	3.03	213	262.95	1.79
29	44.15	1.84	220	275.11	4.46
30	45.17	10.25	228	294.93	3.45
35	50.96	6.57	230	307.02	2.16
42	59.04	8.73	232	313.01	1.61
51	69.10	40.94	234	325.23	3.49
53	64.13	2.07	244	344.52	4.37
59	68.99	54.33	250	362.16	54.50
64	74.16	4.78	257	392.63	13.88
65	75.07	2.90	263	414.60	11.49
84	95.04	3.40	269	444.54	13.33
88	99.89	1.65	271	456.41	0.41
99	113.00	6.11	272	506.05	0.41
110	118.94	19.07	273	506.71	0.41
131	143.98	5.10	274	556.01	0.41
132	145.00	6.94	275	574.22	1.06
145	156.95	1.61	276	623.35	0.37
150	162.95	5.01	277	624.90	0.37
157	174.97	2.16	278	642.67	0.37

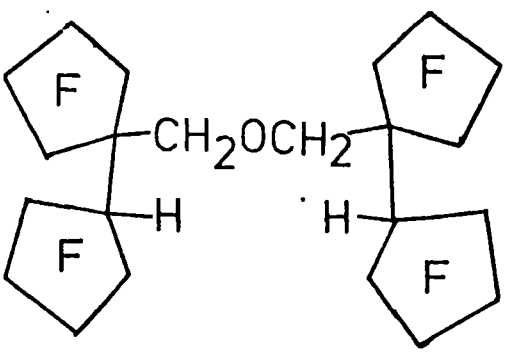


NK211 3 M.Wt.894 No.34.

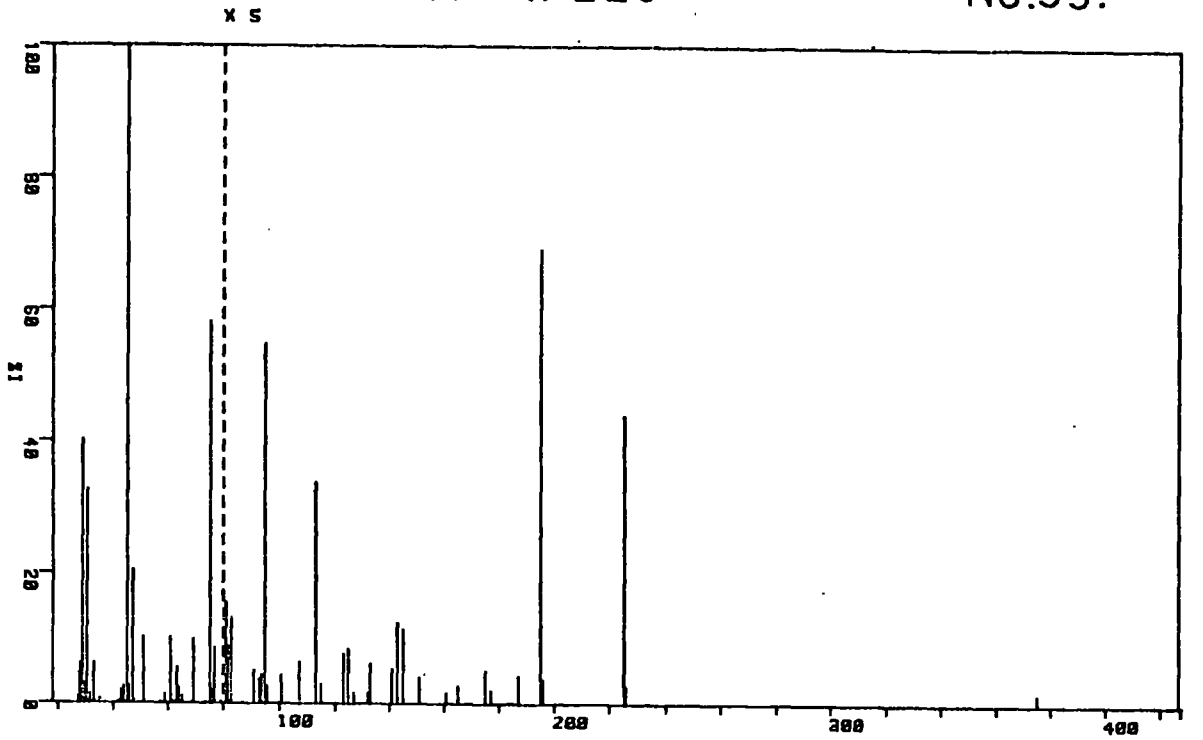


NK211 3 17-OCT-79

PEAK NO.	MASS	% INT BASE			
2	27.12	6.08	50	119.01	8.11
3	27.99	65.86	54	131.01	28.95
4	28.85	14.68	59	144.17	3.08
5	29.70	9.81	60	145.17	4.46
6	30.73	100.00	65	163.20	4.95
7	31.81	26.79	67	169.09	4.30
8	32.92	16.38	69	175.11	12.33
11	38.87	6.49	71	180.11	3.49
13	40.85	22.47	72	181.01	9.41
16	45.09	4.46	73	182.04	15.17
18	49.93	3.33	80	207.04	4.95
19	50.97	21.74	81	213.08	3.24
20	52.06	3.97	85	225.06	8.27
22	54.12	20.28	91	245.14	3.49
23	55.15	5.60	105	319.13	3.08
25	63.08	17.60	111	351.06	5.76
29	68.08	14.36	114	387.18	15.09
30	68.98	60.34	117	399.16	3.65
32	75.14	3.97	118	400.26	0.81
34	77.13	19.55	119	418.94	48.09
35	78.10	3.24	120	439.02	6.89
38	93.14	3.73	121	440.08	1.30
39	95.15	8.43	122	449.16	10.87
41	100.00	7.67	123	450.30	1.22
44	105.14	21.74	124	451.41	1.14
45	106.12	3.24	125	469.19	55.56
48	113.06	11.84	126	472.10	0.73



NK223 5 M. Wt. 226 No.35.



NK223 5 02-OCT-79

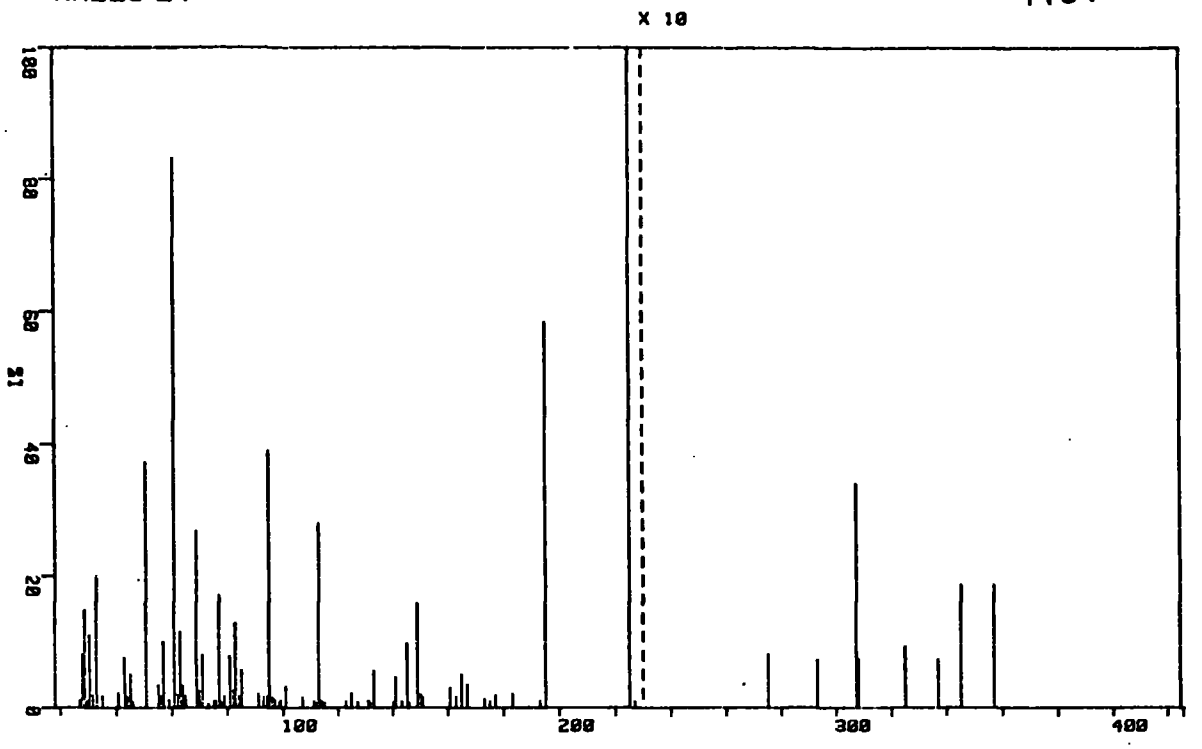
PEAK NO.	MASS	% INT BASE
1	27.17	1.24
2	28.05	6.06
3	28.93	40.31
4	29.77	3.03
5	30.85	32.66
6	31.96	1.51
7	33.07	6.21
10	43.09	2.17
11	44.13	2.64
12	45.15	100.00
13	46.14	2.72
14	47.12	20.43
16	50.93	10.14
18	58.98	1.51
19	60.98	10.14
21	63.07	5.55
22	64.09	2.45
23	65.11	1.20
24	68.97	9.84
26	75.11	50.10
27	76.08	2.17
28	77.04	8.66
30	89.94	3.07
31	91.90	1.79
32	93.01	2.64
33	90.93	1.05
36	95.05	10.95
39	107.03	1.32
40	112.99	6.76
42	122.99	1.55
43	125.04	1.67
46	132.98	1.20
47	140.93	1.07
48	142.99	2.49
49	145.02	2.29
53	175.01	1.01
56	194.98	13.86
58	225.01	8.85
59	226.00	0.58
60	374.95	0.39

$CF_3CFHCF_2CH_2OCH_2OCH_3$

NK223 24

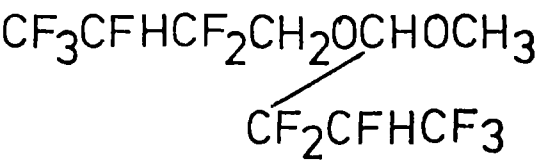
M.Wt. 376

No.36.

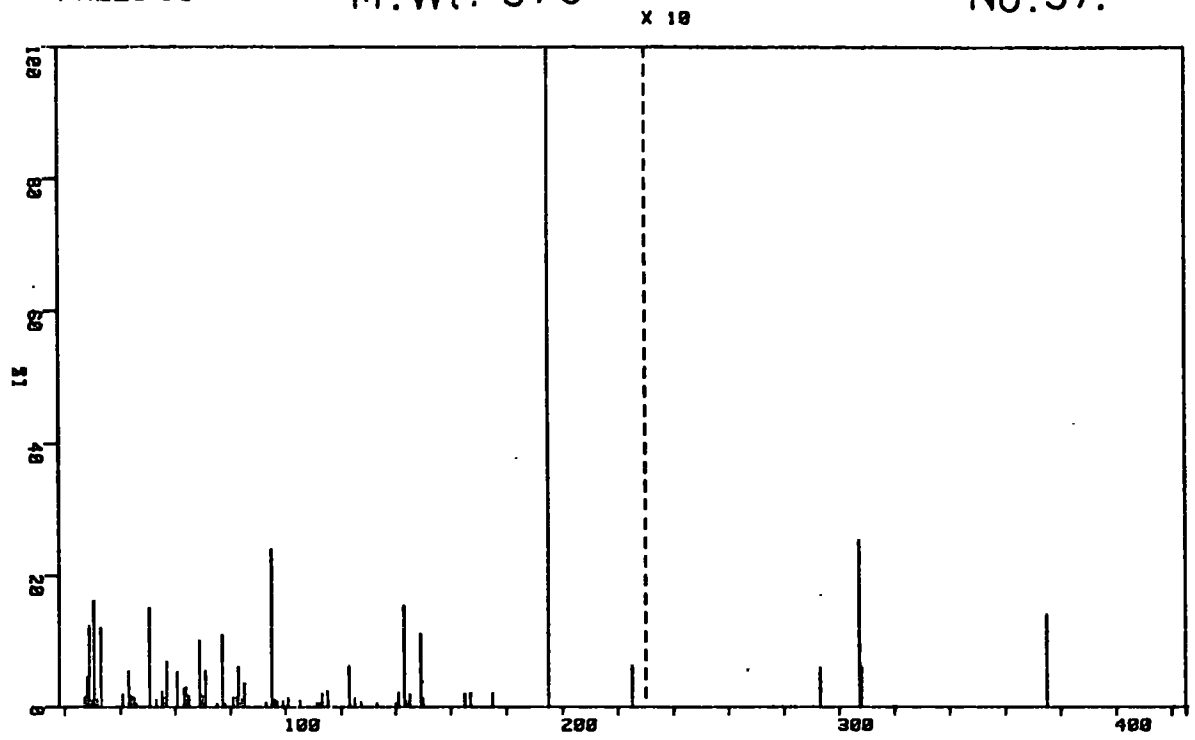


NK223 24 05-OCT-79

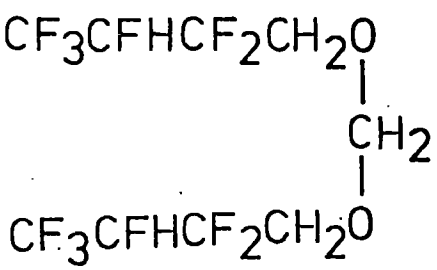
PEAK NO.	MASS	% INT BASE
2	28.05	8.15
3	28.93	14.75
5	30.05	11.06
7	33.08	20.07
10	43.12	7.63
12	45.15	5.06
14	50.94	37.22
15	55.15	3.43
17	57.13	10.03
19	60.97	83.19
21	63.08	11.58
22	64.10	3.34
24	68.98	26.84
26	71.06	7.98
30	77.08	17.15
33	80.98	7.80
35	83.06	12.86
37	85.15	5.66
41	95.07	38.94
46	100.97	3.26
50	113.04	28.04
58	133.03	5.57
60	141.05	4.55
62	145.06	9.69
64	149.00	15.87
67	160.98	3.09
69	165.03	5.06
70	167.05	3.52
75	193.04	0.94
76	195.09	58.40
77	225.09	100.00
78	227.03	1.03
79	275.09	0.86
80	293.15	0.77
81	307.16	3.43
82	308.14	0.77
83	325.03	0.94
84	337.04	0.77
85	344.97	1.89
86	356.99	1.89



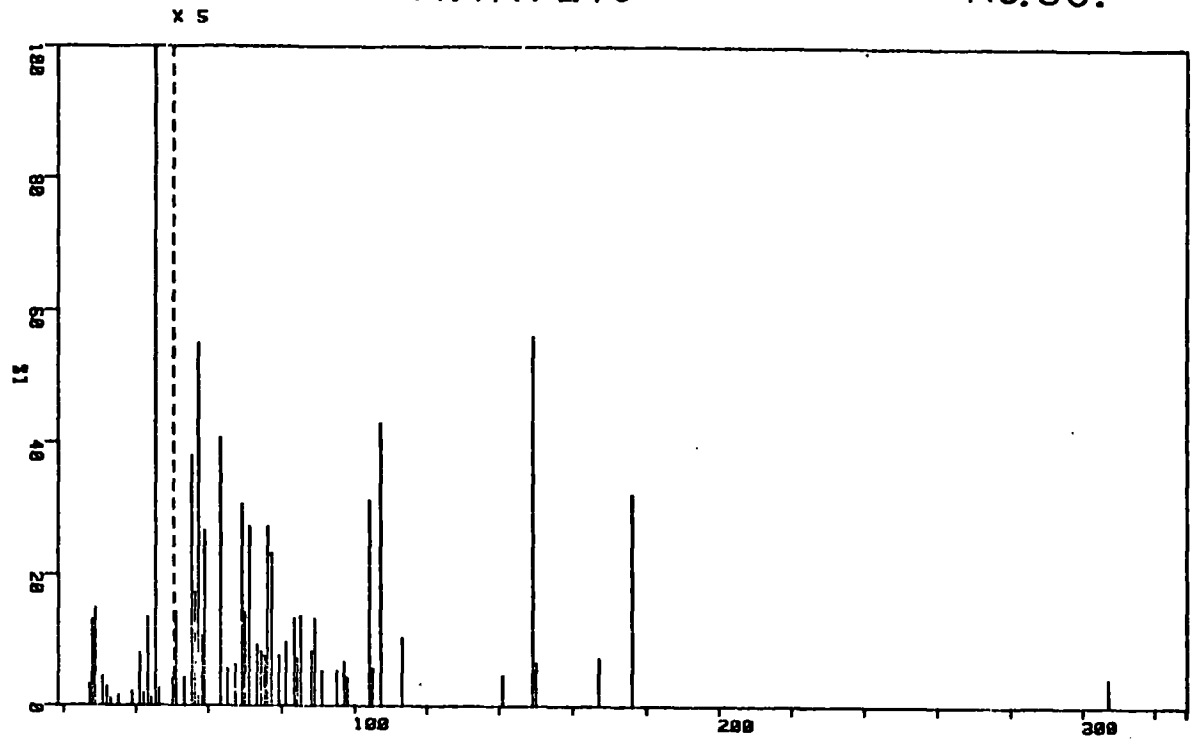
NK223 30 M.Wt. 376 No.37.



