A study of addition products of fluorocarbon olefins

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entitled

A STUDY OF ADDITION PRODUCTS

OF FLUOROCARBON OLEFINS

submitted by

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SUMMARY

Peroxide or γ-ray initiated free radical additions of organic compounds to perfluoro-olefins have been studied. Assessment of the relative efficiency of different groups as chain transfer agents for telomerisation reactions was simplified by use of nonhomopolymerisable olefins.

Highest yields resulted with alcohols and acetaldehyde; ethyl acetate and methanethiol gave low yields; and acids, nitriles, ketones, ethers and amides failed to react. Since radical formation from alcohols, acetaldehyde and ethyl acetate involved α-hydrogen abstraction the resulting adducts were fluorine-containing alcohols, methyl ketones and acetates, while the $CH_3S\cdot$ radical yielded sulphides.

Study of the γ-initiated series of alcohol additions to perfluoropropene pointed to the degree of resonance stabilisation of the α-hydroxyalkyl radical as the most important factor influencing ease of addition.

Thermally initiated addition of trifluoromethyl iodide to perfluorocyclic olefins showed that ease of radical attack upon the olefin decreased in the order:-

(hexagon with F) > (hexagon with F) > (hexagon with F)

whereas reactivity of the resulting radicals, R(olefin)., in the chain transfer step appears to lie in the order:-

$(R = CF_3 \text{ or } CH_2OH)$

explicable on the grounds of a parallel increase in resonance stabilisation of the radicals.

Additions to perfluoropropene gave the isomer CF_3CFHCF_2R exclusively. When R contained an asymmetric carbon atom two optical isomers could be distinguished.

Addition of HR to perfluorocyclic olefins yielded the trans e,e and probably cis a(R),e(H) conformers, identified by n.m.r. spectroscopy.

Dehydrofluorination of CF_3CFHCF_2R yielded both cis and trans isomers of $CF_3CF=CFR$ when R was CH_2OH and $CH(OH)C_2H_5$, but only the trans isomer for the more bulky group, $C(CH_3)_2OH$.

Prolonged treatment of the cyclic adducts with aqueous alkali under conditions sufficiently mild to prevent excessive decomposition, scarcely affected the cis isomers, while cis-elimination of hydrogen fluoride from the trans isomers involved fluorine from the CFR rather than the CF_2 group adjacent to CFH.

C H A P T E R   1.

I N T R O D U C T I O N

INTRODUCTION

As with hydrocarbon olefins, additions to fluoro-olefins may occur by either ionic or free radical mechanisms.

IONIC ADDITIONS

IONIC ADDITIONS   With highly fluorinated olefins electrophilic attack occurs much less readily than with hydrocarbon olefins, owing to inductive electron withdrawal from the double bond by fluorine and fluoroalkyl groups, while nucleophilic attack is correspondingly easier. Thus while hexafluoropropene fails to react with anhydrous hydrogen fluoride at 200°C, it rapidly adds the elements of hydrogen fluoride at 25°C by reaction with potassium fluoride in a protogenic solvent such as formamide, where initial attack is by the fluoride ion rather than the proton.

The direction of ionic addition is as expected from consideration of the polarisation of the olefins , which results from a combination of the mesomeric effect of vinylic fluorine, $\delta-$, $\delta+$,

$$\overset{\curvearrowright}{\underset{/}{\overset{\backslash}{C}}} = \overset{/}{\underset{\underset{\ddot{F}}{\curvearrowleft}}{C}}$$

with inductive,

$$F \leftarrow \overset{\overset{F}{\uparrow}}{\underset{\underset{F}{\downarrow}}{C}} \leftarrow \overset{\delta-}{C^-} = \overset{\delta+}{C\underset{\backslash}{\diagup}}$$
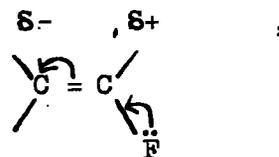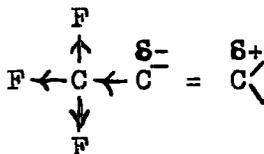
and hyperconjugative effects, $CF_3 - \overset{/}{\underset{/}{C}} = \overset{}{\underset{\backslash}{C}} \longleftrightarrow F^- \quad CF_2 = \overset{}{\underset{/}{C}} - \overset{+}{\underset{\backslash}{C}}\diagup$

e.g. the overall direction of polarisation for a terminal perfluoro-olefin is $R_f \overset{\delta-}{C}F = \overset{\delta+}{C}F_2$.

NUCLEOPHILIC ADDITIONS   Types of compounds successfully added to
fluoro-olefins by a mechanism involving nucleophilic attack include
alcohols and phenols [3,5-24, 28, 30,]   thiols [16, 24-26,]   and
amines [9, 17, 24, 27, 28, 30,]   giving respectively ethers, thio-ethers
and amines.   In most cases use of a basic catalyst such as sodium,
caustic alkali or quaternary ammonium hydroxide is necessary.

Besides allylic substitution products of the type $ROCF_2C:C\langle$ [3,]
many alcohol additions give both saturated, $RO-\overset{|}{\underset{|}{C}}-\overset{/}{\underset{\backslash}{C}}-$, and vinyl, $RO - \overset{/}{C}\overset{}{=}\overset{/}{\underset{\backslash}{C}}$,
ethers.   The ratio of the two has been shown to depend on reaction
conditions [14] and the nature of the alcohol [19] and olefin [14, 18] .
The tendency to form unsaturated products is most pronouced in
fluorinated cyclobutenes [8, 11, 15,]   cyclopentenes [22, 30,]   and
cyclohexenes [28,] where further reaction of the initial unsaturated
product often occurs, leading to 1,2-disubstituted cyclic olefins of the
type
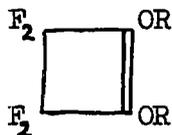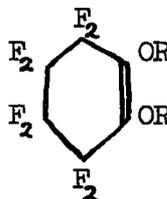
The mechanism has been postulated as direct S_N2 substitution of
vinylic fluorine [8] or stabilisation of an intermediate anion by either
(1) loss of fluoride ion, or (2) proton addition, with subsequent
elimination of Hydrogen fluoride [11] .
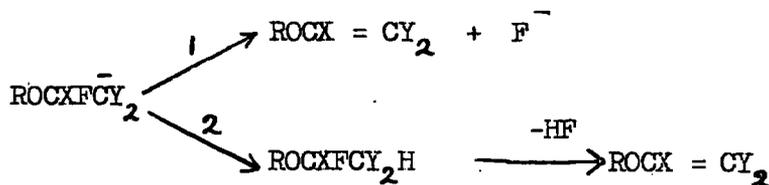
There is insufficient evidence to distinguish between the possibilities, though the addition - elimination mechanism receives support from the fact that vinyl ethers can be obtained from saturated ethers by further treatment with base.

Analogous unsaturated compounds are formed in some thiol [25] and amine [27] additions. With primary amine, ammonia and hydrazine adducts elimination of fluorine and N-hydrogen results in the formation of imidyl fluorides, [27]

$$CFCl: CF_2 \xrightarrow{RNH_2} CHFClCF:NR$$

α-hydrofluoronitrites [17] ,

$$CF_3CF: CF_2 \xrightarrow{NH_4OH} CF_3CFHC:N$$

and α-fluorohydrazones [29]

$$CF_3CF:CF_2 \xrightarrow{PhNHNH_2} CF_3CFH CF: NNHPh$$
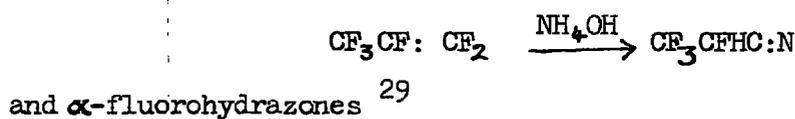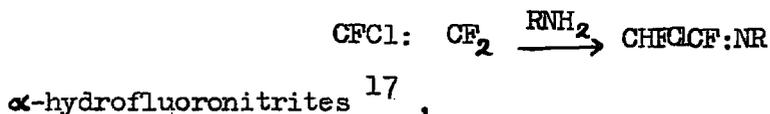
The other major group of nucleophilic additions to fluoro-olefins which has been studied is that involving attack by fluoride ion, often catalyzed by metal fluorides. For example, potassium fluoride in a protogenic solvent gives hydrogen fluoride adducts,[1] while in an inert solvent in the presence of iodine, the elements of iodine and fluorine add to the olefin [31]

$$\underset{/}{\overset{\backslash}{C}} : \underset{\backslash}{\overset{/}{C}} \rightleftharpoons F - \underset{/}{\overset{\backslash}{C}} - \overset{-}{\underset{\backslash}{C}} \xrightarrow{HR \ (or \ I_2)} F-\overset{\backslash}{\underset{/}{C}}-\overset{/}{\underset{\backslash}{C}}-H \ (or \ I) + R^- (or \ I^-)$$

Similarly metal fluoride catalyzed addition of fluoroacyl fluorides yields fluoroketones [32]

$$CF_3 CF : CF_2 \rightleftharpoons \overset{F^-}{} (CF_3)_2 \overset{-}{C}F \xrightarrow{R_fCOF} (CF_3)_2CFCOR_f + F^-$$
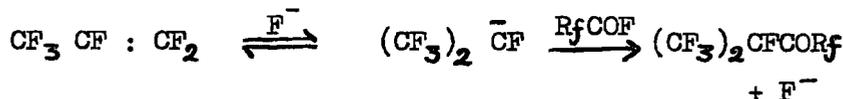
Addition of 'IF' or 'BrF' by reaction of fluoro-olefins with iodine and

and iodine pentafluoride or bromine and bromine trifluoride [33, 34]
is also much more likely to proceed via initial attack by F^- rather
than by I^+ or Br^+.