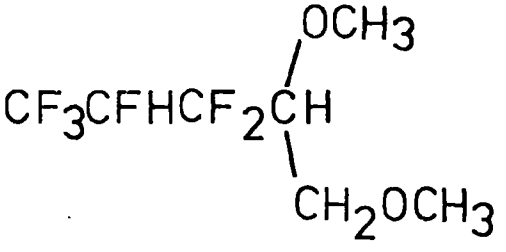
NK223	30	05-OCT-79			
PEAK NO.	MASS	% INT BASE			
1	27.17	1.56	29	82.03	1.56
2	28.05	4.54	30	83.07	6.23
3	28.93	12.40	31	84.14	1.29
4	29.77	1.08	32	85.16	3.66
5	30.84	16.19	34	95.06	23.98
6	31.95	1.22	35	96.08	1.15
7	33.06	12.20	38	100.98	1.42
8	40.95	1.96	42	113.06	2.10
9	43.12	5.49	43	115.07	2.51
10	44.13	1.69	44	123.04	6.30
11	45.14	1.42	45	125.09	1.36
13	50.94	14.97	49	141.14	2.24
14	53.08	1.15	50	143.04	15.45
15	55.16	2.51	52	145.06	1.96
16	56.15	1.49	53	149.01	11.11
17	57.13	6.98	54	149.99	1.29
18	60.95	5.42	55	165.05	1.96
19	63.08	2.91	56	167.07	2.17
20	64.09	3.05	57	175.06	2.17
21	65.11	1.76	58	195.09	100.00
22	68.99	10.16	59	225.07	6.30
23	69.98	1.83	60	293.15	0.61
24	71.06	5.49	61	307.18	2.57
26	77.08	10.91	62	308.11	0.61
28	80.99	1.49	63	375.09	1.42



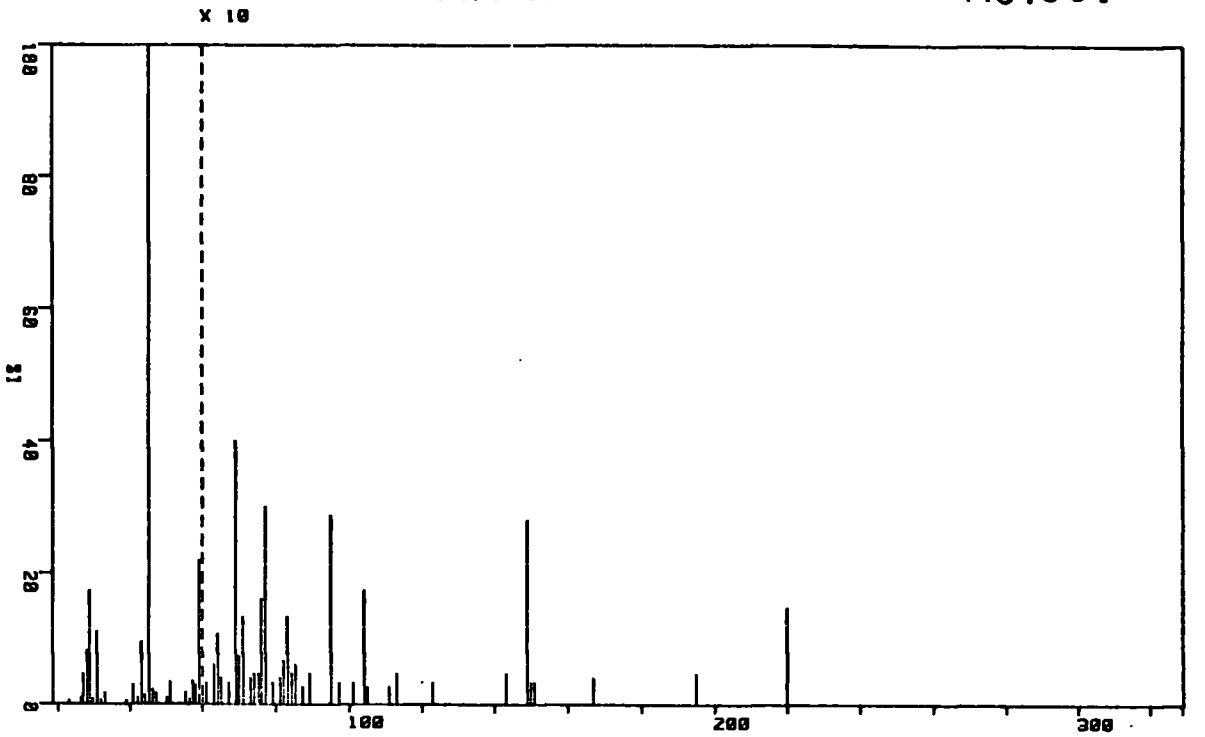
NK201 23 M.Wt. 240 No.38.



NK201	23	04-OCT-79
PEAK NO.	MASS	% INT BASE
1	27.17	3.38
2	28.05	13.23
3	28.93	14.93
4	30.84	4.58
5	31.94	3.08
8	38.96	2.39
9	40.95	8.06
10	42.03	2.09
11	43.10	13.53
13	45.15	100.00
14	46.14	2.79
15	49.88	4.18
16	50.94	2.89
18	55.15	7.66
19	56.15	3.48
20	57.12	11.04
21	58.06	2.19
22	59.00	5.37
23	63.07	8.16
26	69.01	6.17
27	69.98	2.89
28	71.04	5.47
32	76.09	5.47
33	77.07	4.68
35	80.98	1.99
36	83.11	2.69
38	85.15	2.79
40	89.01	2.69
45	104.05	6.27
47	107.04	8.66
48	113.07	2.09
50	148.98	11.24
53	176.04	6.47
54	307.00	0.90



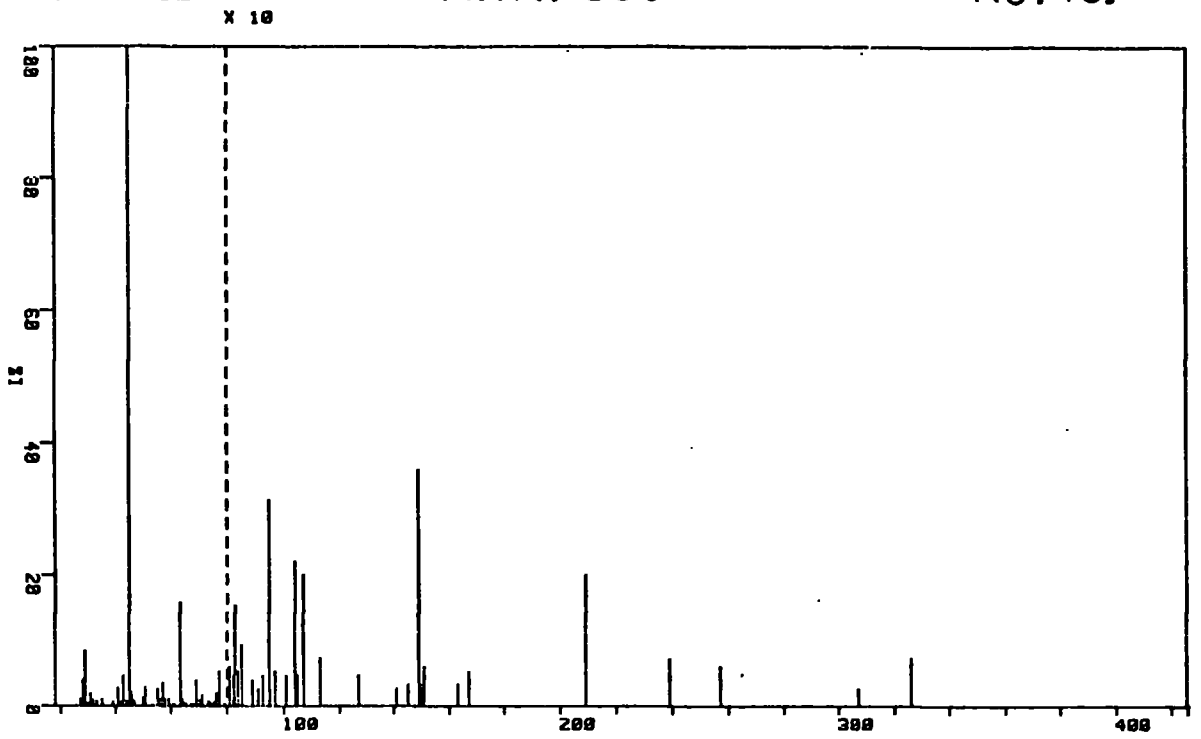
NK201 31 M.Wt.240 No.39.



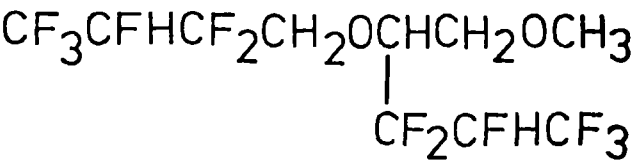
NK201	31	04-OCT-79
PEAK NO.	MASS	% INT BASE
3	27.15	4.60
4	28.05	8.20
5	28.92	17.28
7	30.83	11.04
11	40.93	3.09
13	43.07	9.49
15	45.12	100.00
16	46.12	2.35
19	50.91	3.44
23	57.08	3.64
24	58.03	2.99
25	58.97	21.91
32	68.95	4.02
39	77.03	3.02
48	95.00	2.93
57	140.91	2.86
62	219.86	1.51

$CF_3CFHCF_2CH_2OCH_2CH_2OCH_3$

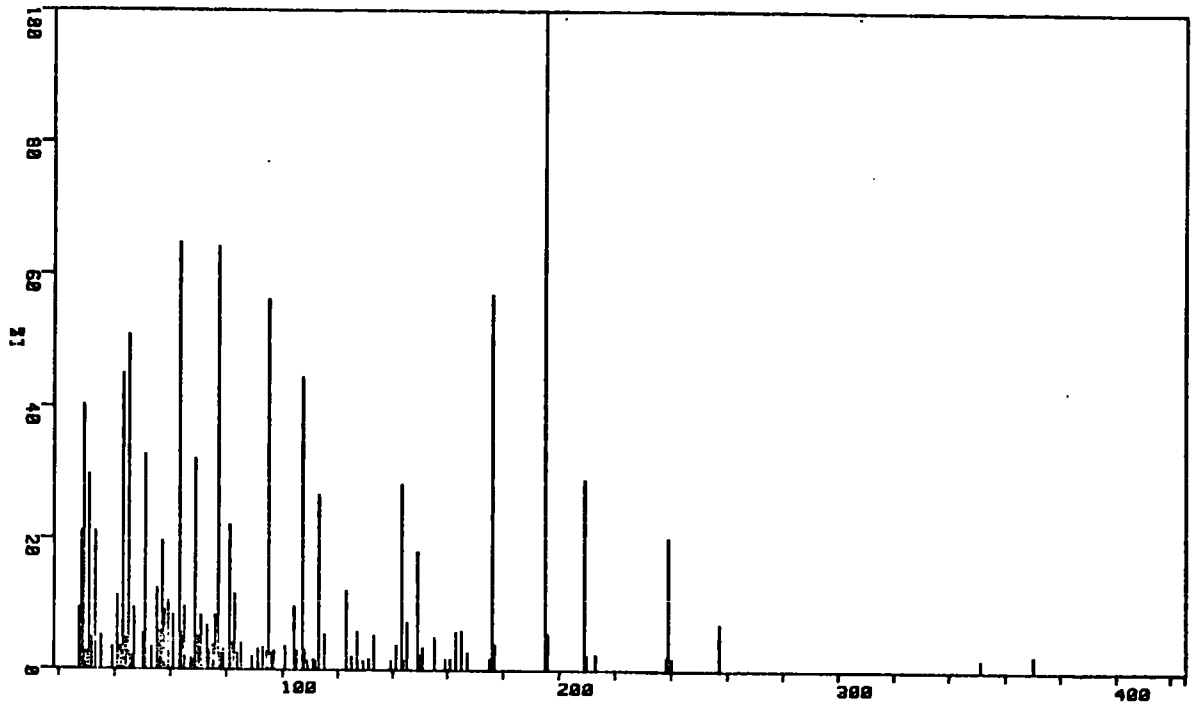
NK201 52 M.Wt. 390 No.40.



NK201	52	04-OCT-79
PEAK NO.	MASS	% INT BASE
2	28.05	4.01
3	28.93	8.52
5	30.84	2.09
10	40.95	2.85
12	43.10	4.73
15	45.15	100.00
16	46.15	2.24
19	50.94	2.93
21	55.15	2.71
23	57.12	3.58
27	63.07	15.82
32	68.99	4.04
38	76.10	2.06
39	77.08	5.34
49	95.06	3.14
52	104.06	2.24
54	107.05	2.02
59	148.98	3.65
64	208.99	2.06
65	239.00	0.76
66	256.99	0.61
67	307.11	0.33
60	325.99	0.79

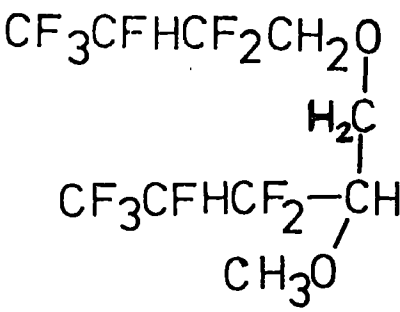


NK201 75 M.Wt. 390 No.41.

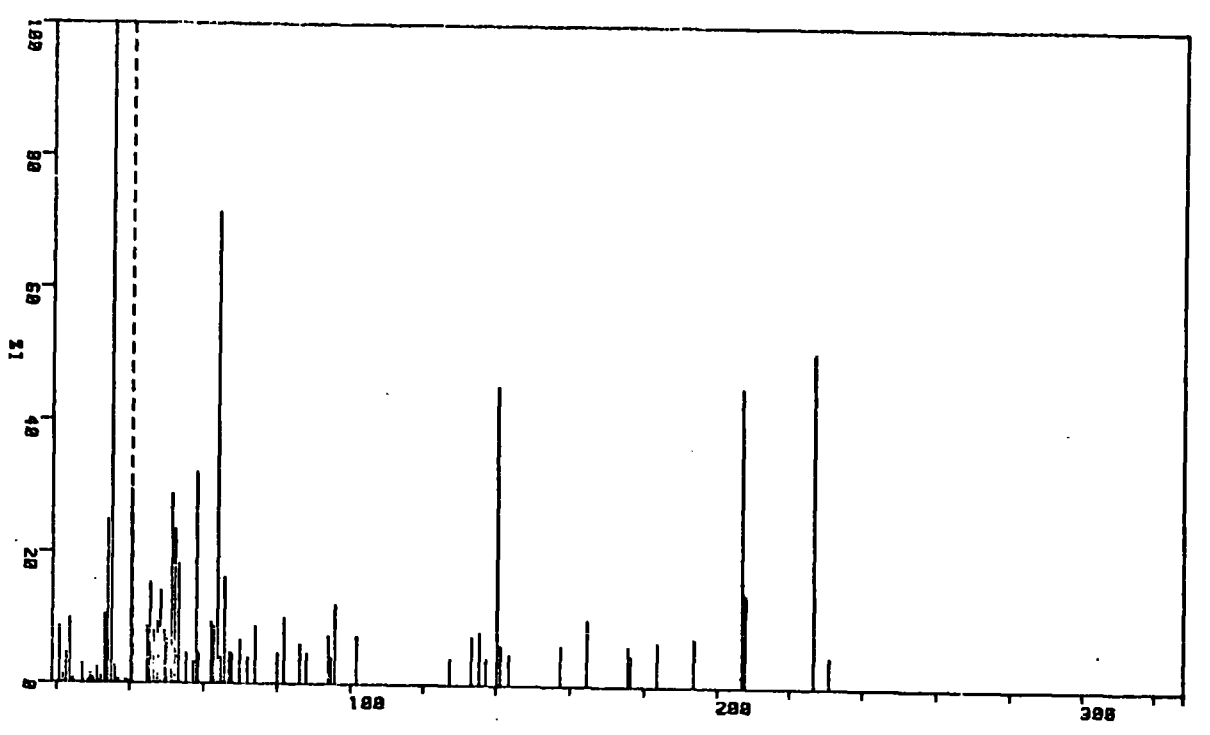


NK201 75 04-OCT-79

PEAK NO.	MASS	% INT BASE						
1	27.17	9.45						
2	28.05	21.06	31	68.99	32.01	62	113.04	26.70
3	28.93	40.30	32	69.98	5.14	63	115.06	5.47
4	29.77	2.82	33	71.05	8.29	64	125.03	12.11
5	30.84	29.68	34	73.08	6.80	65	125.09	2.16
6	31.94	4.81	35	74.10	2.99	66	127.08	5.80
7	33.06	21.06	36	75.10	3.81	69	133.03	5.31
8	35.15	5.31	37	76.11	8.29	71	141.02	3.81
9	38.96	3.48	38	77.08	64.01	72	143.03	28.36
10	40.75	11.28	39	78.05	2.49	74	145.05	7.30
11	42.03	3.65	40	78.98	3.32	75	149.00	18.08
12	43.09	44.94	41	80.98	22.06	76	149.98	2.32
13	44.13	4.81	42	82.02	4.15	77	151.00	3.48
14	45.15	50.75	43	83.07	11.61	78	155.04	4.98
15	46.14	2.16	44	84.14	2.65	81	163.02	5.80
16	47.10	9.45	45	85.15	4.15	82	165.05	5.97
17	49.89	5.47	46	88.99	2.16	83	167.04	2.82
18	50.94	32.67	47	90.96	3.32	85	176.04	56.88
19	53.09	3.48	48	93.04	3.48	86	177.04	3.98
20	55.15	12.44	49	94.07	2.82	87	195.02	100.00
21	56.15	5.80	50	95.06	56.22	88	196.00	5.64
22	57.12	19.57	51	96.07	2.65	89	209.01	29.02
23	58.06	9.12	52	97.11	2.99	90	209.97	2.32
24	59.00	10.45	53	100.98	3.65	91	213.00	2.49
25	60.95	8.46	54	104.07	9.62	92	238.03	1.99
26	63.08	64.68	55	105.07	2.99	93	239.00	20.23
27	64.10	5.64	56	107.06	44.44	94	240.00	1.82
28	65.11	9.62	57	108.05	3.15	95	257.01	7.13
						96	351.04	1.82
						97	370.00	2.49

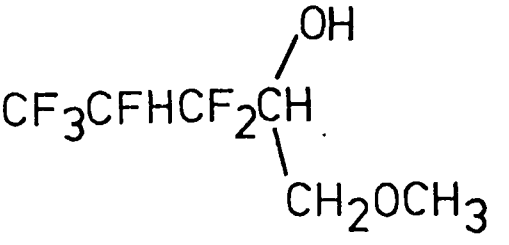


NK2201 5 M.Wt. 226 No.42.



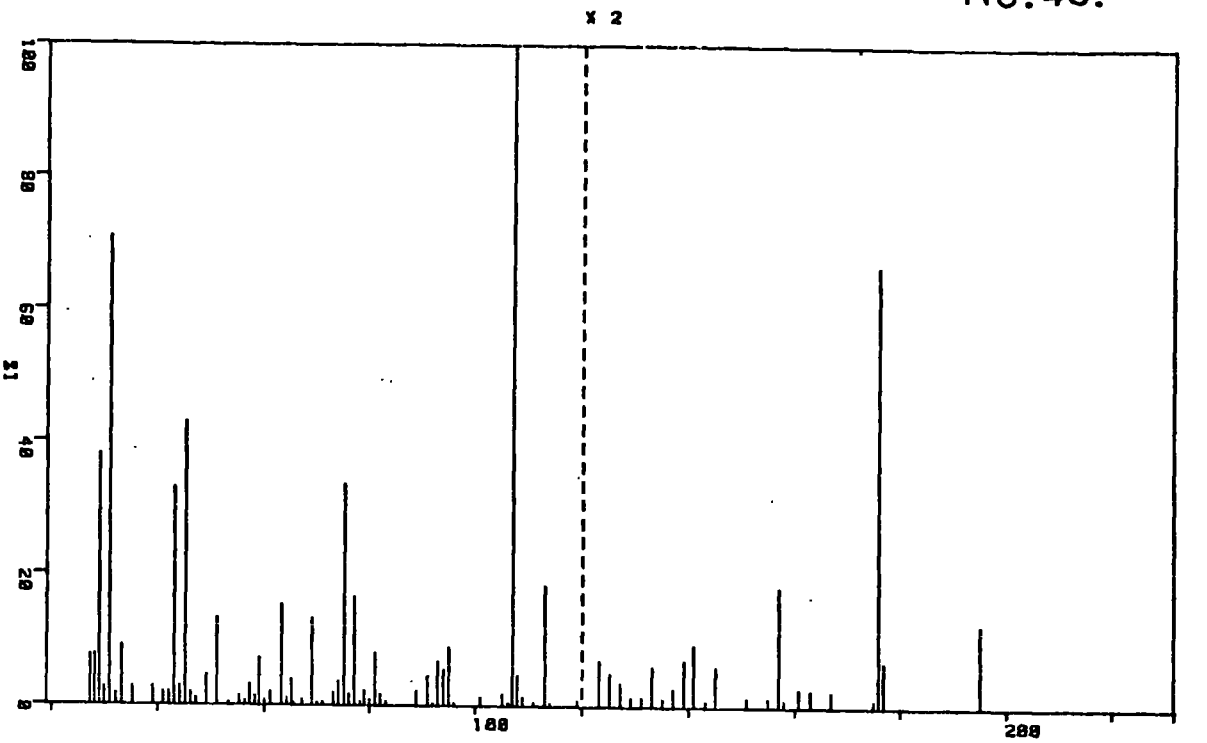
NK2201. 5 22-AUG-71

PEAK NO.	MASS	% INT BASE
1	20.76	8.56
2	21.74	1.38
3	22.68	4.66
4	23.56	9.81
7	26.98	3.12
9	29.38	1.50
13	31.21	2.55
14	32.21	1.18
15	33.16	10.50
16	34.10	24.86
17	35.08	100.00
18	36.02	2.68
22	40.45	2.96
24	45.49	1.54
26	47.38	0.97
27	48.28	1.46
30	51.11	2.88
31	52.13	2.39
32	53.09	1.87
36	57.96	3.20
38	61.85	0.97
40	63.86	7.18
43	65.81	1.66
51	81.65	1.05
56	95.63	1.22
62	140.44	4.58
66	164.49	1.01
71	206.76	4.54
72	207.76	1.42
73	226.81	5.07
74	230.89	0.53



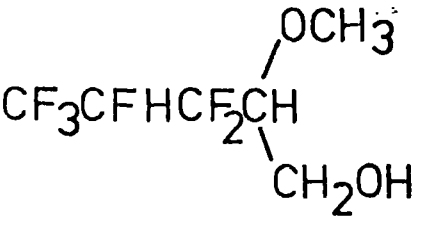
Diastereomer A

NK2203 3 M.Wt.226 No.43.

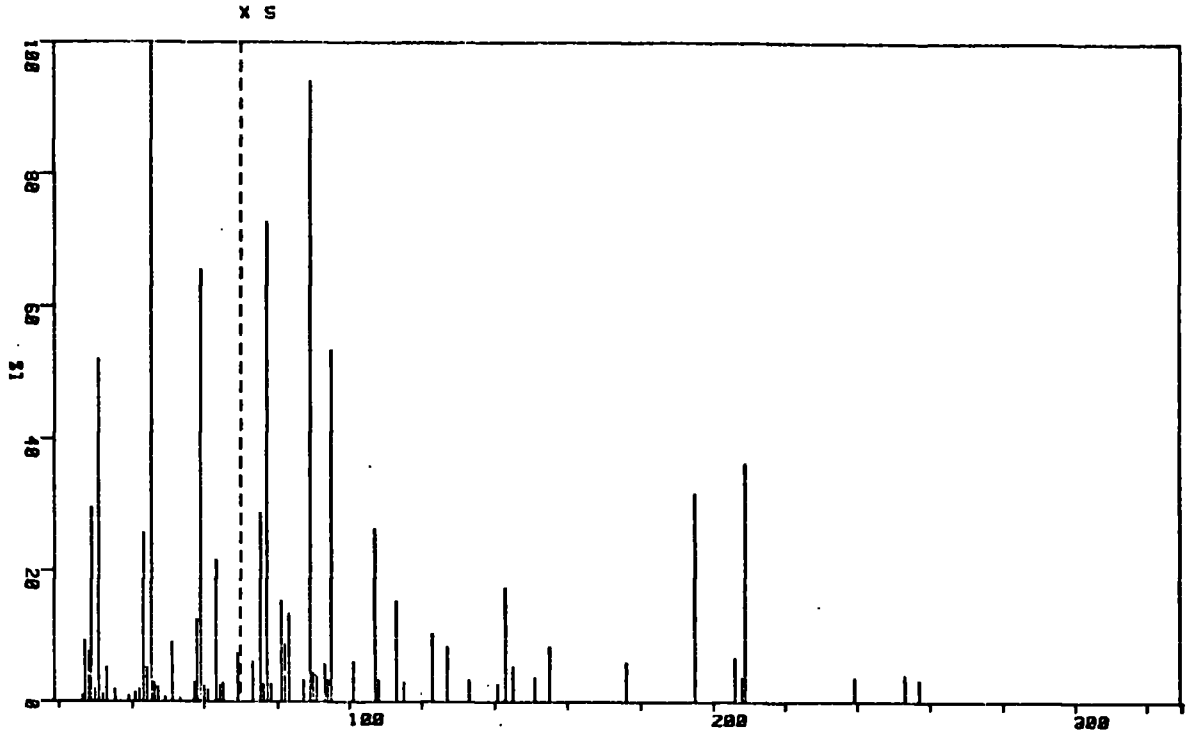


NK2203. 3 11-SEP-71

PEAK NO.	MASS	% INT BASE			
1	27.17	7.61	40	74.08	3.78
2	28.05	7.70	41	75.10	33.66
3	28.93	38.24	43	77.05	16.53
4	29.77	2.80	45	78.95	2.43
5	30.84	70.82	47	80.94	8.12
7	33.07	9.10	50	88.98	2.33
8	35.16	2.85	51	90.93	4.62
9	38.96	2.89	53	93.01	6.77
10	40.94	2.19	54	94.05	5.56
11	42.02	2.19	55	95.04	8.87
12	43.08	33.19	61	107.01	100.00
13	44.13	3.13	63	107.98	4.72
14	45.14	42.90	66	112.98	18.39
15	46.14	1.96	69	122.99	3.50
17	48.96	4.62	70	125.02	2.47
18	50.93	13.45	74	132.97	3.13
22	57.09	3.31	77	138.96	3.55
24	58.97	7.33	78	140.91	4.67
26	60.94	2.24	80	145.00	3.00
27	63.06	15.31	83	156.98	9.01
29	65.09	4.06	89	175.99	33.33
36	68.96	13.31	90	177.00	3.45
39	73.04	2.01	91	194.98	6.30



NK2204 5 M.Wt. 226 No.44.

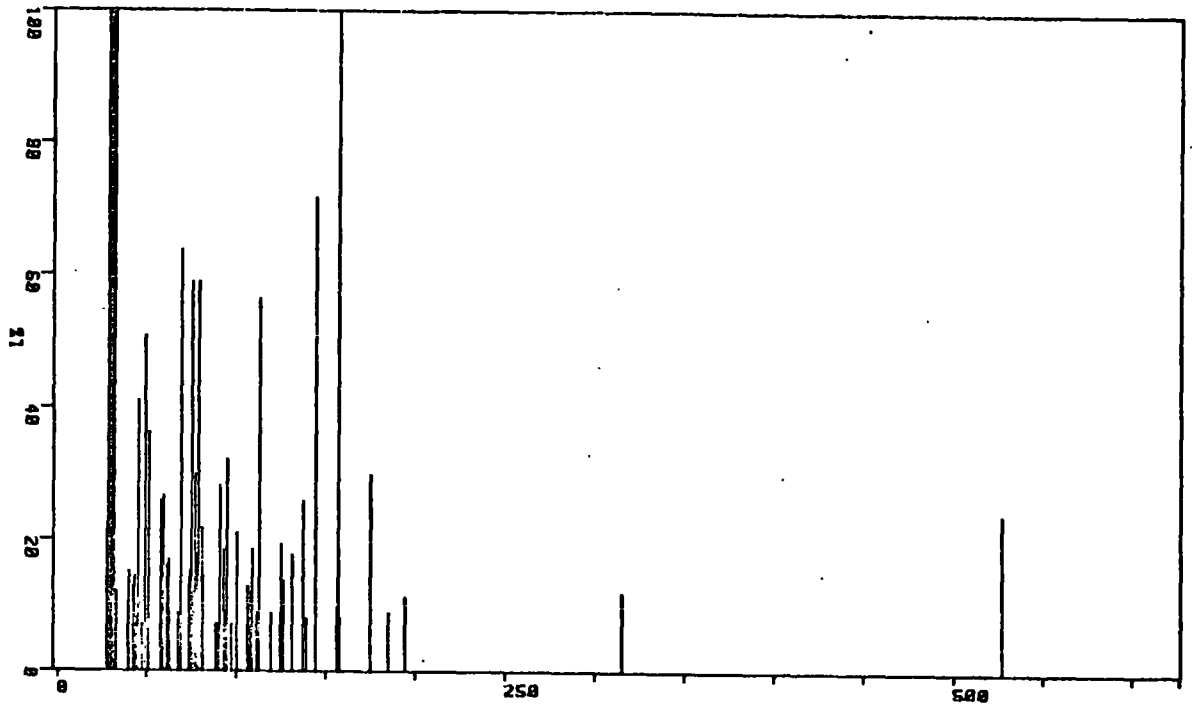


NK2204. 5 03-OCT-79

PEAK NO.	MASS	% INT BASE			
1	26.21	0.90			
2	27.15	9.36	30	73.04	1.24
3	28.05	7.66	31	75.08	5.76
4	28.92	29.67	33	77.04	14.54
5	29.77	1.96	35	80.94	3.08
6	30.83	52.00	36	81.98	1.77
7	31.94	1.24	37	83.01	2.69
8	33.04	5.24	39	88.97	18.86
9	35.14	1.03	42	93.01	1.18
11	40.93	1.51	44	95.01	10.67
12	41.99	1.90	45	100.93	1.24
13	43.06	25.61	46	107.02	5.30
14	44.11	5.24	48	112.99	3.08
15	45.13	100.00	50	122.99	2.10
16	46.12	2.88	51	127.01	1.70
17	47.08	2.29	54	142.97	3.47
19	50.91	8.97	55	145.00	1.11
21	57.07	2.95	57	154.98	1.70
22	58.03	12.57	58	176.01	1.24
23	58.98	65.49	59	194.96	6.35
24	59.90	2.49	60	205.96	1.38
25	60.93	1.90	61	207.94	0.79
26	63.04	21.55	62	208.94	7.27
27	64.06	2.55	63	238.94	0.79
28	65.08	2.88	64	252.97	0.85
29	68.95	7.47	65	256.97	0.72

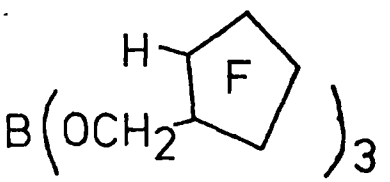
$CF_3CFHCF_2CH_2OCH_2CH_2OH$

NK194 S M.Wt. 740 No.45.

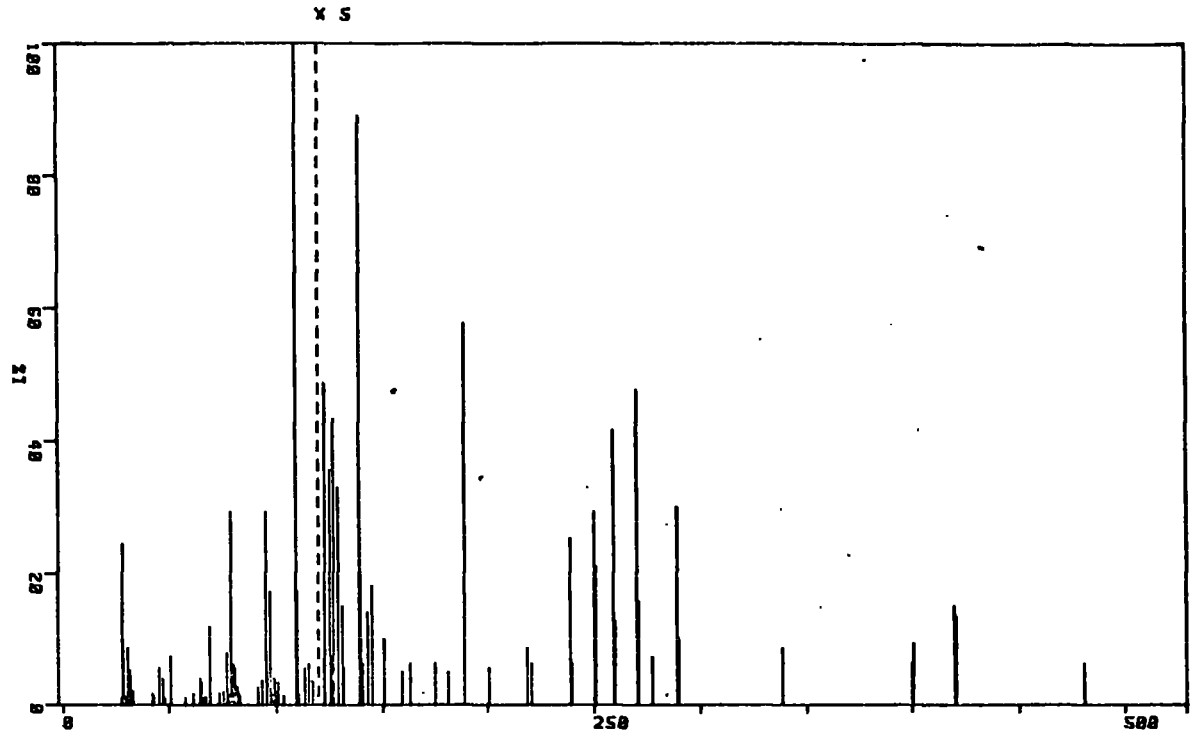


NK194 S 24 OCT-79

PEAK NO.	MASS	% INT BASE
1	27.24	1.64
2	28.12	44.96
3	28.77	15.35
4	29.63	2.69
5	30.72	100.00
6	32.02	9.45
7	33.13	0.82
8	39.00	0.71
9	39.83	1.04
10	42.05	0.88
11	43.12	0.99
12	44.15	0.55
13	45.18	2.80
14	47.08	0.49
15	48.99	3.45
16	50.96	2.47
17	57.11	1.75
18	59.03	1.81
19	61.00	1.10
20	62.05	1.15
21	63.08	0.60
22	67.09	0.60
23	68.99	4.33
24	73.11	0.88
25	74.17	1.04
26	75.11	4.00
27	76.10	0.82
28	77.09	2.03
29	78.06	1.21
30	79.01	4.00
31	81.01	1.48
32	82.04	0.99
33	88.05	0.49
34	89.00	0.49
35	89.95	0.49
36	91.01	1.92
37	93.04	1.26
38	94.07	0.60
39	95.08	2.19
40	97.09	0.49
41	99.94	1.43
42	106.06	0.88
43	107.04	0.88
44	108.02	0.82
45	108.13	0.49
46	109.02	1.26
47	110.98	0.60
48	113.04	3.84
49	118.98	0.60
50	124.04	0.60
51	125.04	1.32
52	126.07	0.93
53	130.97	1.21
54	137.04	1.75
55	139.00	0.55
56	144.03	4.88
57	156.02	0.66
58	157.03	6.00
59	158.03	0.55
60	175.00	2.03
61	185.02	0.60
62	194.03	0.77
63	314.96	0.82
64	526.32	1.64

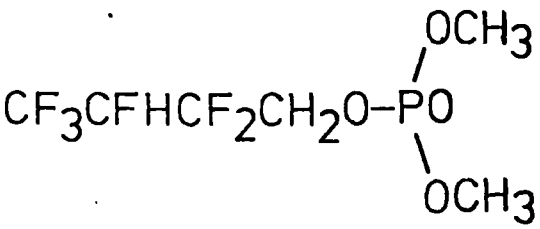


NK2121 4 M.Wt. 290 No.46.