Electrophilic additions   Owing to the reduced electron density at
the double bond few genuine additions of this type are known, though
such a mechanism has been postulated without proof in a number of
cases.

It is reasonable to assume that where a Lewis acid catalyst
e.g. $AlCl_3$, BF_3, is necessary for hydrogen halide addition to occur
an electrophilic mechanism is in operation, and observation of the
deactivating influence of perfluoroalkyl groups attached to vinylic
carbon supports this view [35, 37].   Inductive electron withdrawal will,
in the case of vinylic fluorine, be compensated for by mesomeric
electron release, which explains the relative ease of addition of
hydrogen fluoride to $CF_2 : CH_2$ [35] and $CF_2 : CF_2$ [36], but
replacement of hydrogen or fluorine by the solely electron withdrawing
trifluoromethyl group renders $CF_2 : CHCF_3$ [35] and $CF_3CF : CF_2$ [2]
much more resistant to attack.

In anhydrous hydrogen fluoride, dissociation of metal flurorides
is promoted by strong solvation of F^- to form $H_n F_{n+1}^-$ ions. Since
nucleophilic attack is thereby inhibited, any addition to olefins
which are resistant to hydrogen fluoride must involve attack by the
metal cation followed by fluoride abstraction from the solvent.
Stable fluoroalkyl mercury compounds have been obtained from such
a reaction [2], $HgF_2 + CF_3CH = CF_2 \xrightarrow{HF} (CF_3CH CF_3)_2 Hg$
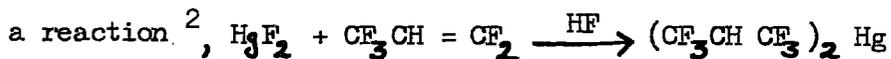
and examination of other metal fluorides under these conditions may produce more examples.

Addition of interhalogen compounds, such as ICl [38, 39, 41, 94] and I Br [40, 41], may also proceed by an electrophilic mechanism, especially with more reactive olefins like vinylidene fluoride [38], but as stated above with regard to 'I F' and 'Br F' additions, a nucleophilic mechanism is more likely in many cases, although as yet there is no conclusive evidence.

FREE RADICAL ADDITIONS   While the most widely studied free radical additions to fluorinated olefins are those of hydrogen bromide, halogens and haloalkanes, [38 – 63, 93, 94], a variety of organic compounds and derivatives of silicon, sulphur and phosphorus have also been successfully added (See Tables I and II).

Table I.   Additions with formation of C-C bond

Olefin	Type of reagent (R = alkyl, Rf = polyfluoroalkyl)	Reference
CF_2 : CF_2	RCH_2OH and RR'CHOH	64, 65
	R_2CO	65, 66
	RCO_2H	65, 66, 67
	$(RCO)_2O$	65, 66
	RCO_2R'	65, 66, 67
	R – O – R'	65, 66, 67, 68, 69
	R H	65. 67., 69
CF_2 : CFCl	RCH_2OH	64
	Rf CHO	70
	Rf_2 CO	70

Table I (Cont)

Olefin	Type of reagent	Reference
$CF_2 : CCl_2$	R CH_2 OH and RR'CH OH	71
	RCHO	72
$CF_2 : CH_2$	R – O – R′	73
CF Cl : CF Cl	RCH_2OH and RR'CHOH	71
	RCHO	72
CF Cl : CCl_2	RCH_2OH and RR'CHOH	71
$CF_2 : CF (CF_2)_2 H$	Rf CHO	70
	Rf COF	70
$CF_2 : CFCF_3$	R CH_2OH	74, 75
	RCHO	74
	Rf CHO	70
	Rf_2CO	70
	Rf COF	70
	R – O – R′	73
$CF_2 = CF C_2F_5$	R CH_2OH	74
	RCHO	74
$CF_2 : CFC_3F_7$	RCH_2OH and RR'CHOH	74
$CF_2 = CFC_5F_{11}$	R CH_2OH	74
	Rf_2CO	70
$CF_2 = CFC_7F_{15}$	R CH_2OH	74
$CF_3CF : CF CF_3$	R CH_2OH	74
$C - C_4F_6$	R CH_2OH	75
$C - C_6F_{10}$	R CH_2OH	75, (74)
$C - 1 : 4 - C_6F_8$	R CH_2OH	75
$C - 1 : 3 - C_6F_8$	R CH_2OH	75

Table II. Additions with formation of C – Si, C – S and C – P bonds.

Olefin \ Reagent	Silanes	Thiols	H S	CF SCl	SF Cl	S Cl	Phosphines	Na HSO
$CF_2 : CF_2$	76 77	65 69 84 85	87 88 121		91		80,92	95
$CF_2 : CFCl$	78 79	85	87 121 89	90	91		80,92	
$CF_2 : CCl_2$							92	
$CF_2 : CF Br$			121					
$CF_2 : CFH$	79	85 121	121	90	91			
$CF_2 : CH_2$		85	88 121	90			80 92	
$CF_2 : CFOCH_3$		85 121	121	90				
$CF_2 : C(CH_3)_2$							92	
$CF_2 : CFCF_3$	78 80	85		90	91		80 92	
$C_5 F_{10}$-1, $C_7 F_{14}$-1								96
$C Cl_2 : CCl CF_3$	78							
$CH_2 : CHF$		86	121			89		
$CH_2 : CFC_2 F_5$	78							
$CH_2 : CHCF_3$	78 81,83							
$CH_2 : CHC_2 F_5$	82, 83							
$CH_2 : CHC_3 F_7$	81, 83 82							
$CH_2 : C(CH_3) C_2 F_5$	82							
$CH_2 : C(CH_3) - C_3 F_7$	82							

Additions to both fluoro- and hydro-carbon olefins follow a similar course, the only difference being in the ease of reaction, especially with radicals of highly polar character. In considering theoretical aspects of free radical additions to fluoro-olefins reference will therefore be made to many reactions involving hydrocarbon olefins, since the principles derived from their study may be profitably applied to this particular class.

This type of reaction proceeds by a chain mechanism with the following steps:-

(1) $R - Y \rightarrow R\cdot + Y\cdot$ Initiation (Y = usually H or halogen)

(2) $R\cdot + \underset{b}{\overset{a}{C}} = \underset{d}{\overset{c}{C}} \rightarrow R - \underset{b}{\overset{a}{C}} - \underset{d}{\overset{c}{C}}\cdot$ Propagation

(3) $R - \underset{b}{\overset{a}{C}} - \underset{d}{\overset{c}{C}}\cdot + R - Y \rightarrow R - \underset{b}{\overset{a}{C}} - \underset{d}{\overset{c}{C}} - Y + R\cdot$ Transfer
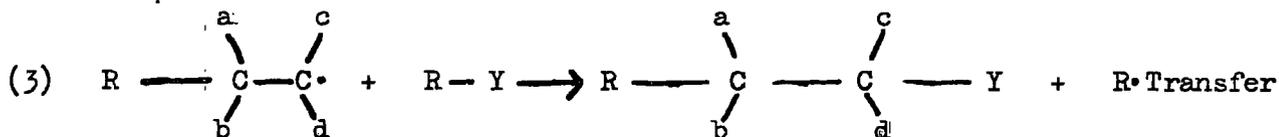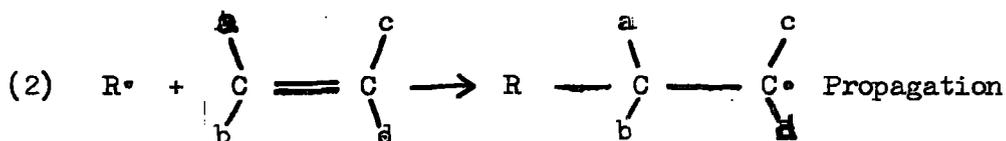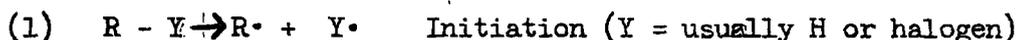
Where the olefin is homopolymerisable step (4) may compete with step (3)