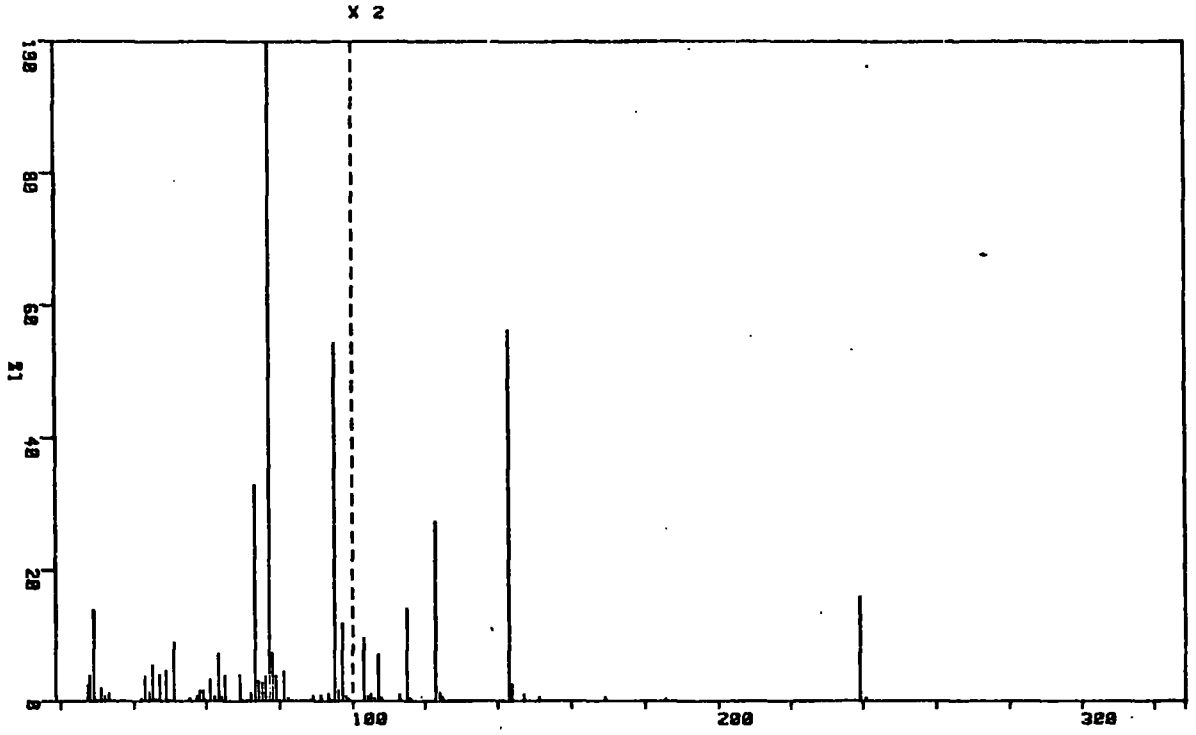


NK2121. 4 06-SEP-79

PEAK NO.	MASS	% INT BASE			
2	20.13	24.41	44	115.03	6.25
3	29.00	0.37	45	117.01	3.66
5	30.93	0.73	47	123.01	9.79
6	32.02	5.31	48	125.02	7.19
7	33.13	2.24	50	127.01	8.73
10	45.17	5.66	51	128.96	6.60
11	47.07	4.13	52	130.95	3.07
13	50.94	7.43	54	138.95	17.81
16	64.10	4.01	55	139.94	4.01
17	65.08	3.42	57	142.98	2.83
20	68.97	11.91	58	144.99	3.66
22	75.07	2.00	59	150.94	2.00
23	77.05	7.90	64	180.90	11.56
25	78.94	29.36	68	238.89	5.07
26	79.89	6.25	70	249.83	5.90
27	80.92	3.54	71	250.93	4.25
28	81.98	2.71	72	258.92	0.37
30	90.94	2.71	73	259.93	2.59
31	92.99	3.77	74	269.90	9.55
32	95.01	29.36	75	270.95	3.18
33	96.01	4.83	77	280.93	6.01
34	96.98	17.22	78	289.91	2.00
36	98.93	4.01	80	399.80	1.30
37	99.89	2.00	81	400.81	1.89
38	100.91	3.42	82	419.79	3.07
40	108.93	100.00	83	420.82	2.71
41	109.89	17.33	84	480.73	1.30
43	113.00	5.54			

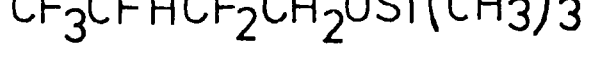


NK235 4 M.Wt. 256 No.47.

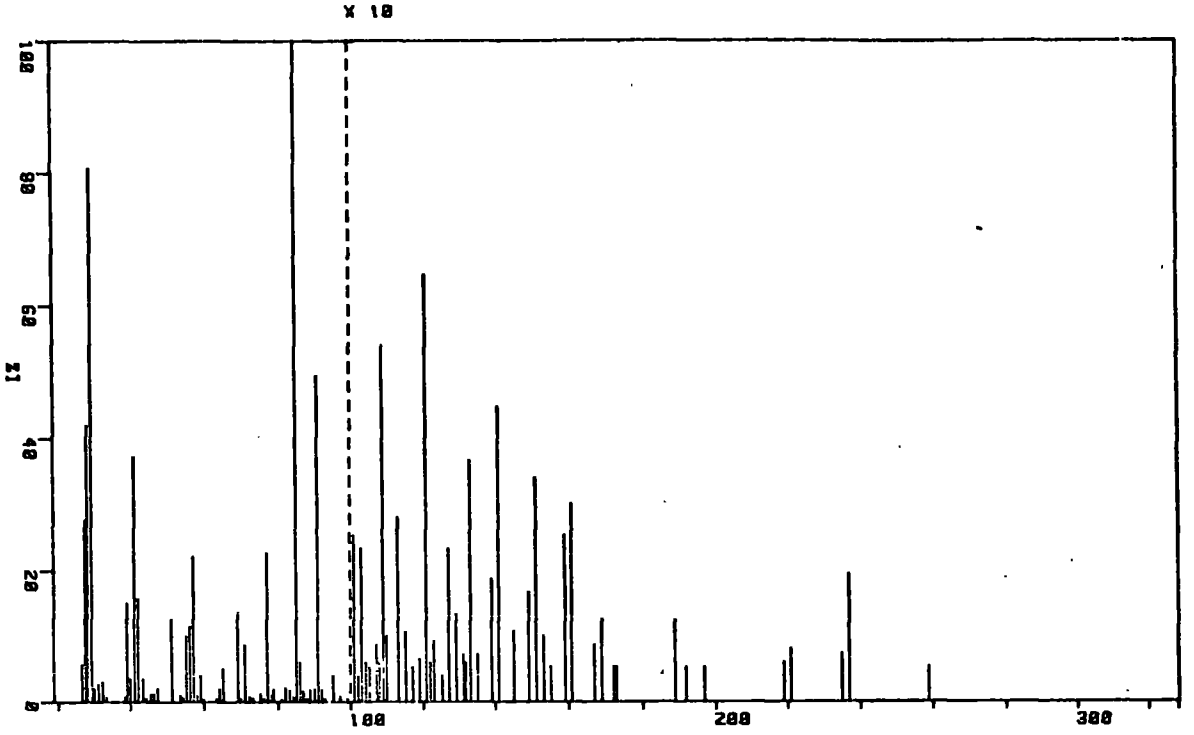


NK235 4 24-OCT-79

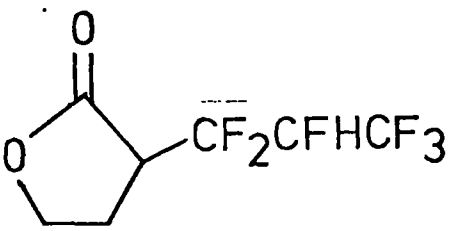
PEAK NO.	MASS	% INT BASE
1	27.24	2.49
2	28.12	3.92
3	28.99	13.83
5	30.98	2.12
7	33.13	1.27
9	43.12	3.82
10	44.16	1.49
11	45.17	5.55
13	47.10	4.16
15	48.98	4.79
17	50.97	8.95
20	58.09	1.67
21	59.03	1.79
23	61.00	3.49
25	63.11	7.37
27	65.13	4.00
28	68.96	4.19
31	72.04	1.37
32	73.09	32.86
33	74.10	3.31
34	75.07	2.08
35	76.05	3.91
36	77.03	100.00
37	78.01	7.40
38	78.95	4.00
40	80.93	4.64
46	93.00	1.24
48	95.04	54.31
49	96.02	1.82
50	97.03	11.80
53	103.06	4.82
57	107.03	3.61
60	115.03	7.07
62	123.01	13.68
65	143.01	28.19
66	144.02	1.30
68	151.02	0.39
69	168.98	0.33
70	239.09	7.98
71	240.96	0.39



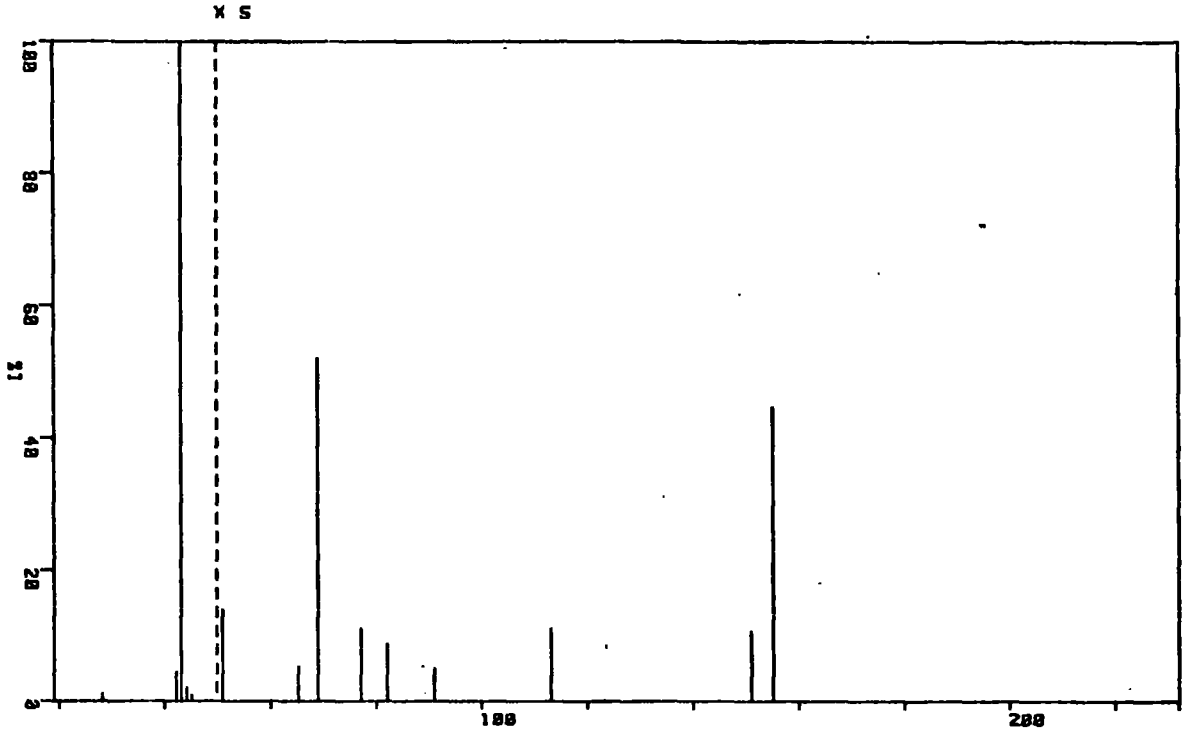
NK231 5 M.Wt. 236 No.48.



NK231	5	06-SEP-71			
PEAK NO.	MASS	% INT BASE			
1	26.30	5.76			
2	27.24	27.73	42	81.93	2.24
3	28.13	42.05	45	84.99	100.00
4	29.00	80.73	46	85.99	6.07
5	29.84	2.09	50	89.85	2.19
6	30.91	2.75	51	90.89	49.44
7	32.00	3.01	52	91.96	1.99
10	38.98	15.04	54	94.98	4.13
11	39.87	3.72	57	100.89	2.55
12	40.96	37.36	59	102.98	2.40
13	42.04	15.75	64	108.89	5.40
14	43.09	3.62	66	112.96	2.80
18	47.09	2.19	70	120.92	6.52
19	50.91	12.54	74	126.96	2.34
22	55.09	10.04	78	132.93	3.72
23	56.09	11.57	81	140.89	4.49
24	57.07	22.17	84	150.87	3.41
26	58.96	4.03	87	158.90	2.60
29	64.06	2.04	88	160.86	3.01
30	65.07	5.20	96	218.87	0.61
31	68.93	13.61	97	220.88	0.87
33	70.93	8.77	98	234.89	0.76
38	77.00	22.48	99	236.87	1.99
40	78.90	2.09	100	250.81	0.56



NK192 5 M.Wt.194 No.49.



NK192 5 24-OCT-79

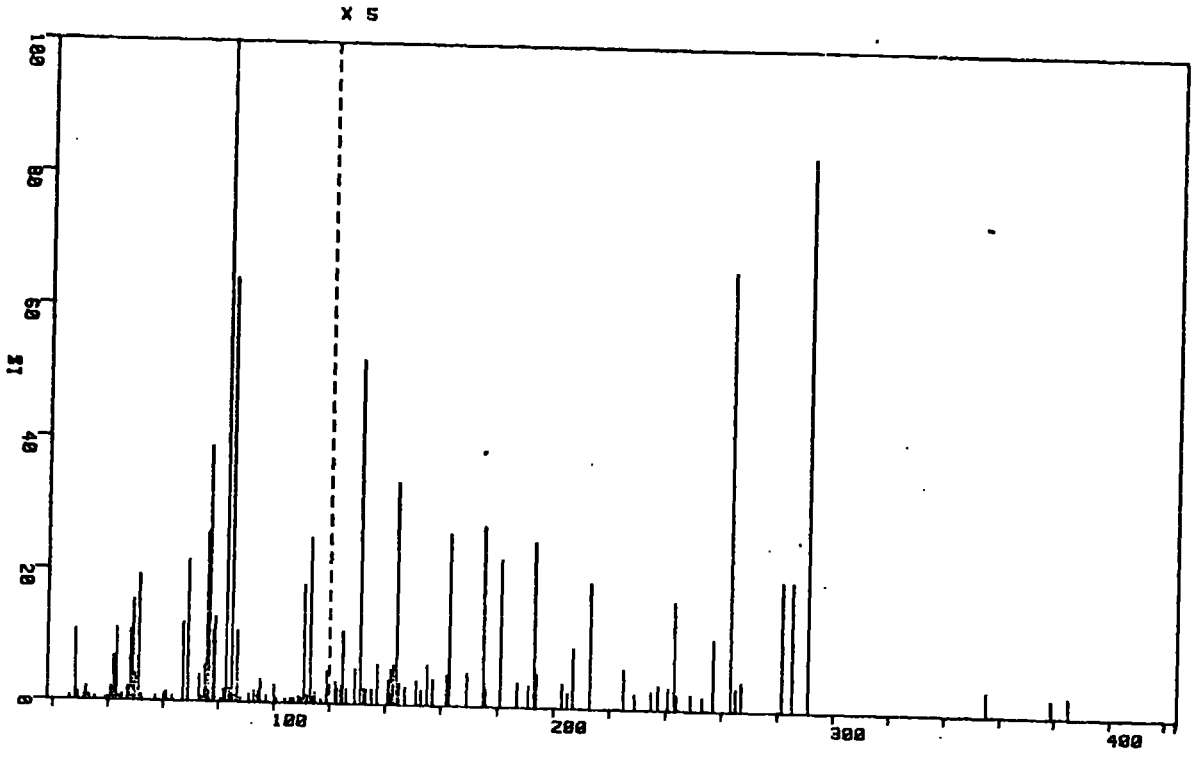
PEAK NO.	MASS	X INT BASE
1	28.12	1.27
2	42.06	4.57
3	43.13	100.00
4	44.17	2.21
5	45.18	1.05
6	50.97	2.85
7	65.15	1.09
8	69.02	10.45
9	77.12	2.25
10	83.07	1.80
11	91.02	1.01
12	113.09	2.21
13	151.08	2.13
14	155.14	8.95

$CF_3CFHCF_2COCH_3$

NK1321 5

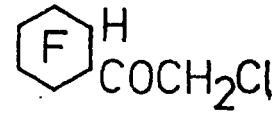
M.Wt. 340.5

No.50.



NK1321. 5 02-NOV-79

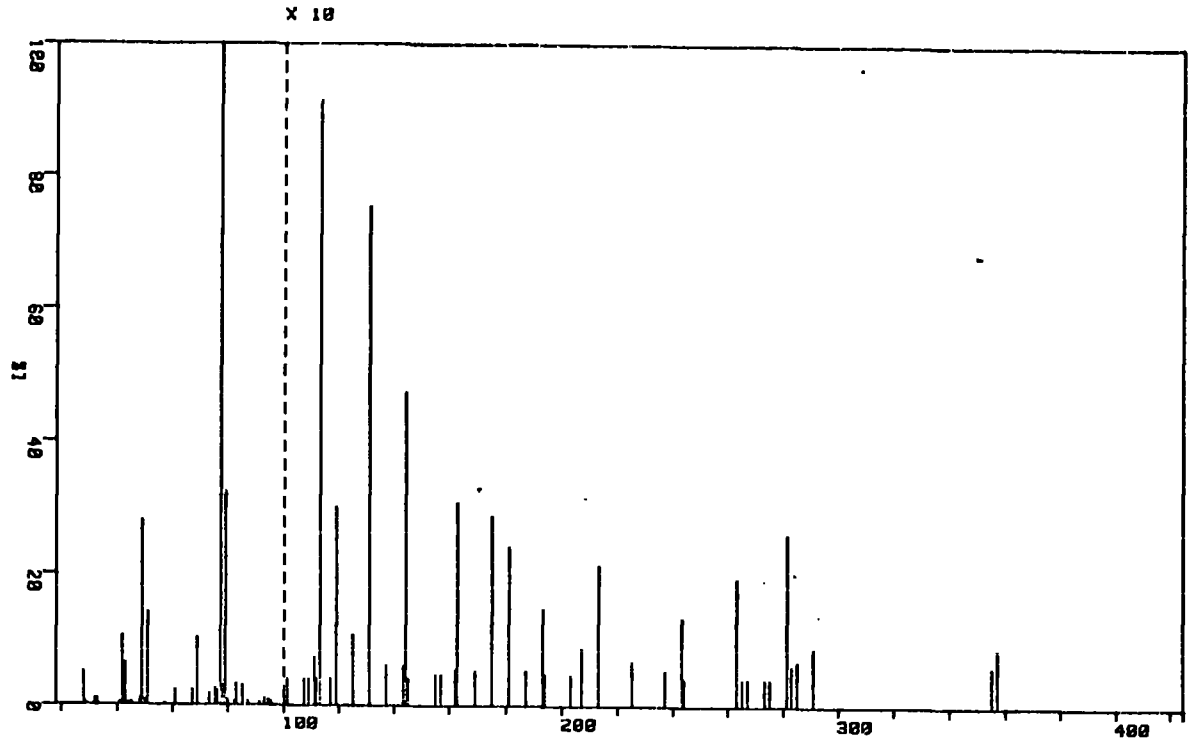
PEAK NO.	MASS	% INT BASE			
2	28.12	10.68	48	99.96	2.74
5	32.01	2.21	55	110.97	17.95
10	40.97	2.16	57	113.06	25.11
11	42.06	6.84	61	119.02	4.89
12	43.13	11.11	65	125.09	2.21
15	47.09	2.26	68	131.04	10.42
16	48.04	10.79	76	144.10	6.79
17	48.97	15.42	84	163.09	5.21
18	49.88	4.05	86	175.09	5.53
19	50.97	19.11	88	181.04	4.47
26	67.09	11.95	91	193.09	5.05
27	69.02	21.42	96	213.06	3.84
28	73.15	4.11	102	243.08	3.32
30	75.14	5.47	106	257.09	2.16
31	76.07	25.74	107	263.15	13.32
32	77.06	38.68	110	281.49	3.95
33	78.04	10.74	111	285.12	3.95
34	78.98	12.89	112	291.03	16.74
37	81.02	100.00	113	355.14	0.74
38	84.04	2.05	114	378.88	0.58
39	85.04	64.11	115	384.99	0.63
41	87.02	10.84	116	776.16	0.63
46	95.07	3.53			

cis 

NK1322 S

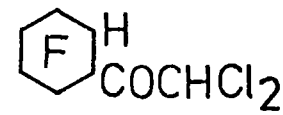
M.Wt. 375

No.51.

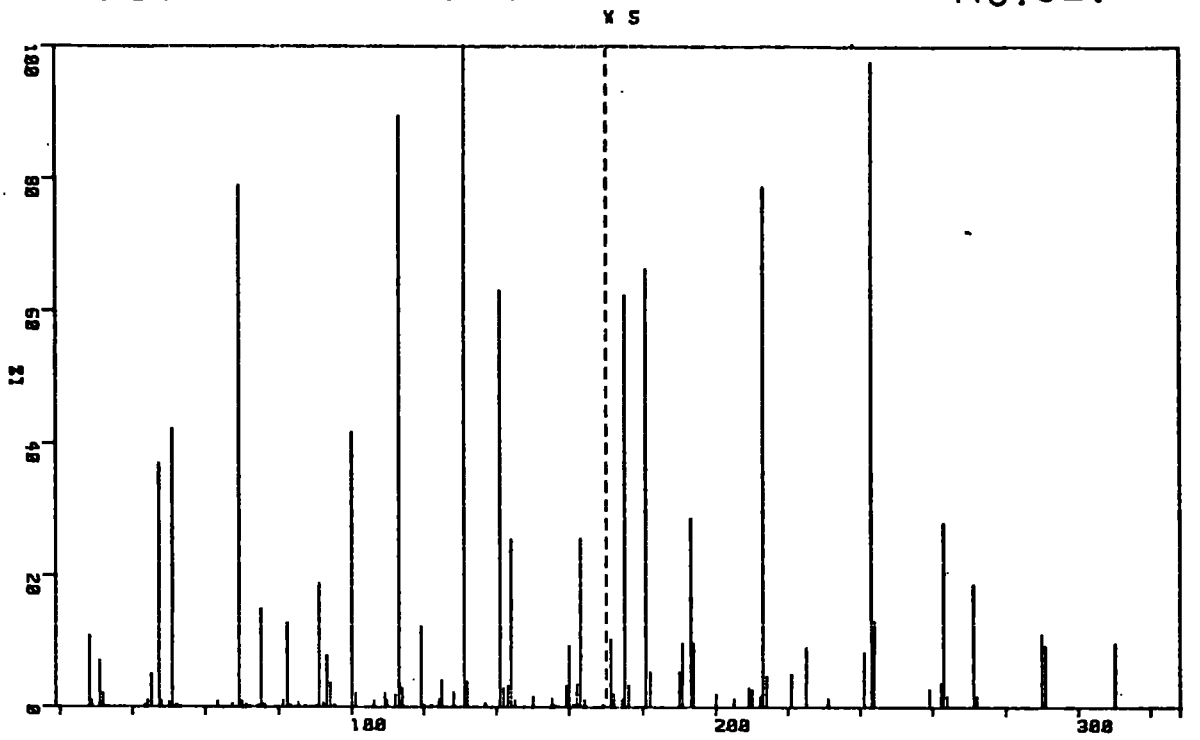


NK1322. 5 02-NOV-79

PEAK NO.	MASS	% INT BASE
1	28.12	5.06
6	42.06	10.58
7	43.13	6.45
11	48.98	27.99
13	50.96	14.02
15	61.01	2.46
16	67.08	2.41
17	69.02	10.40
19	75.14	2.65
20	76.10	2.23
21	77.09	100.00
22	78.07	3.11
23	79.02	32.45
26	83.05	3.30
27	85.09	3.06
39	113.10	9.15
41	119.02	3.02
43	131.02	7.57
46	144.10	4.78
51	163.06	3.11
53	175.09	2.88
54	181.04	2.46
60	213.07	2.14
70	281.35	2.65
74	355.08	0.60
75	357.05	0.80

cis 

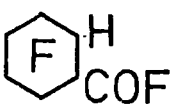
NK202 S M.Wt. 310 No.52.



NK202 5 26-SEP-79

PEAK NO.	MASS	% INT BASE			
1	28.05	10.86	56	144.07	25.52
2	28.93	1.03	57	145.08	1.21
3	30.84	7.10	58	149.99	1.68
4	31.95	2.24	59	155.08	1.34
7	44.10	1.24	61	159.02	3.33
8	45.12	5.14	62	160.00	9.37
9	47.08	37.04	64	162.05	3.49
12	50.94	42.33	65	163.08	25.61
15	63.07	1.03	66	164.10	1.24
17	68.98	78.93	68	171.06	2.09
22	75.10	14.91	71	175.12	12.48
25	80.97	1.15	73	181.02	13.29
26	82.02	12.82	74	182.05	1.09
31	90.98	10.86	75	190.00	1.12
33	93.05	7.87	76	191.02	1.96
34	94.07	3.67	77	193.05	5.79
36	99.94	41.77	78	194.07	1.99
37	100.99	2.21	84	213.07	15.75
39	108.98	2.21	86	221.05	1.06
41	112.02	1.93	87	225.09	1.81
42	113.05	89.51	89	241.05	1.68
43	114.06	2.93	90	243.06	19.58
44	119.00	12.39	91	244.07	2.61
47	124.07	1.28	94	263.08	5.63
48	125.09	4.01	96	271.09	3.77
49	128.04	2.27	98	290.06	2.24
50	131.00	100.00	99	291.08	1.87
51	132.04	3.92	100	310.12	1.96
53	141.01	62.99			
54	142.04	2.96			
55	143.06	3.30			

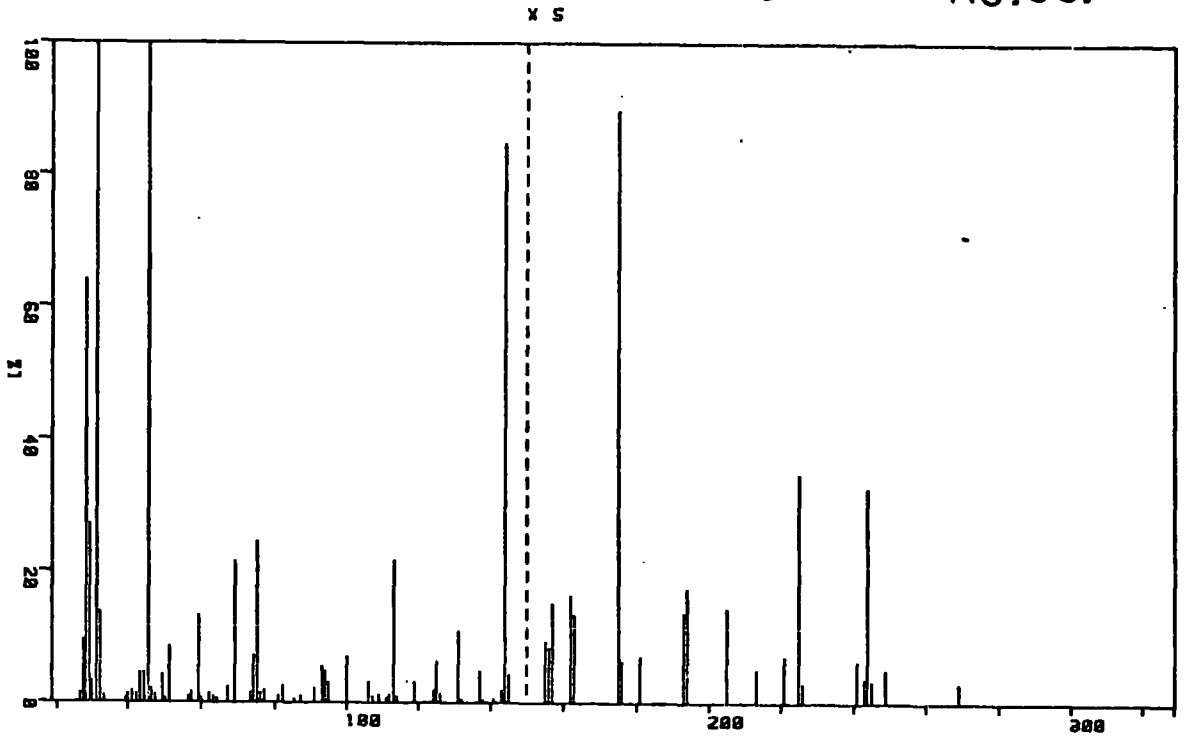
cis



NK204 S

M.Wt. 308

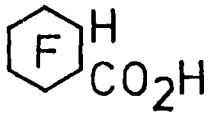
No.53.



NK204 S 24 OCT-79

PEAK NO.	MASS	% INT BASE			
2	27.24	7.53			
3	28.12	50.67	53	125.03	4.97
4	29.00	21.41	55	130.96	8.65
5	29.83	2.67	57	137.01	3.84
6	30.92	100.00	61	144.01	67.06
7	32.01	10.84	62	145.03	3.47
13	43.13	3.63	65	157.00	2.40
14	44.14	3.63	66	161.97	2.62
15	45.15	79.23	68	175.00	14.26
18	48.99	3.42	72	194.00	2.78
20	50.96	6.78	73	204.96	2.30
23	59.04	10.46	74	212.55	0.80
29	68.99	16.98	75	220.91	1.12
31	74.16	5.71	76	224.99	5.50
32	75.07	19.43	77	226.05	0.48
40	93.00	4.48	78	240.91	1.01
41	94.02	3.84	79	242.94	0.59
42	95.05	2.51	80	243.93	5.18
43	99.90	5.50	81	244.94	0.53
44	106.05	2.62	82	248.72	0.80
49	113.03	17.08	83	260.86	0.48
51	118.96	2.62			

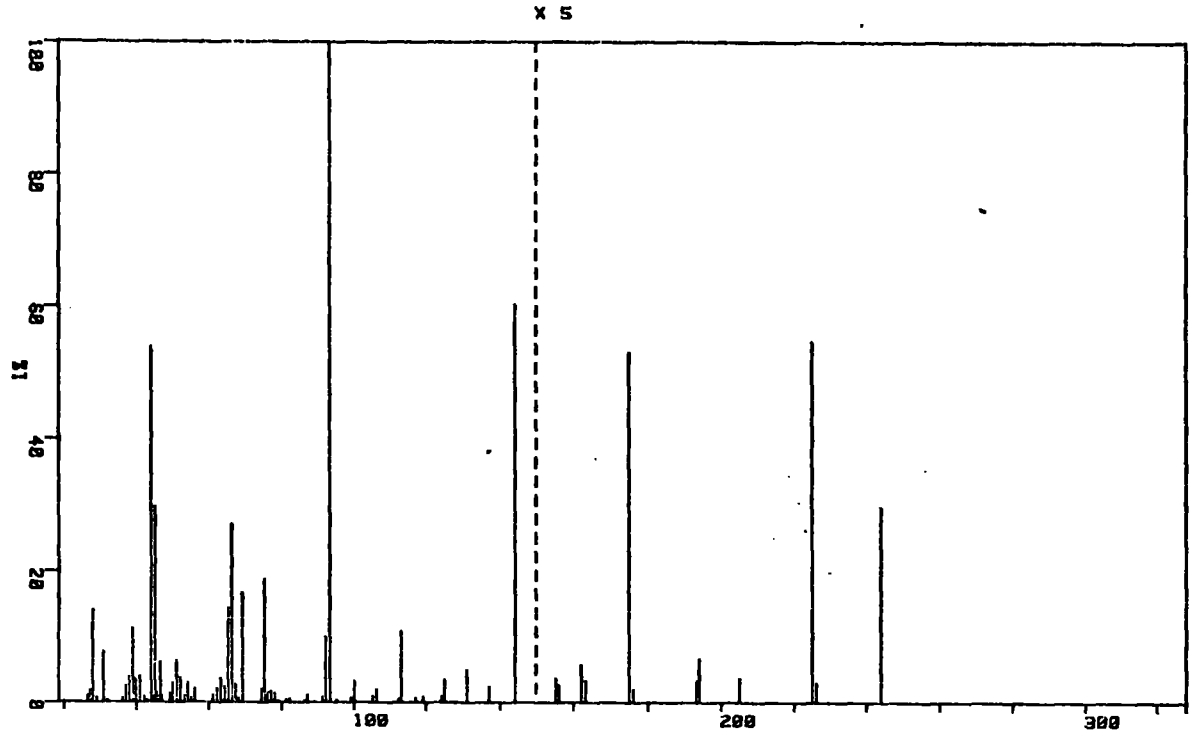
cis



NK204B 7

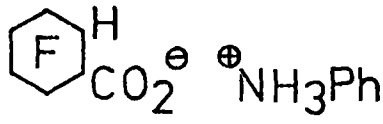
M.Wt. 401

No.54.

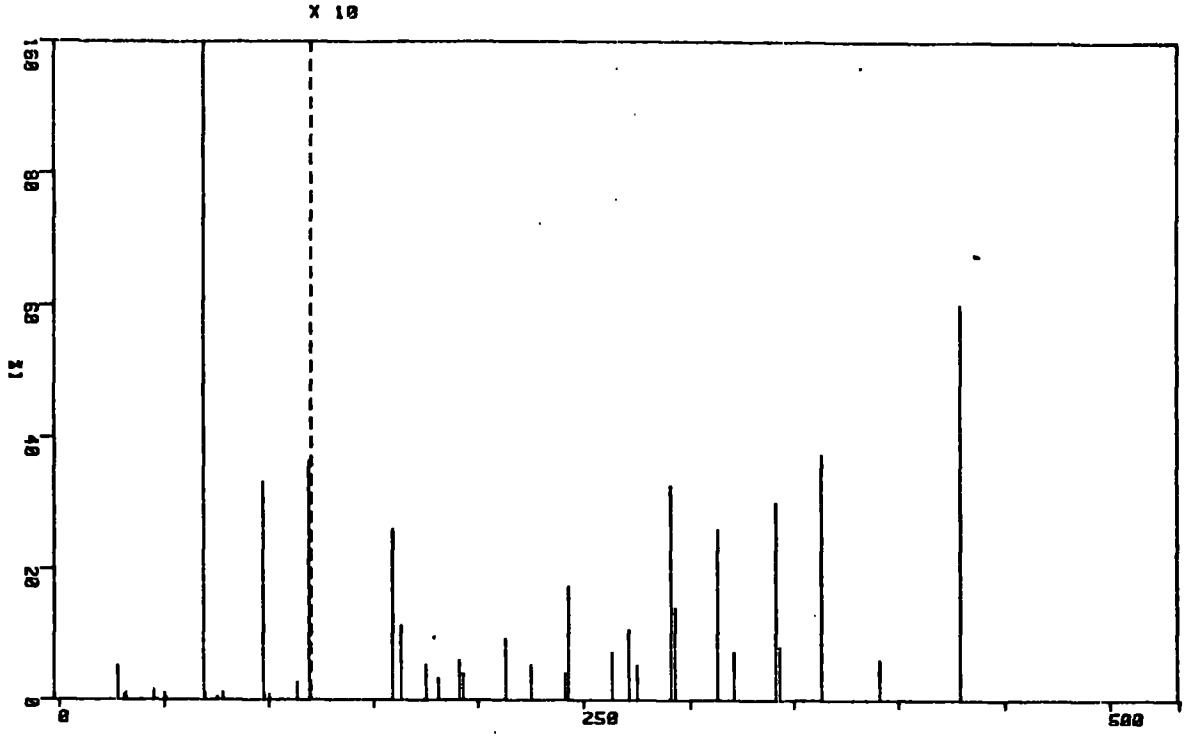


NK204B. 7 02-NOV-79

PEAK NO.	MASS	% INT BASE			
3	27.99	14.03			
5	30.72	7.69	36	67.08	2.85
8	36.97	2.65	38	68.95	16.61
9	37.93	3.95	39	74.08	1.99
10	38.86	11.31	40	75.07	18.67
11	39.79	3.61	50	92.09	10.01
12	40.84	4.05	51	93.21	100.00
15	44.00	53.81	54	99.95	3.32
17	45.03	29.68	58	113.02	10.78
20	46.57	6.20	62	125.06	3.51
23	49.90	2.95	63	130.98	4.97
24	50.96	6.40	64	137.06	2.42
25	52.03	3.85	65	144.06	60.38
27	54.11	2.98	70	175.02	10.64
29	56.08	2.09	74	205.10	0.80
31	62.01	2.16	75	225.03	10.94
32	63.05	3.71	76	226.14	0.66
33	64.08	2.49	77	243.98	5.97
34	65.09	14.32			
35	66.09	27.02			

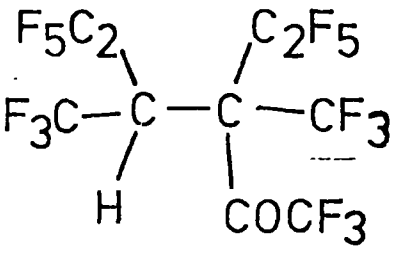
cis 

NK2071 5 M.Wt. 498 No.55.