(4) $R - \underset{b}{\overset{a}{C}} - \underset{d}{\overset{c}{C}}\cdot + \underset{b}{\overset{a}{C}} = \underset{d}{\overset{c}{C}} \rightarrow R - \left[\underset{b}{\overset{a}{C}} - \underset{d}{\overset{c}{C}} \right]_2$ Telomerization
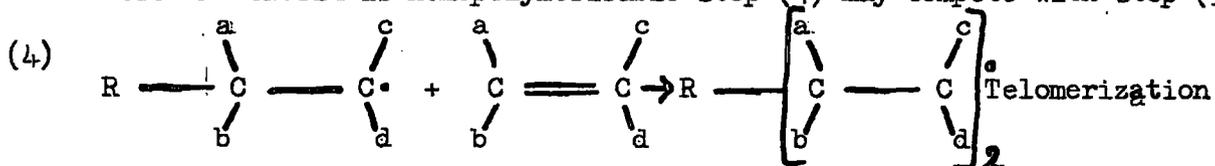
and successive additions of olefin are followed by step (5) to give a telomer molecule

(5) $R - \left[\underset{b}{\overset{a}{C}} - \underset{d}{\overset{c}{C}} \right]_n \cdot + RY \rightarrow R - \left[\underset{b}{\overset{a}{C}} - \underset{d}{\overset{c}{C}} \right]_n - Y + R\cdot$ Transfer
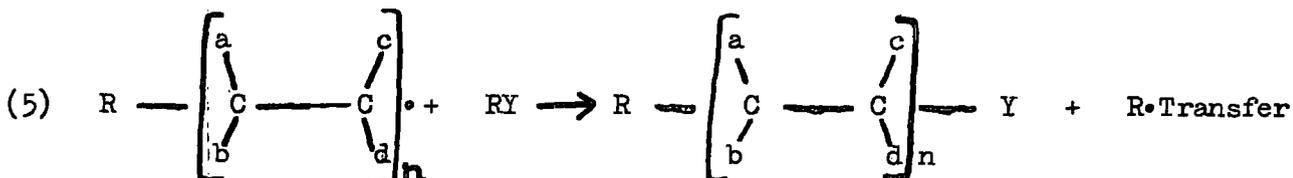
Chain termination may occur by radical combination or disproportionation.

<u>Initiation</u>   Homolytic bond cleavage (Step (1)) may be induced:

a) thermally

b) photochemically

c) by high-energy radiation e.g. α, β, γ and X rays.

These sources may supply directly the energy necessary for rupture of the R - Y bond, or may bring about cleavage of molecules of chemical initiator i.e. compounds containing bonds of low dissociation energy, such as O - O (peroxides), N - N (azo compounds) and S - S (disulphides) The chain carrying species R• is then obtained by reaction of these readily formed free radicals (In •) with RY.

(1)a.   In• +   RY $\longrightarrow$ InY   +   R•

This displacement step is similar to step (3), the major factors influencing its rate being the strength of the R - Y bond and the reactivity of the attacking radical.

In some cases there is evidence that initial attack by the initiator radical is on the olefin, the radical thus formed then reacting with RY. The conversion of 55% of the initiator in the system benzoyl peroxide - cyclohexene - carbon tetrachloride to 2 - chlorocyclohexyl benzoate can only be explained on this basis [97]

$$(PhCO \cdot O)_2 \longrightarrow 2 \, PhCO \cdot O \cdot \; (\longrightarrow 2Ph \cdot + 2CO_2)$$
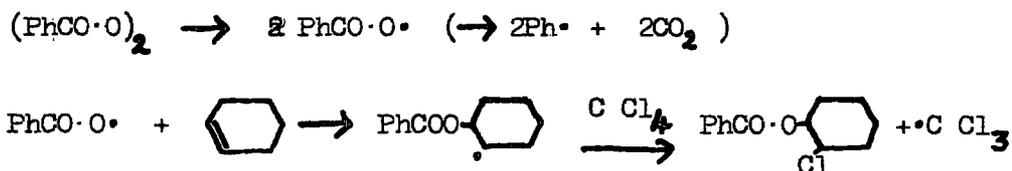
Formation of chlorobenzene by direct abstraction of chlorine by phenyl radicals accounts for only 10% of the initiator.

$$Ph \cdot \; + \; CCl_4 \longrightarrow PhCl \; + \; \cdot CCl_3$$
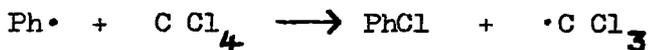
In most organic compounds radical formation involves abstraction of a hydrogen atom from the carbon bearing the functional group. Thus primary and secondary alcohols give α-hydroxyalkyl radicals,

$$RR'CHOH \longrightarrow RR'\overset{\bullet}{C}OH + H\bullet$$

So that the products of free radical additions to olefins are secondary and tertiary alcohols instead of the ethers obtained by nucleophilic additions, while the acyl radicals from aldehydes yield ketones.

$$RCHO \longrightarrow R\overset{\bullet}{C}O + H\bullet$$
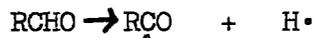
Similarly acids, esters, ethers and amines [98, 99, P.288] add to olefins to give the corresponding α-alkyl substituted compounds.

$$RR'CH-COOR'' \longrightarrow RR'\overset{\bullet}{C}-COOR'' + H\bullet$$

$$RR'CH-OR'' \longrightarrow RR'\overset{\bullet}{C}-OR + H\bullet$$

$$RR'CH\ NR''R''' \longrightarrow RR'\overset{\bullet}{C}NR''R''' + H\bullet$$
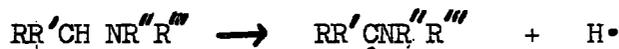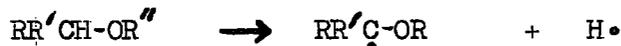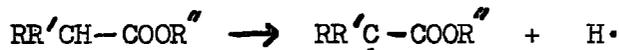
In the case of thiols, however, the S – H bond is more easily broken than the C – H bond, so that thioethers are obtained as from nucleophilic additions.

$$RR'CHSH \longrightarrow RR'CHS\bullet + H\bullet$$
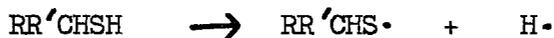
The strength of the bond R – Y which has to be broken (steps (1) and (3)) depends on the nature of both R and Y. For a given R, bond strength decreases in the order Y = H > Cl > Br > I [99 P.50]. Changes in bond strength for a given Y are directly related to the stability of R• , the major contributing factor being resonance stabilisation. The resonance energy of R• can be measured as the difference between the bond dissociation energies of CH_3 – Y and R – Y where Y = H, since in this case contributions from conjugation of Y with R (as in benzyl halides),

steric and polar effects should be at a minimum. The increase in resonance

energy on replacing H by an alkyl group can be accounted for in terms of

hyperconjugation

$$
\begin{array}{c}
CH_3 \\
| \\
\bullet C-CH_3 \\
| \\
CH_3
\end{array}
\longleftrightarrow
\begin{array}{c}
CH_3 \\
| \\
C == CH_2 \quad H\bullet \\
| \\
CH_3
\end{array}
$$
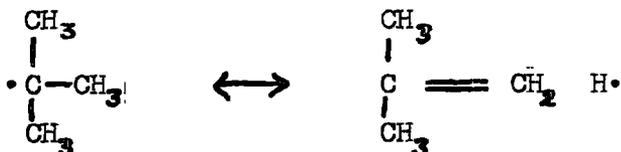
and Tedder [100] suggests that radical formation should also be favoured by

any α-substituent with π electrons (e.g. $-\overset{\overset{O}{\|}}{C}-OR$, $-CH=CH_2$, $-\overset{\overset{O}{\|}}{C}R$) or

non-bonded p-electrons (e.g. halogen, alkoxy) because of the possibilities of

resonance stabilisation.

$$
\text{e.g.} \quad R-\overset{\bullet}{C}H - \overset{\overset{O}{\|}}{C} - OR \longleftrightarrow RCH = \overset{\overset{O\bullet}{|}}{C} - OR
$$

$$
Cl-\overset{\bullet}{C}HR \longleftrightarrow \overset{+}{\bullet}Cl - \overset{-}{C}HR
$$
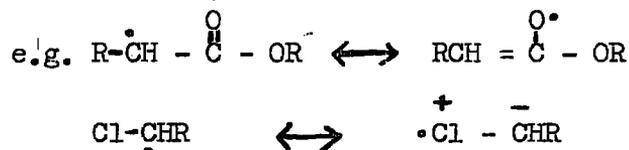
A number of workers have drawn up orders of the relative stabilising powers

of different substituents

e.g. $-Ph \succ -CN \approx -C\ominus- \succ -CO\cdot OEt \approx -CO\cdot OH \succ Me$ [101]

$I \succ Br \succ Cl \succ F \succ H$ [102]

$C_2F_5 \succ CF_3 \succ F$ [102]
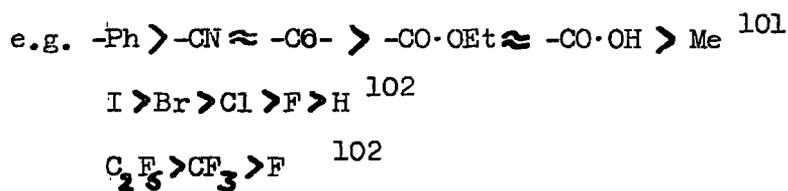
but it should always be borne in mind that such orders may also depend

to a greater or lesser extent upon effects such as the relief of steric

strain as dissociation occurs, which may contribute considerably to the

apparent resonance energies of radicals with bulky substituents.