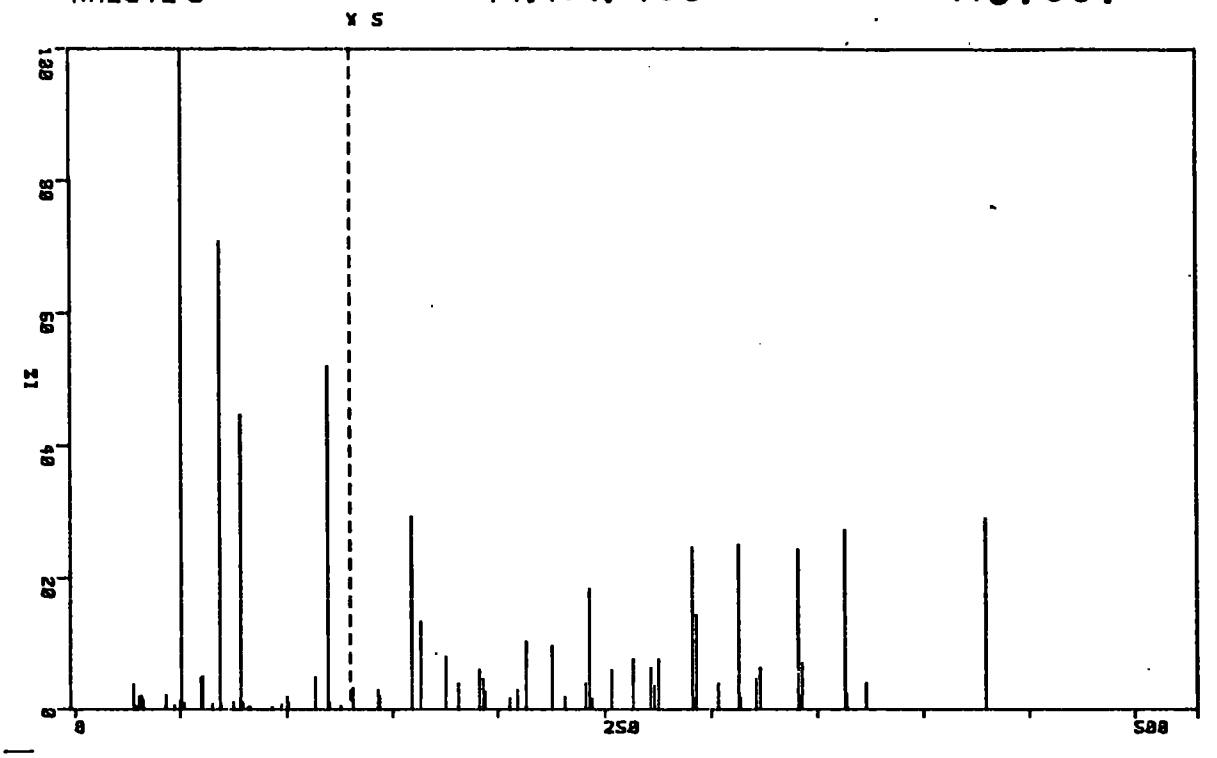


NK2071. 5 02-OCT-79

PEAK NO.	MASS	% INT BASE
1	28.05	5.21
2	30.83	0.84
3	31.94	1.14
4	45.15	1.59
5	49.87	1.19
6	50.74	0.45
7	68.97	100.00
8	69.91	1.04
9	75.09	0.50
10	78.02	1.24
11	97.02	33.22
12	98.01	0.74
13	99.92	0.89
14	113.03	2.68
15	118.96	36.40
16	119.94	0.74
17	150.96	2.63
18	163.01	1.14
19	175.03	0.55
20	180.97	0.40
21	190.97	0.65
22	193.01	0.45
23	213.02	0.94
24	225.02	0.55
25	240.96	0.45
26	242.98	1.74
27	263.02	0.74
28	270.97	1.09
29	275.02	0.55
30	290.96	3.20
31	292.96	1.44
32	312.97	2.63
33	320.98	0.74
34	340.98	3.03
35	342.97	0.84
36	362.94	3.77
37	390.95	0.65
38	429.05	6.06

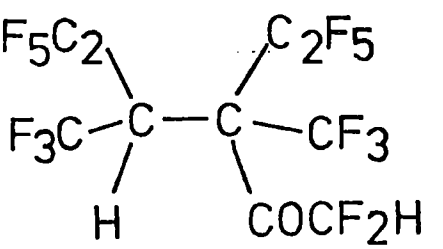


NK2872 5 M.Wt. 480 No. 56.

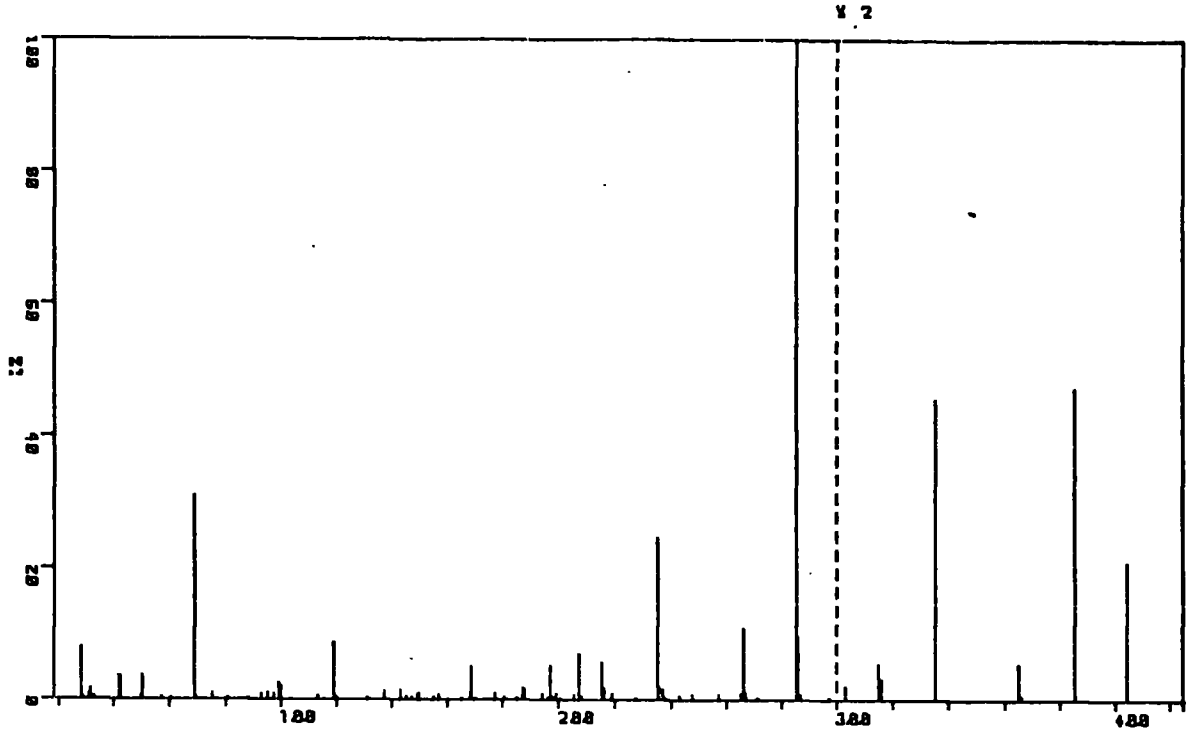


NK2072. 5 26-SEP-79

PEAK NO.	MASS	% INT BASE			
1	28.05	3.83			
4	30.04	1.97	38	191.03	1.23
5	31.96	2.22	43	213.08	3.10
6	33.06	1.52	44	225.11	1.93
7	43.09	2.30	47	243.08	3.70
9	49.88	1.44	49	253.08	1.23
10	50.94	100.00	50	263.10	1.56
11	52.02	1.11	51	271.09	1.28
12	59.90	4.81	53	275.12	1.56
13	60.96	5.06	54	291.05	4.94
15	68.99	70.84	56	293.07	2.92
17	75.10	1.19	57	303.11	0.86
18	78.03	1.69	58	313.10	5.06
19	78.99	44.71	59	314.10	0.37
20	79.94	0.99	60	321.06	0.99
25	99.94	1.97	61	323.13	1.28
26	101.00	1.11	62	341.06	4.90
27	113.07	4.90	63	342.10	0.45
28	119.01	52.08	64	343.09	1.44
29	119.98	1.15	65	363.08	5.47
34	159.03	5.88	66	364.12	0.49
35	163.11	2.67	67	373.17	0.86
36	175.11	1.65	68	429.20	5.04

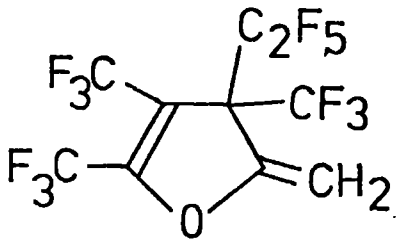


NK81 4 M.Wt. 404 No.57.



NK81 4 26-SEP-79

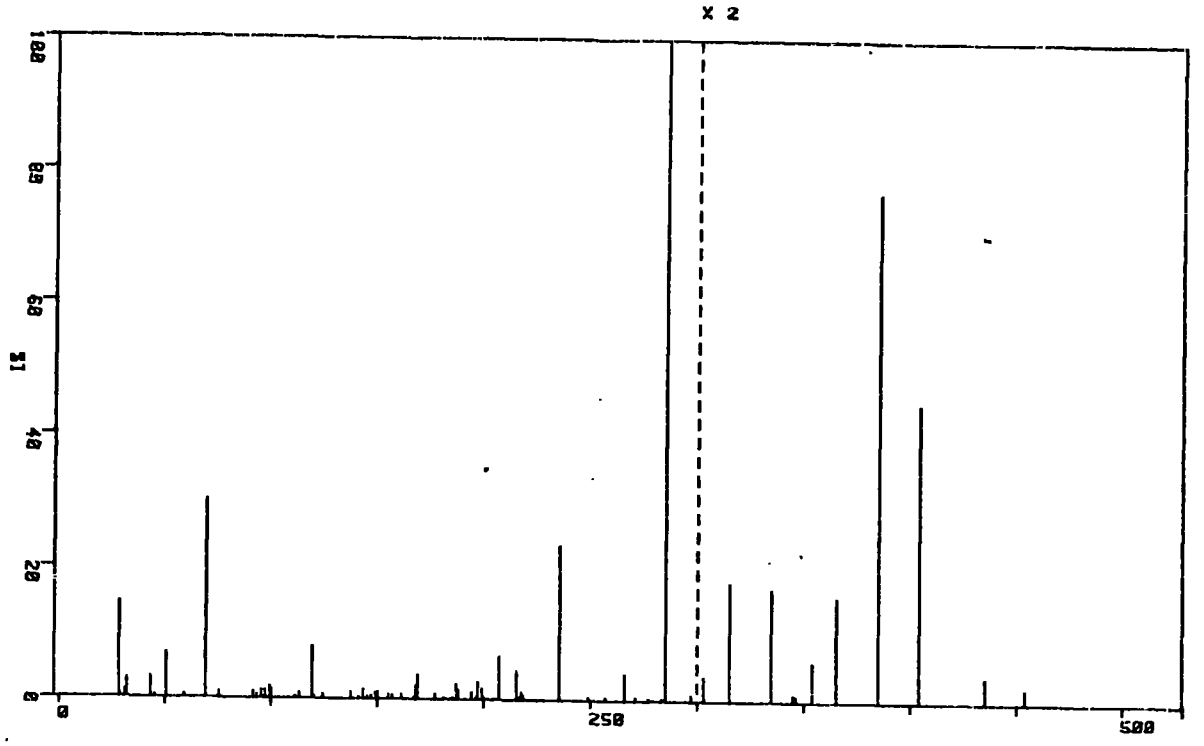
PEAK NO.	MASS	% INT BASE
1	28.05	7.99
5	31.94	1.62
7	42.02	3.66
8	43.09	3.43
10	50.94	3.69
13	68.99	31.06
15	75.10	1.17
19	95.09	1.24
21	99.00	2.60
22	99.95	2.22
24	119.03	8.78
27	137.08	1.36
28	143.07	1.51
32	150.02	1.09
36	160.10	1.02
37	169.09	5.05
39	177.13	1.13
42	187.08	1.92
43	188.09	1.62
46	197.06	5.24
48	199.06	1.09
51	207.08	6.94
53	215.10	5.77
54	216.12	1.81
58	235.08	24.69
59	236.10	2.00
60	237.06	1.62
65	265.09	1.02
66	266.09	10.89
67	267.09	1.21
69	285.06	100.00*
70	285.99	9.76*
73	303.11	1.09
74	315.10	2.79
75	316.10	1.62
76	335.15	22.80
77	365.04	2.79
78	366.04	0.34
79	385.23	23.67
80	404.14	10.52



NK138 5

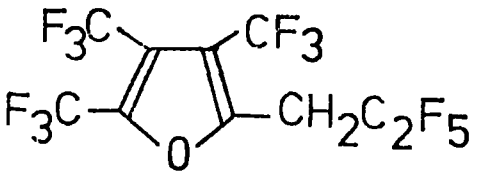
M.Wt. 404

No.58.

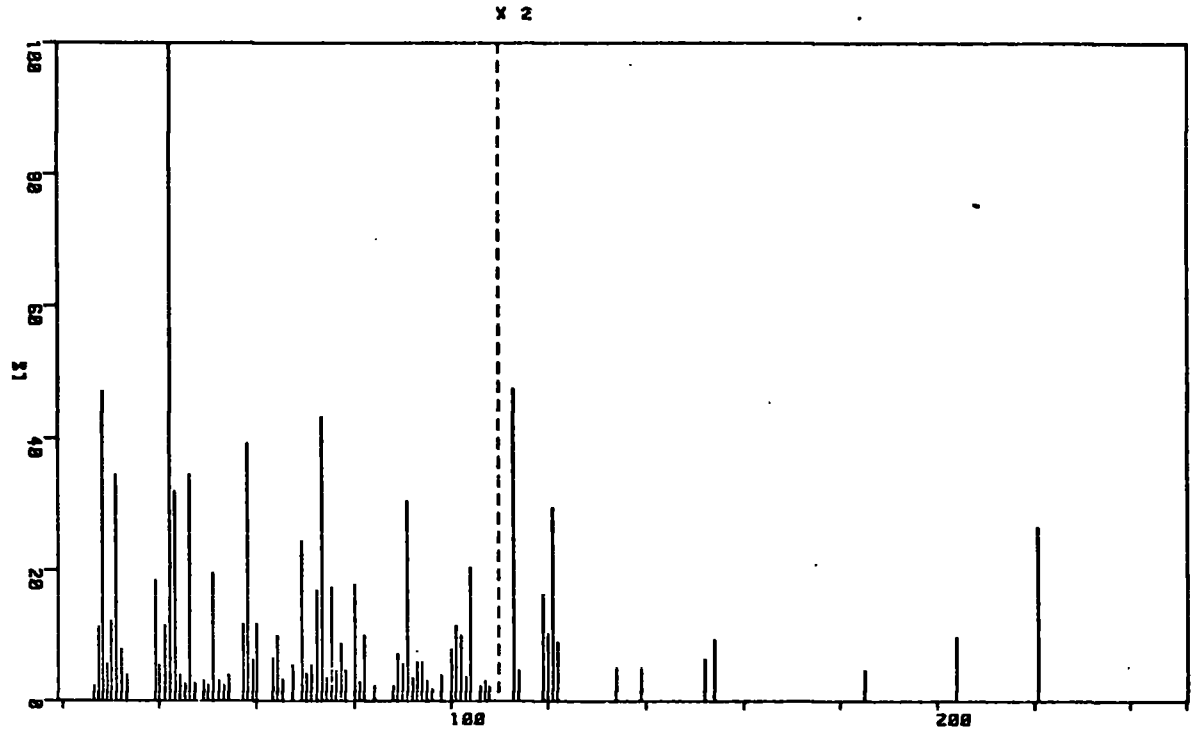


NK138 5 02-NOV-79

PEAK NO.	MASS	% INT BASE
1	28.12	14.56
4	32.02	2.90
5	43.13	3.25
7	50.97	6.74
9	69.02	30.00
19	119.08	7.87
33	168.11	2.02
34	169.05	3.69
38	187.09	2.36
42	197.11	2.71
46	207.12	6.64
47	215.25	4.43
51	235.32	23.46
54	265.97	4.13
58	285.05	100.00
60	302.99	1.92
61	315.15	8.95
62	334.82	8.51
63	344.92	0.54
64	345.59	0.49
65	346.07	0.39
66	346.49	0.44
67	354.03	2.95
68	365.07	7.92
69	384.95	38.42
70	403.97	22.58
71	434.96	1.97
72	464.85	1.10

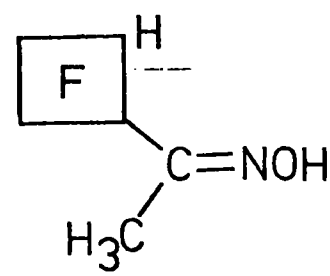


NK1551 5 M.Wt.221 No.59.



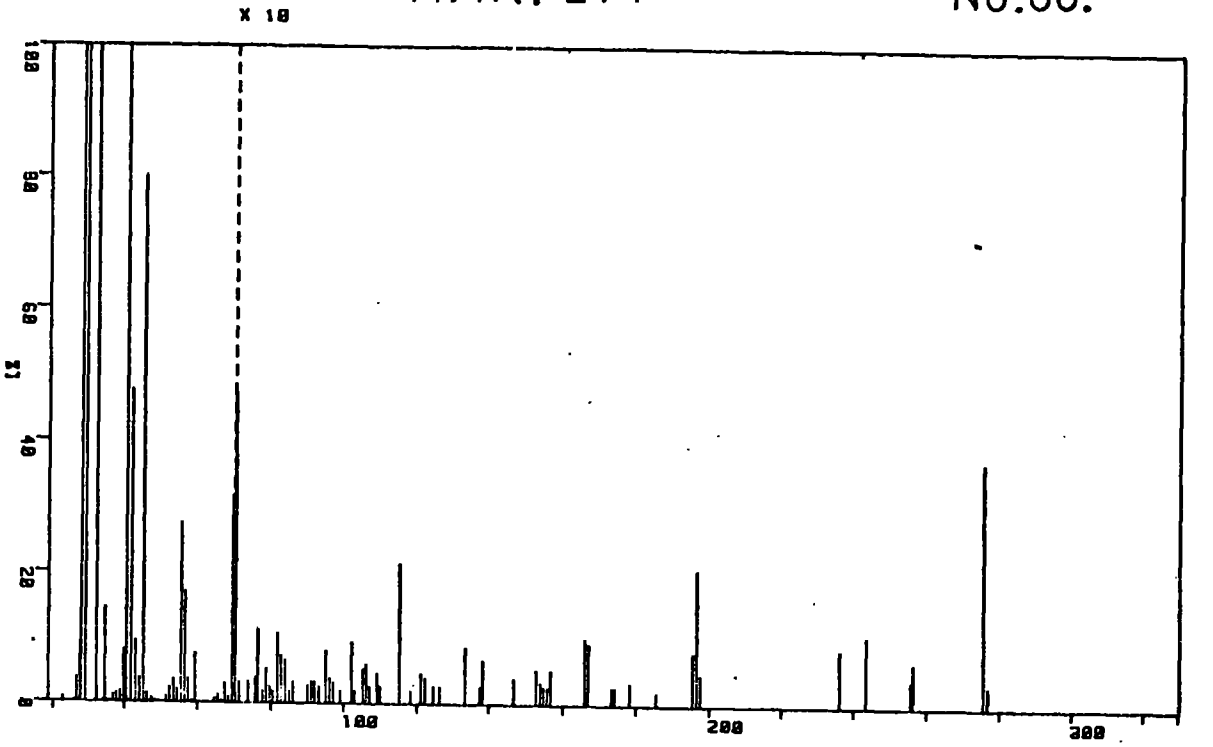
NK1551. 5 12-OCT-79

PEAK NO.	MASS	% INT BASE
2	27.17	11.35
3	28.05	47.11
4	28.93	5.78
5	29.77	12.21
6	30.83	34.48
7	31.94	7.92
8	33.06	4.07
9	38.96	18.42
10	39.85	5.57
11	40.93	11.56
12	42.03	100.00
13	43.07	31.91
14	44.11	4.07
16	46.12	34.48
20	50.93	19.49
23	54.11	4.07
24	57.07	11.78
25	58.03	39.19
26	58.98	6.42
27	59.88	11.78
28	63.04	6.64
29	64.08	10.06
31	67.05	5.57
32	68.96	24.41
33	69.91	4.28
34	70.97	5.57
35	72.02	16.92
36	73.06	43.25
38	75.06	17.34
39	76.06	4.71
40	77.05	8.78
41	78.00	4.71
42	79.90	17.77
44	81.99	10.06
47	88.95	7.28
48	89.91	5.78
49	90.94	30.41
51	92.99	6.00
52	94.02	6.00
55	97.97	4.07
56	99.90	7.92
57	100.95	11.56
58	102.00	10.06
59	103.02	3.85
60	104.03	20.34
64	112.99	23.77
66	118.96	8.14
67	119.91	5.14
68	120.96	14.78
69	121.99	4.50
73	153.99	4.71
75	203.94	4.93
76	220.90	13.28



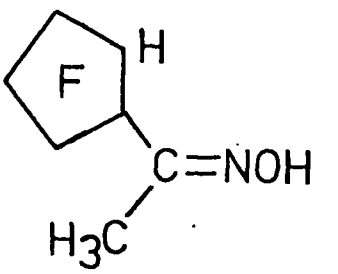
trans

NK1554 5 M.Wt. 271 No.60.



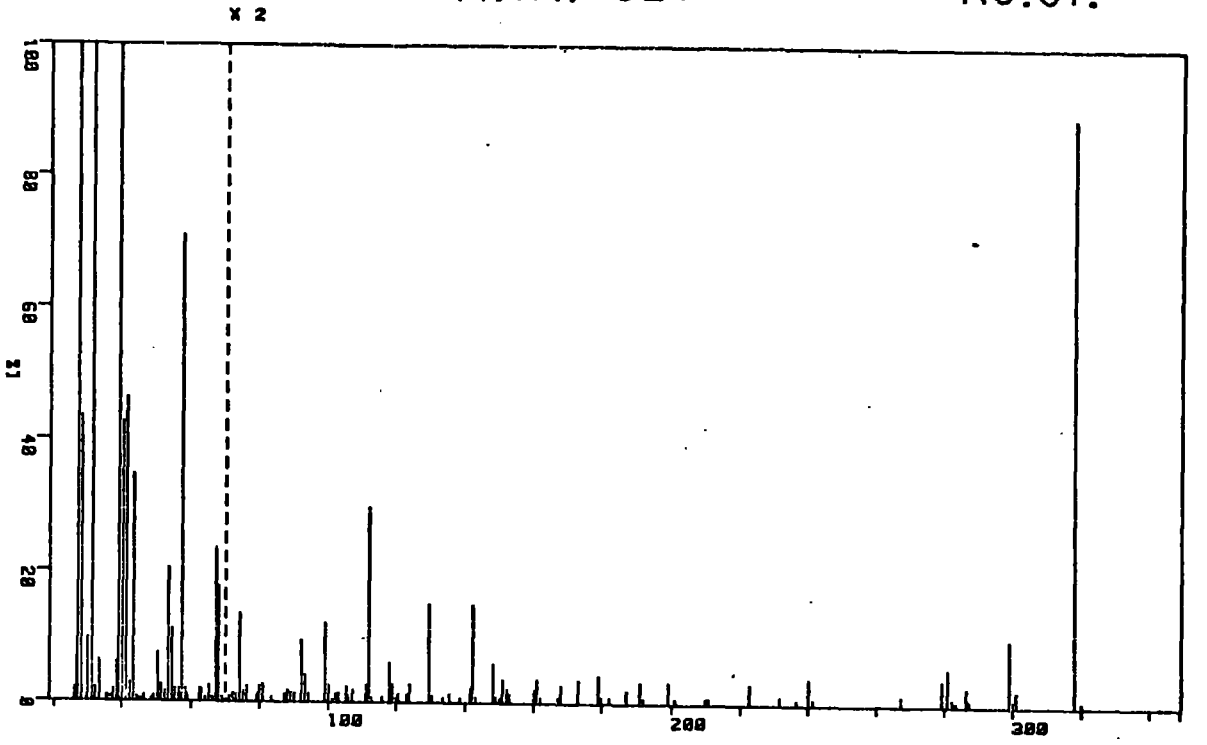
NK1554. 5 12-OCT-79

PEAK NO.	MASS	% INT BASE			
3	26.70	3.91			
5	27.62	9.18			
6	27.99	100.00			
7	29.06	100.00	48	67.33	3.15
8	32.11	100.00	49	68.31	1.15
10	34.64	14.51	50	69.29	31.67
17	36.67	1.22	51	70.17	4.79
18	37.69	1.49	55	76.38	1.20
19	38.63	1.76	60	81.45	1.07
20	39.58	8.03	80	115.06	2.17
22	40.54	100.00	95	165.97	1.05
26	41.74	47.62	97	167.01	0.98
27	42.82	9.47	103	196.49	2.10
28	43.88	3.86	105	236.12	0.88
29	44.90	80.10	106	243.26	1.12
31	45.94	1.56	107	255.42	0.46
35	50.95	1.03	108	256.42	0.71
36	52.02	2.42	109	275.64	3.74
37	53.08	3.59	110	276.81	0.39
38	54.15	2.17			
39	55.16	27.47			
40	56.17	16.97			
41	57.11	3.79			
43	59.09	7.59			
46	65.30	1.37			



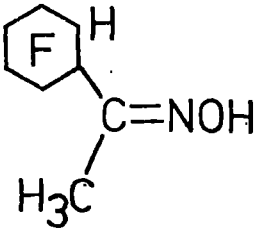
cis

NK1555 5 M.Wt. 321 No.61.



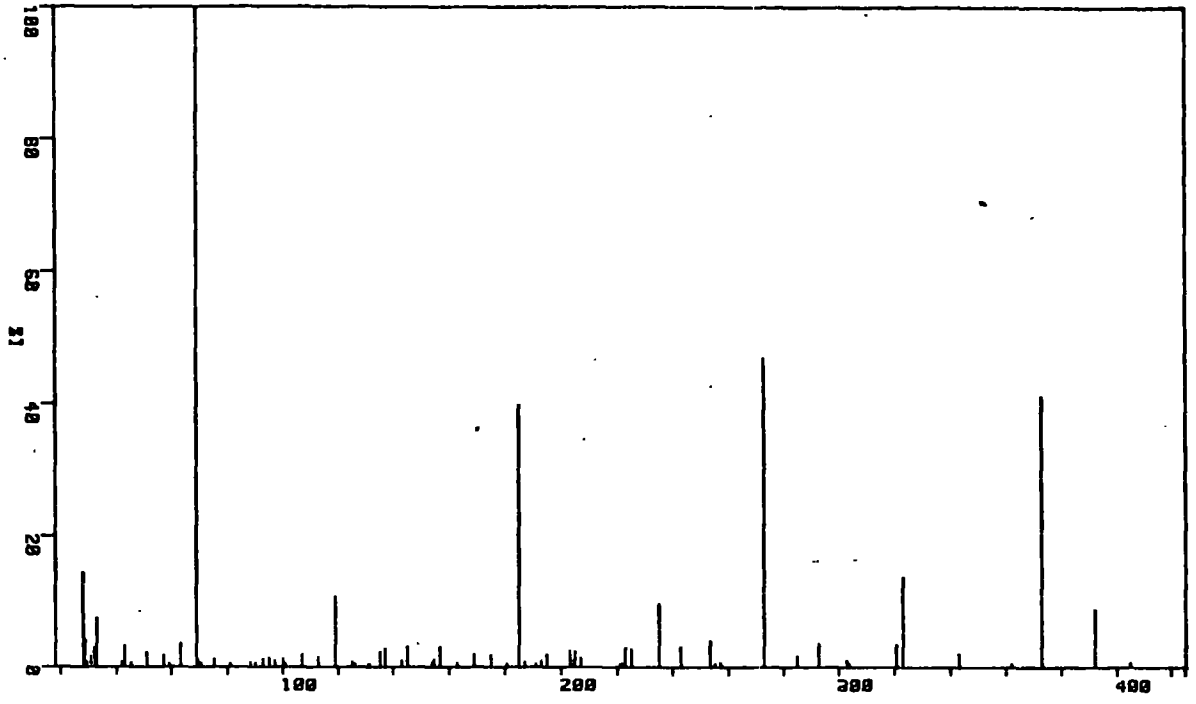
NK1555. 5 12-OCT-79

PEAK NO.	MASS	% INT BASE			
1	25.76	1.37	38	58.13	1.34
2	26.67	4.13	40	62.06	1.32
4	27.30	100.00	41	63.07	1.29
5	27.99	26.89	43	65.10	1.61
10	30.12	4.03	45	67.05	14.48
11	31.18	100.00	46	67.96	10.89
13	32.30	1.42	52	73.96	4.18
14	33.34	3.91	63	91.71	2.95
17	37.32	1.27	64	92.84	1.32
18	38.26	3.74	66	98.71	3.74
19	39.12	61.73	75	111.61	9.21
21	40.09	26.40	78	117.60	1.90
22	41.18	28.62	84	129.38	4.66
23	42.25	1.93	90	142.29	4.62
24	43.25	21.37	92	140.18	1.83
30	50.09	4.64	104	178.80	1.34
31	51.16	1.66	117	240.33	1.27
33	53.24	12.65	121	280.88	1.76
34	54.25	6.96	126	298.63	3.10
35	55.22	1.34	127	299.06	0.37
36	56.22	1.39	128	300.80	0.76
37	57.17	43.76	129	317.47	27.55
			130	319.76	0.27



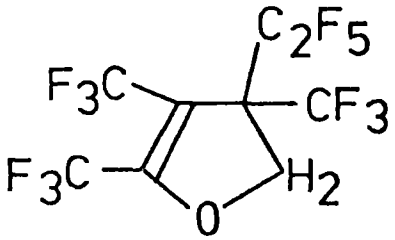
cis

NK34R3 5 M.Wt. 392 No.62.

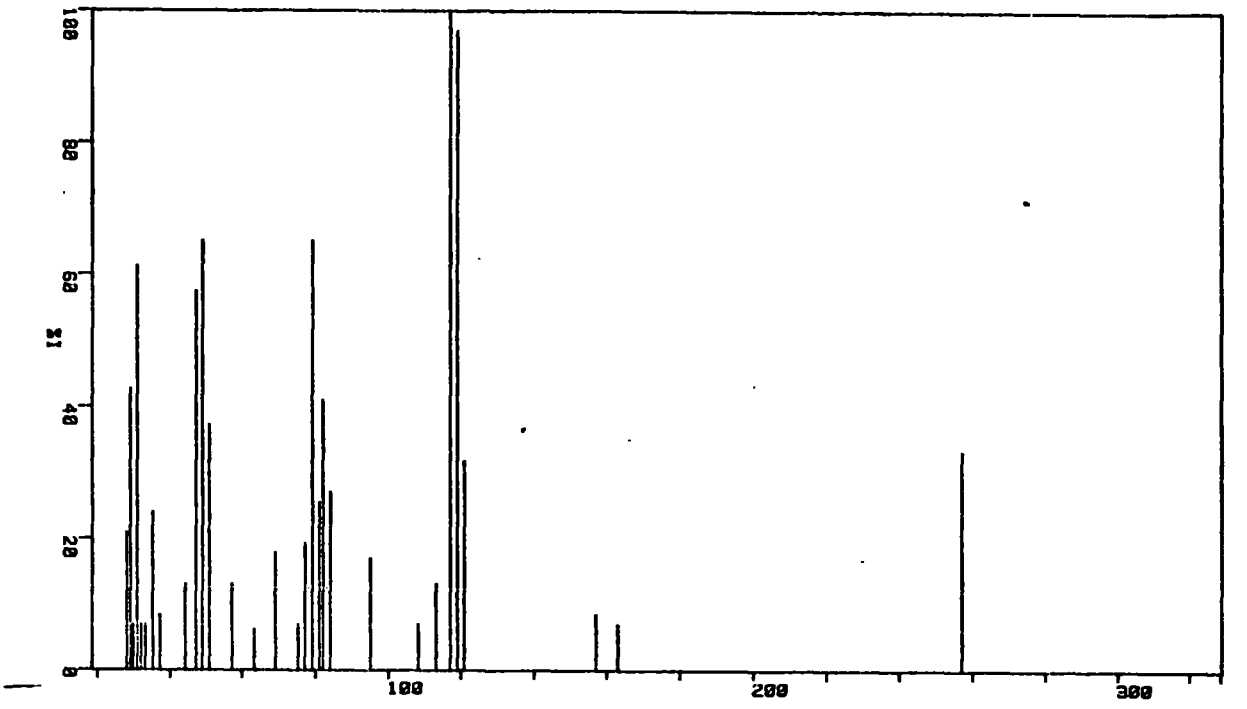


NK34R3. 5 24-OCT-79

PEAK NO.	MASS	% INT BASE
1	28.12	14.37
2	28.99	4.22
5	32.01	3.00
6	33.13	7.49
8	43.12	3.27
13	63.11	3.61
14	68.99	100.00
28	118.98	10.69
35	145.04	3.20
38	157.03	3.13
43	185.00	39.78
54	222.99	3.00
56	235.05	9.60
57	242.94	3.13
58	253.35	4.09
61	272.82	46.87
63	292.87	3.61
64	302.93	1.23
65	303.99	0.68
66	320.92	3.47
67	323.03	13.69
68	342.00	2.25
69	361.94	0.68
70	373.06	41.21
71	391.91	8.86
72	404.86	0.82

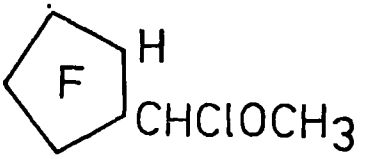


NK119 23 M.Wt. 292.5 No.63.



NK119 23 24-OCT-79

PEAK NO.	MASS	% INT BASE
1	28.12	20.93
2	28.99	42.64
3	29.83	6.98
4	30.92	61.24
5	32.02	6.98
6	33.13	6.98
7	35.16	24.03
8	37.11	8.53
9	44.17	13.18
10	47.08	57.36
11	48.96	65.12
12	50.94	37.21
13	57.10	13.18
14	63.09	6.20
15	68.99	17.83
16	75.11	6.98
17	77.10	19.38
18	79.00	65.12
19	80.98	25.58
20	81.98	41.09
21	84.03	27.13
22	95.00	17.05
23	100.04	6.98
24	113.05	13.18
25	116.95	100.00
26	118.90	96.90
27	120.89	31.78
28	157.05	8.53
29	163.03	6.98
30	257.03	33.33



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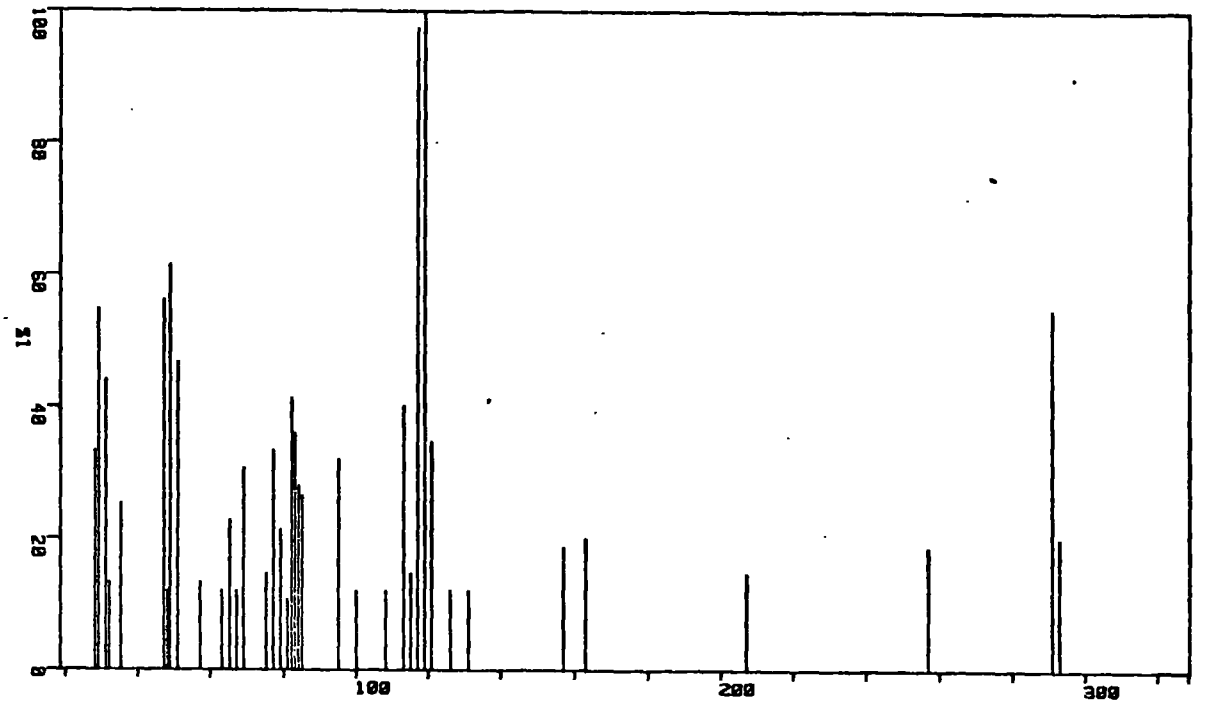
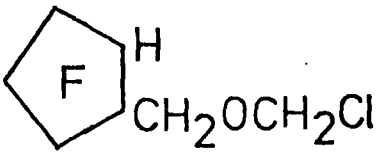
NK119 35 M.Wt. 292.5 No.64.