<u>Propagation and transfer</u> In order for steps (2) and (3)

(2) $R\bullet + $ olefin $\rightarrow R$ (olefin)$\bullet$

(3) R (olefin)$\bullet + RY \rightarrow R$(olefin) $Y + R\bullet$
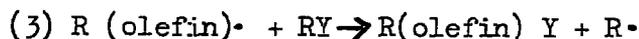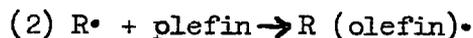
to form part of a rapid chain reaction they must have low activation energies,

and as these cannot be less than ΔH for the step involved, radical

additions are generally observed only when both steps are exothermic.

Where the R - C bond to be formed on addition is weak e.g. C -'I, step

(2) tends to be endothermic, and therefore radical additions of I_2 and HI do

not occur. Any substituent which stabilises the radical R(olefin)•

will however lead to a decrease in ΔH for this step, so that it will be

energetically more favoured. At the same time ΔH for the displacement

step (3) will be increased since the stabilised radical will be less

reactive, and exothermic reactions will be limited to cases where the

R - Y bond is relatively weak. This simple picture is complicated

by contributions to the reaction rate from steric and polar factors, but

it can be used to obtain a qualitative indication of the effects of

substituents on the extent of radical additions which is in good

agreement with experimental observations.

Considering step (2) in more detail it is evident that its rate

will depend upon the reactivity of both R• and the olefin.

<u>Reactivity of R•</u>   The greater the resonance energy of R• the greater

will be the activation energy for the addition step, owing to loss of

resonance energy on reacting, but only in the cases of very stable

radicals, such as the acyl radicals from α - β unsaturated aldehydes [103]
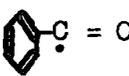
e.g.   , is the decrease in reactivity sufficient to

prevent chain propagation.

The occurrence of coulombic repulsion between the p-electron of the

attacking radical and the π-electrons of the double bond means that the

rate of addition will also be affected by the presence of electron supplying or withdrawing groups in both radical and olefin. In as far as changes in R• are concerned, reactivity with an olefin with electron supplying substituents should increase with increasing electrophilic character of the radical e.g. in going from •CH_3 to •CF_3, and vice versa for olefins with electron withdrawing substituents [104].

In the case of non-terminal olefins or those with bulky substituents the size of R may also become a critical rate determining factor.

<u>Reactivity of olefin</u>   Much information on the relation between structure and reactivity in free radical additions has been derived from co-polymerization studies carried out by Mayo and Walling [105]. Szwarc etal [104, 106 - 108] have added further data by their comparisons of the methyl and trifluoromethyl affinities of a number of olefins, and Kharasch [109 - 110] has considered trichloromethyl attack. All these results give good agreement on the way in which resonance stabilisation, steric and polar effects influence olefin reactivity.

Resonance stabilisation of free radicals has been considered in the section on initiation (P.12), and formation of the intermediate radical R(olefin)• will be favoured by the types of substituents mentioned. Such groups will however also conjugate with the double bond of the olefin, thus decreasing its reactivity. Walling [99, P.121] has shown from co-polymerization studies that although these effects are parallel, a given substituent is more effective in stabilizing a radical than in stabilizing the olefin from which that radical is formed −

Substituent X	Stabilization (K cal/mole)			
	Olefin $\begin{pmatrix} \overset{a}{\underset{b}{C}} = \overset{c}{\underset{x}{C}} \end{pmatrix}$		Radical $\begin{pmatrix} R - \overset{a}{\underset{b}{C}} - \overset{c}{\underset{x}{C}} \end{pmatrix}$	
-OAc, - Me	2.5		4	
-CH:CH$_2$, - C$_6$H$_5$	3-4		25	

This suggests that an unpaired electron is more easily delocalized than one forming part of a double bond. The net result is that olefin reactivity is increased by such substituents.

The influence of steric hindrance is clearly seen when 1 - substituted olefins are compared with those bearing an additional 2 - substituent, as in the following example given by Szwarc [106].

Olefin	Methyl affinity (Benzene = 1)
PhCH:CH$_2$	1630
PhMeC:CH$_2$	1390
Ph$_2$C:CH$_2$	2240
trans-PhCH:CHPh	205
Ph$_2$C:CHPh	85
Ph$_2$C:CPh$_2$	< 25

Substituents in the 1 - position increase reactivity through resonance stabilization, but in the 2 - position their stabilizing effect is more than counteracted by the resulting steric hindrance, since this is the preferred position for radical attack (see P.20) Similar effects are observed with other substituents, and this is probably the main reason for the decreased reactivity of internal olefins, especially cyclic ones, as

compared with terminal ones [38,111,112].

In the example given above the steric effect was working in direct opposition to resonance stabilisation, but cases are also known where reactivity is decreased through steric inhibition of resonance. Cis-stilbene is only half as reactive as the trans isomer we considered in the above series, since only one phenyl group at a time can assume the coplanarity with the double bond necessary for resonance stabilisation; and the greater reactivity of fumaric as compared with maleic esters can be accounted for on similar grounds [113].

The polar effects arising from the presence of electron withdrawing or supplying substituents on the olefin cannot always be clearly distinguished from the accompanying resonance and steric effects, but the evidence available supports the postulate that reactivity between an olefin and an "electron donor" radical is increased by substitution of electron attacking groups in the olefin, since such groups reduce the electron density at the double bond. Electron supplying substituents decrease reactivity through increased coulombic repulsion (opposing the resonance stabilising effect of these groups, so that the net result is a smaller increase in reactivity than expected). Most examples have come from co-polymerization studies [105] but simpler systems e.g. with the slightly nucleophilic methyl radical [104, 107] have provided added confirmation.

Since fluoroalkyl groups are extreme examples of electron withdrawing substituents it is to be expected that fluoroolefins will be especially

reactive with radicals of the "electron donor" type. Acyl and
α-hydroxyalkyl radicals are considered to belong to this class, since
the corresponding carbonium ions which would result on complete loss
of an electron, $R\overset{+}{C}:O$ and $R_2\overset{+}{C}\cdot OH \leftrightarrow R_2\overset{+}{C}:OH$, are fairly stable; and
the additions of aldehydes and alcohols to fluoroolefins [74] have
been found to give considerably better yields than with most hydrocarbon
olefins [99] P.274, [114].

Reactions with "electron acceptor" radicals e.g. $\cdot CF_3$ [38], [104],
$\cdot CCl_3$ [110], $\cdot SR$ [111], [115], $\cdot Si\ Cl_3$ [78], have received more attention, and
the expected reverse order of olefin reactivity has been observed e.g.
$CH_2 : CH_2 > CF_2 : CH_2 > CF_2 CF_2 > CF_2 CF : CF_2 > CF_3 CF : CFCF_3$ [38]. As with electrophilic
ionic additions replacement of vinylic hydrogen by fluorine or fluoroalkyl
decreases ease of attack, and so fluoroolefins are less susceptible
than hydrocarbon ones to these types of reagents.

Reactions competing with chain propagation

a) Reaction of R· with initiator   The specificity of initiator observed for
certain free radical additions has been accounted for on the grounds of
preferential reaction of R· with a molecule of initiator rather than
with the olefin. For example alkyl peroxides are effective for additions
of alcohols to hydrocarbon olefins but diacyl peroxides are not [114].
Since benzoyl peroxide is known to decompose rapidly in primary and
secondary alcohols [116], probably by the sequence:

(i) $(Ph\cdot CO\cdot O)_2 \longrightarrow 2\ Ph\cdot C\Theta\cdot O\cdot$

(ii) $Ph\cdot CO\cdot O\cdot\ +\ R_2 CHOH \rightarrow Ph\cdot COOH\ +\ R_2\overset{\bullet}{C}OH$

(iii) $R_2\overset{\bullet}{C}OH\ +\ (Ph\cdot CO\cdot O)_2 \rightarrow R_2 C(OH)O\cdot COPh\ +\ PhCO\cdot O\cdot$
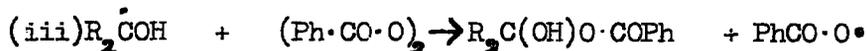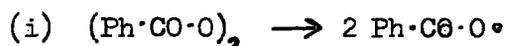
it is not surprising that step (iii) competes successfully with the

propagation step, R• + olefin →R(olefin)•. That this is probably

due to some extent to polar factors is supported by the fact that

alcohol additions to fluoro-olefins can be initiated by benzoyl

peroxide, indicating that affinities for α-hydroxyalkyl radicals lie

in the order: fluoro-olefin > benzoyl peroxide > hydrocarbon olefin.

b) <u>Allylic substitution</u> With an olefin with one or more hydrogen

atoms on the α-carbon, formation of an allyl radical by hydrogen

abstraction can compete with addition.

$$\text{>CH} - \overset{|}{\text{C}} = \overset{|}{\text{C}} \ + \ R\bullet \quad \overset{K_s}{\underset{K_a}{\rightrightarrows}} \quad \begin{cases} \overset{|}{\underset{|}{\text{C}}}\bullet - \overset{|}{\text{C}} = \overset{|}{\text{C}} \ + \ RH \\ \text{CH} - \overset{|}{\underset{\bullet}{\text{C}}} - \overset{|}{\text{C}}R \end{cases}$$
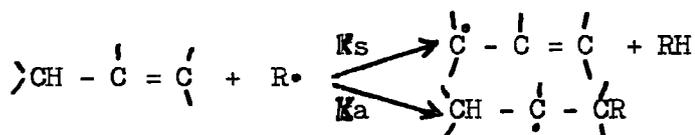
Unless the allyl radical is too stable to continue the chain, reaction

with RY results in allylic substitution products.

$$\bullet\overset{|}{\underset{|}{\text{C}}} - \overset{|}{\text{C}} = \overset{|}{\text{C}} \ + \ RY \longrightarrow \overset{|}{\underset{|}{\text{C}}}Y - \overset{|}{\text{C}} = \overset{|}{\text{C}} \ + \ R\bullet$$
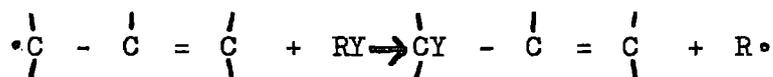
Changes in the rate-ratio K_s/K_a with changes in olefin structure

can be explained on the basis of the factors considered earlier,

viz. resonance stabilisation, steric and polar effects [112].

Where these are such as to decrease the reactivity of the olefin

towards addition, K_a will be smaller and substitution will be

correspondingly more important. Thus Huyser [112] attributes the

more prominent part played by substitution in radical reactions of

bromotrichloromethane with 2-pentene and 3-heptene, as compared with

1-octene and 1-decene, to the greater steric hindrance of addition to

the non-terminal olefins. (As K_s values for these terminal olefins are

very low, the effect of the increased statistical possibility of

allylic substitution in the corresponding non-terminal olefins should

not be significant).

Since C - H bond strengths decrease in the order primary>secondary
>tertiary, owing to resonance stabilization of the resulting radicals,
ease of abstraction of allylic hydrogen (and therefore K_s) will increase
in the same order. Therefore while addition to olefins is favoured by
stabilizing vinylic substituents, allylic substituents decrease the
extent of addition owing to increased ease of formation of the allyl
radical.

Orientation of Addition From a consideration of the factors influencing
olefin reactivity the predicted direction of addition to an unsymmetrical
olefin would be that in which :-

a) the more stable of the two possible intermediate radicals,
$R(olefin)\cdot$, is formed.

b) the initial attack is at the less sterically hindered end of
the double bond.

c) the point of attack by strongly polar radicals is influenced by
the direction of polarisation of the double bond (assuming this to be
the same as for ionic additions).

Haszeldine's studies of the free radical addition of trifluoroiodomethane
to a wide range of unsymmetrical olefins [51] have shown that the direction
of addition is in fact independent of the polarisation of the double
bond, since all olefins of the type $RCH:CH_2$ give predominantly
$RCHI\cdot CH_2CF_3$ regardless of whether polarisation is in the direction
$\overset{\delta+}{R}CH:\overset{\delta-}{CH_2}$ (R = Me,Cl or F) or $\overset{\delta-}{R}CH:\overset{\delta+}{CH_2}$ (R = CF_3, CN or CO_2 Me).
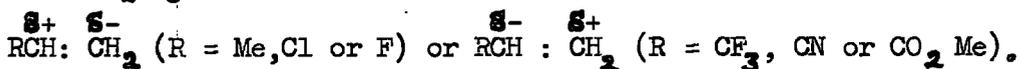
The fact that attack occurs at the terminal carbon atom is in agreement with postulate (b), although there should be little difference on these grounds between the two carbons of vinyl fluoride. Some examples have however been found in which attack occurs on the more hindered carbon,

$$\text{e.g. } CH_3CH:CF_2 + RY \longrightarrow CH_3CHRCF_2Y \quad [37]$$

$$(R \div Y = CF_3- I, C Cl_3 - Br \text{ or } Br - H)$$
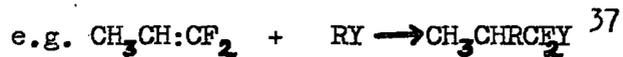
indicating that while steric effects may play a significant part in determining the direction of addition there are other factors of even greater importance.

With the assumption that in general radical stability decreases in the order tertiary $>$ secondary $>$ primary (where the terms primary, secondary and tertiary indicate the number of atoms or groups other than hydrogen attached to the carbon atom formally carrying the lone electron) [37] and bearing in mind the relative stabilising powers of different substituents (see examples P. *12*), postulate (a) has been found to be generally applicable in cases where addition goes exclusively in one direction.

A number of examples are known in which both possible isomers are formed, and consideration of these throws valuable light upon the relative importance of the factors determining the direction of addition. Patrick [117] and Huang [101] have obtained both isomers from addition of aldehydes to derivatives of β,β-dimethylacrylic acid, $Me_2C:CHX$, attributing this to the balance between the steric and stabilization effects operating at either end of the double bond. Huang has used the change in isomer ratio with change in X as a measure of the relative

stabilising influence of different groups upon the intermediate radical,
since other contributing effects remain constant in the series.
Where X = CO_2Et or CO_2H the balance is only 3:1 in favour of attack at the
$-CMe_2$ end of the double bond, but on passing to X = COMe the ratio shifts
to 10:1, and with the even more strongly stabilising group X = CN, attack
occurs exclusively in this direction.

Two isomers are formed in the addition of diethyl malonate to
oct-2-ene [118]

$$C_5H_{11}CH:CHMe \nearrow C_5H_{11}\overset{\bullet}{C}HMeCH(CO_2Et)_2 \rightarrow C_5H_{11}CH_2CHMe\ CH(CO_2Et)_2$$
(2 parts)

$$\searrow C_5H_{11}\overset{\bullet}{C}HCHMe \rightarrow C_5H_{11}CHCH_2Me$$
$$\underset{CH(CO_2Et)_2}{|} \quad \underset{CH(CO_2Et)_2}{|}$$
(1 part)
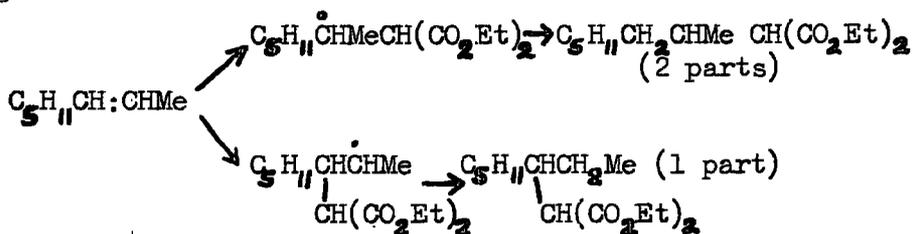
and the observed ratio has been attributed to the influence of steric
factors, since the two possible intermediate radicals should be of
similar stability as both are secondary; whereas with terminal olefins,
$RCH = CH_2$, one of the possible intermediates is a primary radical, and
attack occurs exclusively in the direction giving the more stable
secondary radical.
In the only other examples so far known (Table III), the olefins concerned
are ones in which there is little difference between stability and steric
factors favouring either direction of addition.

Table III

Olefin	Radical	% attack on C*	Reference
* $CF_2:CFCF_3$	$\cdot C_3F_7$	100[†]	59
	"	98	39
	$\cdot SiMe_3$	96	80
	$\cdot SiHMe_2$	95	80

Olefin	Radical	% attack on C*	Reference
	$\cdot SCH_3$	91	85
	$\cdot CF_3$	At least 85 [†]	53,59
	"	80	80
	"	92	39
	$\cdot SiH_2Me$	76	80
	$\cdot SCH_2CF_3$	70	85
	$\cdot PH_2$	66	80
	$\cdot Br$	At least 90 [†]	53
	"	58,62	63
	$\cdot SiH_3$	60	80
	$\cdot SF_5$	50	91
	$\cdot SCF_3$	45	85
$CF_2 : CFH$ [*]	$\cdot CFCl_2$	Mainly	119
	$\cdot SCF_3$	98	85
	$\cdot SH$	85	121
	$\cdot CF_2Br$	80	62
	$\cdot CF_3$	80	57
	$\cdot SCH_3$	75	85
	$\cdot Br$	60	57
	"	57	63
$CF_2 : CH_2$ [*]	$(\cdot SCF_3)$	(100)	(85)
	$\cdot C_3F_7$	95	120
$CF_2 : CFCl$ [*]	$\cdot CF\,Cl\,CF_2Cl$	Mainly	39

([†] Refined techniques have invalidated early claims that radical attack occurred exclusively on the CF_2 group of C_3F_6[53, 59] indicating the need for caution in considering the data at present available.)