NK119 35 24-OCT-79

PEAK NO.	MASS	% INT BASE
1	28.12	33.33
2	28.99	54.67
3	30.93	44.00
4	32.02	13.33
5	35.16	25.33
6	47.08	56.00
7	48.04	12.00
8	48.96	61.33
9	50.96	46.67
10	57.11	13.33
11	63.05	12.00
12	65.09	22.67
13	67.06	12.00
14	69.00	30.67
15	75.11	14.67
16	77.09	33.33
17	79.00	21.33
18	80.98	10.67
19	81.99	41.33
20	83.01	36.00
21	84.02	28.00
22	85.04	26.67
23	95.10	32.00
24	99.94	12.00
25	108.04	12.00
26	113.04	40.00
27	115.02	14.67
28	116.96	97.33
29	118.91	100.00
30	120.90	34.67
31	126.08	12.00
32	130.98	12.00
33	157.04	18.67
34	163.03	20.00
35	207.02	14.67
36	256.99	18.67
37	290.87	54.67
38	292.93	20.00



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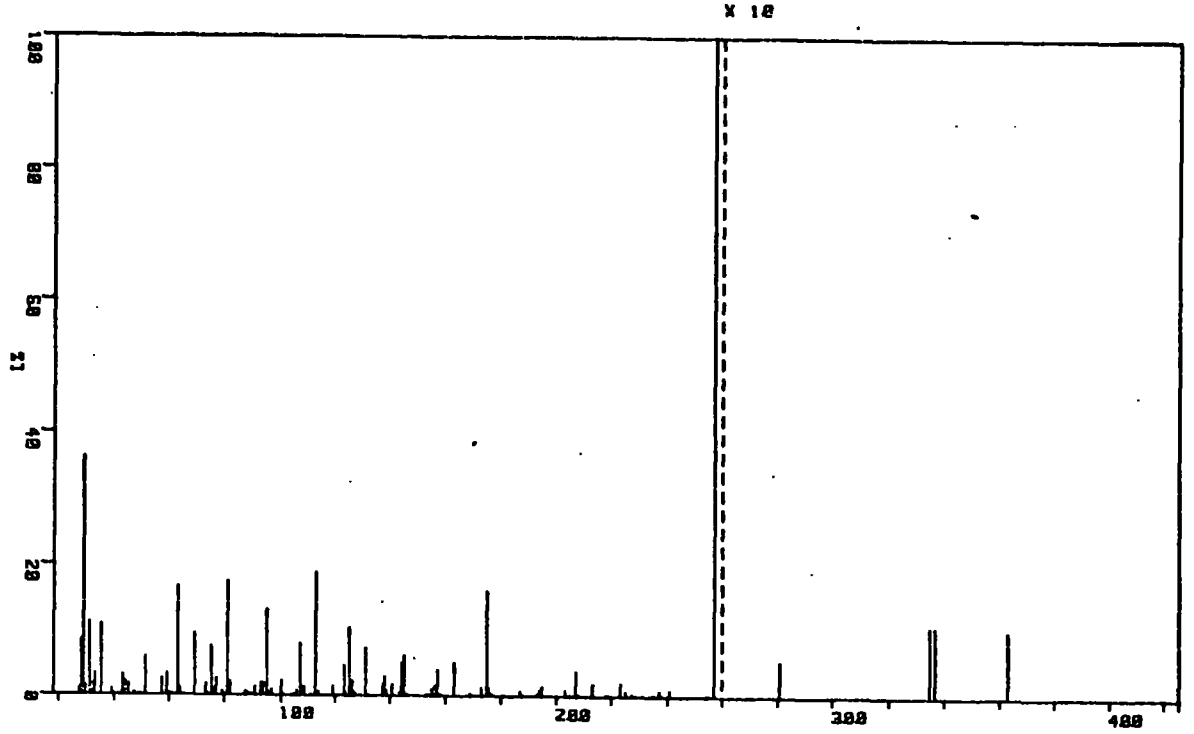
+ cis

NK127 5 M.Wt. 335 No.65.



NK127 5 24-OCT-79

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3	28.98	36.23
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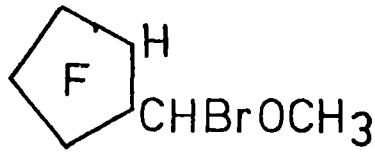
7	33.13	3.45
8	35.21	10.78
11	43.12	3.27
16	50.96	5.89
17	59.01	3.45
23	63.10	16.61
26	68.96	9.58
30	75.07	7.57
35	80.96	17.40
44	95.04	13.03
52	107.03	7.91
57	113.00	18.77
60	122.96	4.64
62	125.00	10.35
66	130.93	7.36
73	144.00	5.13
74	144.99	6.20
80	156.99	4.06
82	160.96	5.07
86	174.99	15.96
99	206.95	3.82
112	254.51	0.27
113	257.04	100.00
114	260.82	0.58
115	304.73	1.10
116	336.75	1.13
117	362.94	1.04



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APPENDIX IV

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

(a) all research colloquia, research seminars and lectures (by external speakers) arranged by the Department of Chemistry during the period of the writer's residence as a postgraduate student;

(b) all research conferences attended and papers read out by the writer of the thesis, during the period when the research for the thesis was carried out;

and (c) details of the first-year induction course.

Events in (a) which were attended are marked *.

Research Colloquia, Seminars and Lectures

1. University of Durham Chemistry Colloquia

1977

* 26 Jan. Dr. A. Davis (ERDR), "The Weathering of Polymeric Materials".

* 2 Feb. Dr. A. M. Falk(NRC Canada), "Structural Deductions from the Vibrational Spectrum of Water in Condensed Phases".

* 9 Feb. Professor R.O.C. Norman (U. of York), "Radical Cations in Organic Reactions".

23 Feb. Dr. G. Harris (U. of St. Andrews), "Halogen Adducts of Phosphines and Arsines".

25 Feb. Professor H. T. Dieck (Frankfurt U.), "Diazadienes - New Powerful Low-Valent Metal Ligands".

2 Mar. Dr. F. Hibbert (Birkbeck Coll., London), "Fast Reaction Studies of Slow Proton Transfers Involving Nitrogen and Oxygen Acids".

4 Mar. Dr. G. Brink (Rhodes U., R.S.A.), "Dielectric Studies of Hydrogen Bonding in Alcohols".

* 9 Mar. Dr. I. O. Sutherland (Sheffield U.), "The Stevens Rearrangement: Orbital Symmetry and Radical Pairs".

18 Mar. Professor H. Bock (Frankfurt U.), "Photoelectron Spectra and Molecular Properties: A Vademecum of the Chemist".

* 30 Mar. Dr. J. R. McCallum (U. of St. Andrews), "Photooxidation of Polymers".

* 20 Apr. Dr. D.M.J. Lilley (G.D. Searle, Research Div.), "Tails of Chromatin Structure - Progress Towards a Working Model".

27 Apr. Dr. G.C. Tabisz (U. of Manitoba), "Collision Induced Light Scattering by Compressed Molecular Gases".

* 11 May Dr. R.E. Banks (UMIST), "The Reaction of Hexafluoropropene with Heterocyclic N-Oxides".

* 18 May Dr. J. Atwood (U. of Alabama), "Novel Solution Behaviour of Anionic Organoaluminium Compounds: the Formation of Liquid Clathrates".

25 May Professor M.M. Kreevoy (U. of Minnesota), "The Dynamics of Proton Transfer in Solution".

1 June Dr. J. McCleverty (U. of Sheffield), "Consequences of Deprivation and Overcrowding on the Chemistry of Molybdenum and Tungsten".

6 July Professor J. Passmore (U. of Brunswick), "Adducts between Group 5 Pentahalides and a Postscript on S_7I^+ ".

* 27 Sept. Dr. T.J. Broxton (La Trobe U., Australia), "Interaction of Aryldiazonium Salts and Arylazoalkyl Ethers in Basic Alcoholic Solvents".

* 19 Oct. Dr. B Heyn, (U. of Jena, D.D.R.), "Sigma-organo Molybdenum Complexes as Alkene Polymerisation Catalysts".

* 27 Oct. Professor R.A. Filler (Illinois Institute of Technology, U.S.A. "Reactions of Organic Compounds with Xenon Fluorides".

2 Nov. Dr. N. Boden (U. of Leeds), "NMR Spin-Echo Experiments for Studying Structure and Dynamical Properties of Materials Containing Interacting Spin-$\frac{1}{2}$ Pairs".

9 Nov. Dr. A.R. Butler (U. of St. Andrews), "Why I Lost Faith in Linear Free Energy Relationships".

7 Dec. Dr. P.A. Madden (U. of Cambridge), "Raman Studies of Molecular Motions in Liquids".

14 Dec. Dr. R.O. Gould (U. of Edinburgh), "Crystallography to the Rescue in Ruthenium Chemistry".

1978

* 25 Jan. Dr. G. Richards (U. of Oxford), "Quantum Pharmacology".

* 1 Feb. Professor K.J. Ivin (Queens U., Belfast), "The Olefin Metathesis Reaction: Mechanism of Ring Opening Polymerisation of Cycloalkenes".

3 Feb. Dr. A. Hartog (Free U., Amsterdam), "Surprising Recent Studies in Organo-magnesium Chemistry".

22 Feb. Professor J.D. Birchall (Mond Division, I.C.I.), "Silicon in the Biosphere".

* 1 Mar. Dr. A. Williams (U. of Kent), "Acyl Group Transfer Reactions".

3 Mar. Dr. G. van Koten (U. of Amsterdam), "Structure and Reactivity of Arylcopper Cluster Compounds".

15 Mar. Professor G. Scott (U. of Aston), "Fashioning Plastics to Match the Environment".

* 22 Mar. Professor H. Wahrenkamp (U. of Frieburg, Germany), "Metal-Metal Bonds in Organometallic Complexes".

19 Apr. Dr. M. Barber (UMIST), "Secondary Ion Mass Spectra of Surfaces and Absorbed Species".

16 May Dr. P. Ferguson (C.N.R.S., Grenoble), "Surface Plasma Waves and Adsorbed Species on Metals".

18 May Professor M. Gordon (U. of Essex), "Three Critical Points in Polymer Chemistry".

* 22 May Professor D. Tuck (U. of Windsor, Ontario), "Electrochemical Synthesis of Inorganic and Organometallic Compounds".

24 & 25 May Professor P. von R. Schleyer (U. of Erlangen, Nurnberg),

* I "Planar Tetra-coordinate Methanes, Perpendicular Ethenes, and Planar Allenes".

* II "Aromaticity in Three Dimensions".

* III "Non-classical Carbocations".

* 21 June Dr. S.K. Tyrlik (Acad. of Sci., Warsaw), "Dimethylglyoxime-Cobalt Complexes - Catalytic Black Boxes".

23 June Professor W.B. Pearson (U. of Florida), "Diode Laser Spectroscopy at 16μm".

30 June Professor G. Mteescu (Case Western Reserve U., Ohio), "A Concerted Spectroscopy Approach to the Characterisation of Ions and Ion-pairs: Facts, Plans and Dreams".

* 8 Sept. Dr. A. Diaz (I.B.M., San Jose, California), "Chemical Behaviour of Electrode Surface Bonded Molecules".

15 Sept. Professor W. Siebert (Marburg, W. Germany), "Boron Heterocycles as Ligands in Transition Metal Chemistry".

22 Sept. Professor T. Fehlner (Notre Dame, U.S.A.), "Ferraboranes: Synthesis and Photochemistry".

* 12 Dec. Professor C.J.M. Stirling (U. of Bangor), "Parting is such Sweet Sorrow - the Leaving Group in Organic Chemistry".

1979

* 31 Jan. Professor P.D.B. de la Mare (U. of Aukland, New Zealand), "Some Pathways Leading to Electrophilic Substitution".

14 Feb. Professor B. Dunnell (U. of British Columbia), "The Application of NMR to the Study of Motions of Molecules in Solids".

* 14 Mar. Dr. J.C. Walton (U. of St. Andrews), "Pentadienyl Radicals".

28 Mar. Dr. A. Reiser (Kodak Ltd.), "Polymer Photography and the Mechanism of Cross-link Formation in Solid Polymer Matrices".

25 Apr. Dr. C.R. Patrick (U. of Birmingham), "Chlorofluorocarbons and Stratospheric Ozone: an Appraisal of the Environmental Problem".

1 May Dr. G. Wyman (European Research Office, U.S. Army), "Excited State Chemistry of Indigoid Dyes".

2 May Dr. J.D. Hobson (U. of Birmingham), "Nitrogen-centred Reactive Intermediates".

8 May Professor A. Schmidpeter (Inst. of Inorg. Chem., Munich U.), "Five-membered Phosphorus Heterocycles Containing Dicoordinate Phosphorus".

9 May Professor G. Maier (Lahn Giessen U.), "Tetra-tert-butyltetrahedrane".

9 May Dr. A.J. Kirby (U. of Cambridge), "Structure and Reactivity in Intramolecular and Enzymic Catalysis".

16 May Dr. J.F. Nixon (U. of Sussex), "Some Recent Developments in Platinum-metal Phosphine Complexes".

* 23 May Dr. B. Wakefield (U. of Salford), "Electron Transfer in Reaction of Metals and Organometallic Compounds with Polychloropyridine Derivatives".

* 13 June Dr. G. Heath (U. of Edinburgh), "Putting Electrochemistry in Mothballs".

14 June Professor I. Ugi (U. of Munich), "Synthetic Uses of Super Nucleophiles".

* 25 Sept. Professor R. Soulen (Southwestern U., Texas), "Applications of HSAB Theory to Vinylic Halogen Substitution Reactions and a Few Copper Coupling Reactions".

2. Durham University Chemical Society

1977

18 Jan. Professor I. Fells (U. of Newcastle), "Energy Storage: the Chemist's Contribution to the Problem".

* 8 Feb. Dr. M.J. Cleare (Johnson Matthey Research Centre), "Platinum Group Metals as Anti-Cancer Agents".

1 Mar. Professor J.A.S. Smith (Q.E. Coll., London), "Double Resonance".

* 8 Mar. Professor C. Eaborn (U. of Sussex), "Structure and Reactivity".

* 13 Oct. Dr. J.C. Young and Mr. A.J.S. Williams (U. of Aberystwyth), "Experiments and Considerations Touching Colour".

* 20 Oct. Dr. R.L. Williams (Metropolitan Police Forensic Science Dept.), "Science and Crime".

* 3 Nov. Dr. G.W. Gray (U. of Hull), "Liquid Crystals - Their Origins and Applications".

24 Nov. Mr. G. Russell (Alcan), "Designing for Social Acceptability".

* 1 Dec. Dr. B.F.G. Johnson (U. of Cambridge), "Chemistry of Binary Metal Carbonyls".

1978

* 2 Feb. Professor R.A. Raphael (U. of Cambridge), "Bizarre Reactions of Acetylenic Compounds".

* 16 Feb. Professor G.W.A. Fowles (U. of Reading), "Home Winemaking".

* 2 Mar. Professor M.W. Roberts (U. of Bradford), "The Discovery of Molecular Events at Solid Surfaces".

* 9 Mar. Professor H. Suschitsky (U. of Salford), "Fruitful Fissions of Benzofuroxans".

4 May Professor J. Chatt (U. of Sussex), "Reactions of Coordinated Dinitrogen".

* 9 May Professor G.A. Olah (Case Western Reserve U., Ohio), "Electrophilic Reactions of Hydrocarbons".

* 10 Oct. Professor H.C. Brown (Purdue U.), "The Tool of Increasing Electron Demand in the Study of Cationic Processes".

19 Oct. Mr. F.C. Shenton (Public Analyst, Co. Durham), "There is Death in the Pot".

26 Oct. Professor W.J. Albery (Imperial Coll., London), "Photogalvanic Cells for Solar Energy Conversion".

* 9 Nov. Professor A.R. Katritsky (U. of E. Anglia), "Some Adventures in Heterocyclics".

* 16 Nov. Dr. H.C. Fielding (I.C.I. Ltd., Mond), "Fluorochemical Surfactants and Textile Finishes".

* 23 Nov. Dr. C. White (Sheffield U.), "The Magic of Chemistry".

1979

18 Jan. Professor J.C. Robb (Birmingham U.), "The Plastics Revolution".

8 Feb. Mr. C.G. Dennis (Vaux Ltd.,), "The Art and Science of Brewing".

1 Mar. Professor R. Mason (Govt. Scientific Advisor), "The Scientist in Defense Policy".

10 May Professor G Allan (Chairman SRC), "Neutron Scattering for Polymer Structures".

18 Oct. Dr. G. Cameron (Aberdeen), "Synthetic Polymers- Twentieth Century Polymers".

25 Oct. Professor P. Gray (Leeds), "Oscillatory Combustion Reactions".

1 Nov. Dr. J Ashby (I.C.I. Toxicological Laboratory), "Does Chemically-Induced Cancer make Chemical Sense?"

8 Nov. Professor J.H. Turnbull (RMC Shrivenham), "Luminescence of Drugs".

15 Nov. Professor E.A.V. Ebsworth (Edinburgh), "Stay Still, You Brute: The Shape of Simple Silyl Complexes".

Research Conference Attended

IXth International Symposium On Fluorine Chemistry, Avignon, 3 - 7 September 1979.

First Year Induction Course

In each part of the course, the use and limitations of the various services available are explained by the people responsible for them.

Departmental organisation	Dr. E.J.F. Ross
Safety matters	Dr. M.R. Crampton
Electrical appliances and infra-red spectroscopy	Mr. R.N. Brown
Chromatography and microanalysis	Mr. T.F. Holmes
Library facilities	Mr. W.B. Woodward (Keeper of Science Books)
Atomic absorptiometry and inorganic analysis	Mr. R. Coult

Mass spectrometry	Dr. M. Jones
N.m.r. spectroscopy	Dr. R.S. Matthews
Glassblowing technique	Mr. W.H. Fettis and Mr. R. Hart

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