For all the olefins in Table III attack on C* should give the more stable intermediate radical (since stabilising ability decreases in the series Cl, $CF_3 > F > H$[102]), and such attack will also be the less subject to steric hindrance. Since these directing influences are not much stronger than those operating in the reverse direction, it is not surprising that some attack at the other end of the double bond does occur. More remarkable is the variation in the extent of its occurrence with different attacking radicals. In order to account for these differences in isomer ratios, Harris and Stacey[85] and Haszeldine[80] have found it necessary to reintroduce the once discarded polarisation theory (c).

The observed variations are obviously dependent upon the nature of the radicals, and can be correlated with their relative electrophiticities, which increase in the series $\cdot SCH_3 < \cdot SCH_2CF_3 < \cdot SCF_3, \cdot SF_5$ and $\cdot SiMe_3 < \cdot SiMe_2H < \cdot SiMeH_2 < \cdot SiH_3$. Preferential attack by a radical with electron withdrawing groups might be expected at the end of the double bond where electron density is greater. As polarisation of C_3F_6 during ionic additions is in the direction $CF_2^{\delta+} : CF CF_3^{\delta-}$, with electrophilic radicals the polar effect will be working in opposition to the stability and steric effects, favouring attack on the CF group rather than on the CF_2^*. The fact that less than 50% attack by $\cdot SCF_3$ occurs on C* indicates the overiding importance of the polar directing effect in this case; but its
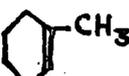
influence should become less pronounced as the electrophilicity of the radical decreases, and the proportion of addition in the direction favoured by stability and steric factors does in fact increase in this order for the thiol and silane series given above. (The anomalous positions of certain strongly electrophilic radicals e.g. $\cdot CF_3$ and $\cdot C_3F_7$ show that the present theory is not entirely adequate.)

Where the polar effect reinforces the weak directing influences of the other two effects i.e. in $CF_2 : \overset{*}{C}FH$ and $CF_2 : \overset{*}{C}H_2$,
$\delta+ \quad \delta- \quad \delta+ \quad \delta-$
nearly 100% attack on C^* occurs with strongly electrophilic radicals, but with less electrophilic ones there is a greater probability of addition in the unexpected direction.

The influence of the polar effect is only seen in cases where the normally predominating effects are weak, and even in the most extreme example available it is insufficient to direct more than 55% of the attack to the other end of the double bond. It may therefore be concluded that the most powerful influence on the direction of the free radical addition to unsymmetrical olefins is that exerted by the preferential formation of the more stable intermediate radical, and only as the energy difference between the two intermediates becomes small do steric and then polar effects become to any extent the deciding factors.

Stereochemistry of Radical Additions. The study of the stereochemical aspects of radical additions is a relatively recent addition to the field of free radical chemistry. The results of this work have been reviewed by Bohm and Abell [127], and attention will here be confined to additions to cyclohexene derivatives, which are summarised in Table IV.

Table IV

Olefin.	Reagent.	% Trans Addition.	Reference.
	NO_2Cl	62	122
	N_2O_4	58	122
	$n\text{-}C_3F_7I$	cis and Trans) no	128
	$i\text{-}C_3F_7I$	cis and Trans) figures given	128
	H Br	99.5	124,123
	H Br	99.7	124
	C_6H_5SH	94 - 99*	125
	H_2S	75 - 93*	125
	CH_3COSH	66 - 73*	125
	N_2O_4	100	122
	H Br	100	123
	C_6H_5SH	Predominantly	126
	CH_3COSH	85	126

* Stereospecificity increases as ratio thiol olefin increases.

It is seen that trans-addition predominates even though with RH this
type of addition to 1-substituted cyclohexenes gives the thermo dynamically
less stable cis isomer [129],
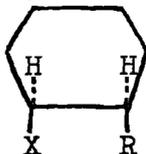
Any satisfactory explanation of this preference for a trans mechanism must
account for the decrease in stereospecificity in passing from H Br to thiols

and fluoroalkyl iodides; the influence on stereospecificity of changes
in thiol:olefin ratios; and the non-stereospecifidty of additions
to cyclohexene as compared with 1-methylcyclohexene.

Radical additions to cyclic olefins proceed by the chain mechanism
discussed earlier. It was originally thought that the attacking radical
would enter the less sterically hindered equatorial position in the
intermediate radical R (olefin).[123] . However it is now generally
agreed that an attacking radical approaches an olefin from a direction
perpendicular to the axis of the double bond, and as far cyclohexene the
least hindered route is that corresponding most nearly to an axial
direction, R is more likely to assume such a position in the cyclohexyl
radical.
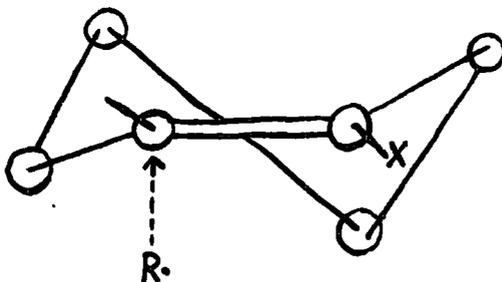
If the carbon bearing the odd electron has a pyramidal rather than a
planar configuration, (a postulate favoured by Bordwell and Hewett [126]
and Brand and Stevens [122]), reaction of R•with $\bigcirc^X$ will be
expected to give initially an intermediate of conformation (a) with X
occupying an equatorial position.

(a) X H R

(b) H R X

(c) X H R

(d) H R X
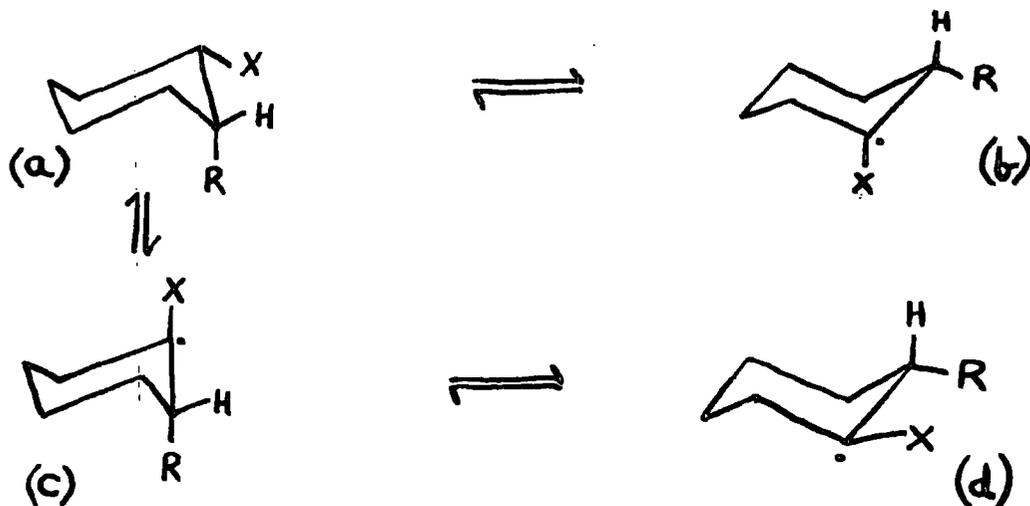
Inversion at the trigonal carbon may then occur to give (c), and both (a) and (c) may undergo ring inversion to (b) and (d) respectively. Brand and Stevens [122] ignore the latter two conformations on the assumption that ring inversion occurs much more slowly than chain transfer, and this step is considered to occur only with (a) and (c), resulting in trans and cis-addition respectively.

The extent to which cis-addition takes place will depend on the relative speeds of chain transfer and radical inversion. With efficient chain transfer agents e.g. H Br, or high concentrations of adding reagent, a high degree of stereospecificity is likely, since chain transfer will occur before (a) can be converted to (c). When ability for chain transfer is lessened e.g. with thiols, or with lower concentrations of reagent, there will be a greater chance of inversion of configuration occurring before the transfer step, so that some cis addition results by participation of conformation (c). The rate of radical inversion may also be affected by substituents on the cyclohexene ring, and the stereospecificity of addition to 1-methylcyclohexene can be explained by considering the increase in the energy of (c) as compared with (a)

resulting from steric factors, when X = methyl rather than H.

Brace [128] has determined the actual conformations of the fluoroalkyl iodide-cyclohexene adducts from a study of their N.M.R. spectra. The trans - n - C_3F_7I adduct is assigned the conformation with n-C_3F_7- and I both axial, which is to be expected if addition proceeds via the intermediate radical (a). With i-C_3F_7I however, the trans-adduct has both i-C_3F_7- and I in equatorial positions, so that addition could either have proceeded via intermediate (b), or ring inversion could have occurred after chain transfer. The preference of the bulky perfluoroisopropyl group for the equatorial position is not surprising on steric grounds, and in the case of the cis-adducts, both i-C_3F_7- and N-C_3F_7- are found to occupy equatorial positions, while iodine is in the more hindered axial position, indicating that here too ring inversion has occurred either before or after chain transfer.

So although the theory outlined above explains the data in Table IV, Brand and Steven's assumption that no ring inversion is involved is not valid when the size of R is such as to lead to considerable steric strain when it is situated axially. (The influence of steric effects has also been demonstrated with norbornene derivatives, where severe hindrance of trans-addition can result in preferential cis-addition) Other theories which have been propounded to account for the occurrence of stereospecific trans-addition include the participation of a bridged intermediate radical [123] e.g.
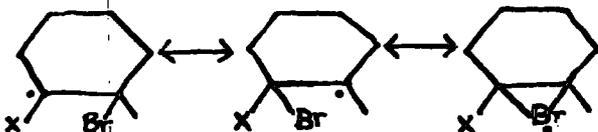
or of a π-complex [124]. Present available evidence does not substantiate these mechanisms, but further investigation is necessary before they can be dismissed entirely.

ADDITIONS OF ORGANIC MOLECULES

1. Alcohol additions Free radical additions of alcohols to fluoro-olefins have been initiated by peroxides [64, 74], AZO compounds [64] and γ-irradiation [71,75]. In all reported cases radical formation involved cleavage of an α C-H bond

$$R_2CHOH \longrightarrow R_2\overset{\bullet}{C}OH \quad + \quad H\cdot$$
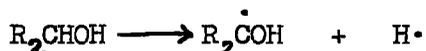
Using benzoyl peroxide Lazerte and Koshar [74] found yields of 1:1 adduct with a given olefin decreased with increasing molecular weight of the alcohol, secondary alcohols being more reactive than the isomeric primary ones, e.g. with perfluoropentene - 1 they obtained the following results:-

Alcohol	% conversion of olefin
Methanol	89
ethanol	70
i-propanol	40
n-propanol	20
s-butanol	20
n-butanol	< 5
i-butanol	< 5

On the other hand Muramatsu's results with γ-ray initiated additions show little dependence on the molecular weight of the alcohol, but an increase in reactivity (as measured by the yields of 1:1 adduct with $CFCl : CFCl$ and $CF_2 : CCl_2$) in the order:- methanol < other primary

alcohols $<$ secondary alcohols. This parallels the order of increasing

ease of chain transfer found by Urry [114] for t-butyl peroxide and

ultra-violet induced telomerizations with hydrocarbon olefins, and is

consistent with increasing resonance stabilisation and consequent ease

of formation of the α-hydroxyalkyl radicals concerned. (The change in

order of reactivity to $CH_3OH < C_3H_7OH < (CH_3)_2 CHOH < C_2H_5OH$ for additions

to $CFCl:CCl_2$ is explicable on the grounds of decreased reactivity of the

primary and secondary propanols owing to steric hindrance by the bulky

Cl atoms.)

Since there are no complicating factors involved in γ-ray initiated

additions, the order of alcohol reactivity for such reactions may be

considered as the true one, and it seems likely that the anomalous results

obtained with benzoyl peroxide arise from some competing reaction involving

this particular initiator. During the course of a study of the

decomposition of benzoyl peroxide in a number of solvents, Bartlett and

Nozaki [116] obtained the following results:-

Alcohol	% Decomposition of 0.2M Benzoyl Peroxide at 80°	
	5 min.	10 min.
methanol	33	46
ethanol	71	82
i-propanol	87	95
n-butanol	20	35

If the postulated reaction of $R_2\overset{\bullet}{C}OH$ with the peroxide,

$$R_2\overset{\bullet}{C}OH + (PhCOO)_2 \rightarrow R_2C-(OH)-OCOPh + PhCOO\cdot$$
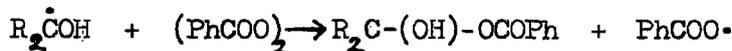
competes with the propagation step,

$$R_2\overset{\bullet}{C}OH + RfCF:CF_2 \rightarrow RfC\overset{\bullet}{F} CF_2C(OH)R_2$$
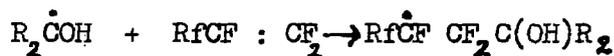
the greatest reduction in yield of adduct is likely for those alcohols

in which benzoyl peroxide shows the greatest induced decomposition rate,

and this could conceivably result in reversal of the normal order of

reactivity (i-propanol $>$ ethanol $>$ methanol). The inadequacies of this

explanation are seen in its failure to account for the low yields

obtained with n-butanol, which Urry found to have a transfer constant

of the same order as that of ethanol. The observed order of reactivity

may well involve contributions from effects such as the degree of

solubility of the olefin in the alcohol, in addition to those from

the factors already considered.

The structures of adducts derived from unsymmetrical olefins, as

determined by chemical methods [71] or n.m.r. spectroscopy [74], are

consistent with addition in the direction favoured by all three factors

influencing orientation, viz. stability, steric and polar effects;

and there is no reported formation of the less favoured isomer.

e.g. $CF_3CF : CF_2$ + $CH_3OH \longrightarrow CF_3CFH \ CF_2CH_2OH$ [74]

$CCl_2 : CFCl$ + $CH_3OH \longrightarrow CCl_2H \ CFCl \ CH_2OH$ [71]

$CCl_2 : CF_2$ + $CH_3OH \longrightarrow CCl_2H \ CF_2CH_2OH$ [71]
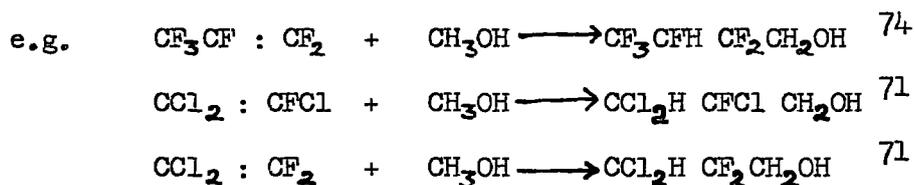
<u>Properties of alcohol adducts.</u>   As a result of the inductive effect

of fluorine and fluoroalkyl groups, the acidity of fluorinated alcohols

is greater by a factor of 10^4 than that of their hydrocarbon

analogues [130, 131]. More vigorous conditions are therefore generally

required for esterification of these alcohols, but it can usually be

accomplished by reaction with the acid halide [132], or with the acid

itself mixed with trifluoroacetic anhydride [136] or in the presence of an

acid catalyst e.g.p- toluene sulphonic acid [133].

Reactions of fluoroalcohols with sulphuric or chlorosulphonic acid [134]

$$RfCH_2OH \quad + \quad H_2SO_4 \longrightarrow Rf\ CH_2OSO_3H$$

and p-toluene sulphonic acid [135]

$$Rf\ CH_2OH \quad + \quad HOSO_2C_6H_4CH_3 \longrightarrow RfCH_2OSO_2C_6H_4CH_3$$
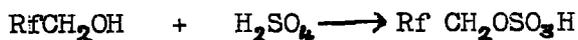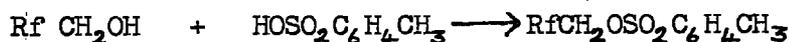
occurs fairly readily giving fluoroalkyl hydrogen sulphates and p-toluene sulphonates respectively, the latter compounds being useful fluoroalkylating agents. Phosphoric acid esters can also be prepared by reaction of the alcohol with phosphorus oxychloride, in the presence of an acid acceptor such as pyridine, or with phosphorus pentoxide [137]. Reaction conditions can be adjusted to give mono-, di- or tri-alkyl esters.

Conventional methods of ether synthesis e.g. the Williamson reaction, and reaction with diazomethane, have been successfully applied to fluorinated alcohols [10].

e.g. $CF_3CH_2ONa \quad + \quad CF_2ClCH_3 \longrightarrow CF_3CH_2OCF_2CH_3 + NaCl$

$CF_3CH_2OH \quad + \quad CH_2N_2 \longrightarrow CF_3CH_2OCH_3 \quad + \quad N_2$
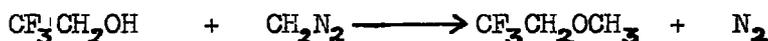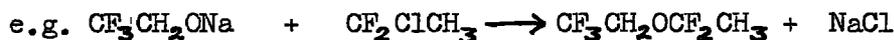
The primary alcohols obtained by addition of methanol to fluoro-olefins can be oxidised to acids by use of permanganate in glacial acetic acid [64,138], or dichromate in sulphuric acid [71, 74].

$$Rf\ CFH\ CF_2\ CH_2OH \longrightarrow Rf\ CFH\ CF_2COOH$$

Higher primary alcohols add to olefins to give secondary alcohols which are oxidised to ketones by dichromate [71, 74].

$$Rf\ CFH\ CF_2\ CHROH \longrightarrow Rf\ CFH\ CF_2COR$$
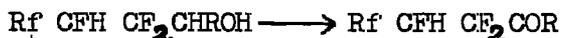
Ketones can also be obtained by photochlorination of secondary fluoroalcohols, but under these conditions oxidation of primary alcohols goes only as far as the aldehyde [139, 140]

$$Rf\ CH_2OH \xrightarrow[h\nu]{Cl_2} Rf\ CHO \quad + \quad \text{other products.}$$
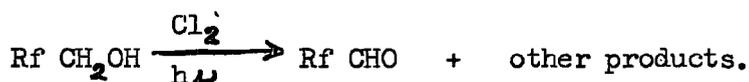
The influence of the inductive effect of fluorine upon the strength of the carbinol C - O bond is such as to render fluoroalcohols particularly resistant to dehydration. Tertiary alcohols have been dehydrated by heating them with concentrated sulphuric acid [141] or phosphorus pentoxide [71,74], but McBee found the former method ineffective for secondary alcohols, and observed cracking of the molecule rather than dehydration when samples were passed over alumina at 300 - 500 C [142]. Low yields of olefin have been obtained by use of phosphorus pentoxide at elevated temperatures [71, 74,141, 142].

$$Rf\ CH\ (OH)\ CH_2\ R \xrightarrow{P_2O_5} Rf\ CH \quad = \quad CHR$$
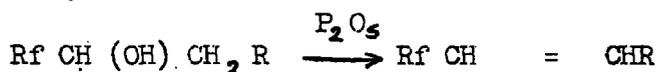
The presence of hydrogen on the γ-carbon of the alcohol adducts, Rf CFH CF CHROH (or in the case of telomers of the type H $(CF_2 CF_2)_n$-
-CHROH, on the ω-carbon) has little effect upon their chemistry, as the reactions considered above occur with both di- and tri-hydroperfluoroalkanols. The only significant difference between them is that while the former are stable to alkali, the latter undergo decomposition e.g. with 0·2N NaOH or 10% Na_2CO_3 at 100°C [74]. The source of this instability is evidently the γ-H, which can be eliminated with a vicinal fluorine by basic reagents, whereas the two α-H atoms are unreactive. Intermolecular attractive forces involving the γ or ω-H exert some influence upon physical properties of the trihydro-alcohols and their derivatives [133], so that they have higher boiling points, refractive indices and viscosities than their dihydro-analogues.

2. Aldehyde additions La Zerte and Koshar[74] and Muramatsu and Inukai [72] have obtained fluorinated ketones by peroxide initiated addition of

hydrocarbon aldehydes to fluoro-olefins.

$$Rf\ CF : CF_2 + RCHO \longrightarrow Rf\ CFH\ CF_2 COR$$

$$(R = CH_3, C_2H_5, n\text{-}C_3H_7, i\text{-}C_3H_7)$$
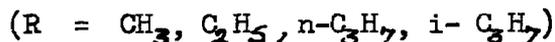
With i-butyraldehyde some halohydrocarbon formation was also observed, probably resulting from the side reaction:

$$(CH_3)_2\ CHCO \longrightarrow (CH_3)_2CH + CO$$

$$(CH_3)_2CH + CF_2 : CFCl \longrightarrow (CH_3)_2CHCF_2C\ Cl_2$$
$$\downarrow (CH_3)_2\ CHCHO$$
$$(CH_3)_2\ CHCF_2CCl_2 H + (CH_3)_2CHCO$$
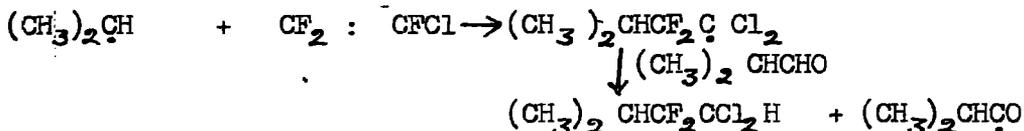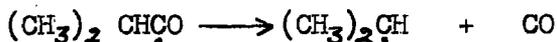
That addition to unsymmetrical olefins occurs in the direction favoured by stability, steric and polar factors, is confirmed by the interconvertibility, by oxidation and reduction, of the ketones and the corresponding alcohols of known orientation [74].

When Harris and Coffman [70] attempted the ultra-violet initiated addition of perfluoroaldehydes to fluoro-olefins, they obtained fluorotrimethylene oxide derivatives instead of ketones.

$$Rf\ CHO + Rf'CF : CF_2 \xrightarrow{h\nu}$$

$$
\begin{array}{ccc}
O & \!\!\!\!\!-\!\!\!\!- & CHRf \\
| & & | \\
F_2C & \!\!\!\!\!-\!\!\!\!- & CFRf'
\end{array}
$$
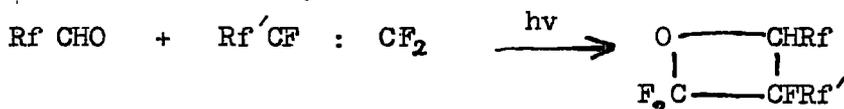
The production of analogous hydrocarbon compounds has been reported for additions of certain hydrocarbon aldehydes to di-, tri- and tetra-substituted hydrocarbon olefins [143]. In the latter examples the aldehydes concerned were ones yielding strongly resonance stabilised acyl radicals e.g. Ph-CO, which have little tendency to propagate the chain, while in the case of fluoroaldehydes hydrogen abstraction to give the acyl radical is likely to be difficult owing to the inductive effect of the fluoroalkyl group. For these cases where the usual radical chain reaction is not favoured, an alternative mechanism involving a diradical has been suggested.

$$
RCHO \longrightarrow RHC \!-\!\!-\! O \xrightarrow{\ >C = C<\ } RHC - O
$$
$$
\begin{array}{cc}
& \quad\quad\quad\quad\quad | \quad\quad | \\
& \quad\quad\quad\quad\quad >C - C<
\end{array}
$$
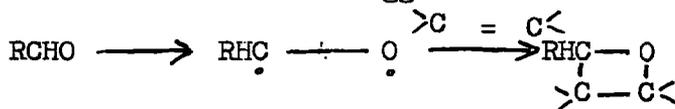
<u>Properties of aldehyde adducts</u>   The inductive effect of fluorine results in decreased electron density at the carbonyl group of fluorinated ketones.

$$Rf \longleftarrow \underset{\underset{\delta+}{\overset{R}{|}}{C} \underset{\delta-}{=\!=\!=\!O}$$
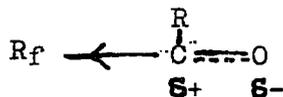
The enhanced electrophilicity of the carbonyl C favours nucleophilic additions, so that even hydrate formation occurs very readily; while the accompanying decrease in nucleophilicty of the carbonyl O reduces the solubility of fluoroketones in acids [147] .

Typical carbonyl addition reactions such as the Reformatsky and Knoevenagel reactions yield only saturated products with fluoroketones (in contrast with the α - β unsaturated esters and acids obtained with hydrocarbon ketones), owing to the resistance to dehydration derived from the increased C - O bond strength e.g.

$$C_3F_7COEt + CH_2Br\,CO_2Et \xrightarrow{Zn} \underset{Et}{C_3F_7}C(OH)\,CH_2CO_2Et \qquad [144]$$

$$CF_3COCH_3 + CH_2(CO_2H)_2 \longrightarrow CF_3(CH_3)C\,(OH)\,CH_2CO_2H \qquad [145]$$
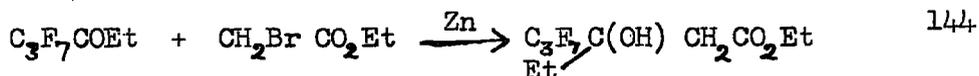
Aldol formation has been accomplished using sodamide or sodium ethoxide in organic solvents at low termperatures [146] .

$$2CF_3COCH_3 \longrightarrow CF_3(CH_3)C(OH)CH_2COCF_3$$
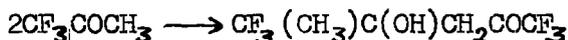
but with dilute aqueous alkali haloform cleavage predominates [146,147]

$$Rf\,COR \xrightarrow{NaOH} RfH + RCOONa$$
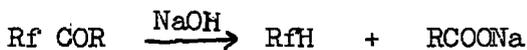
Most fluoroketones form normal 2,4-dinitrophenyl hydrazones, but when the α-carbon bears a halogen other than fluorine the intermediate hydrazone is converted to the hydrazone of the α-diketone [72] .

$$CHFClCFClCOR + 2NH_2NH\,C_6H_3(NO_2)_2$$

$$\downarrow H_2SO_4$$

$$\left[\begin{array}{c} R\,C - CFClCFClH \\ \parallel \\ N-NHC_6H_3(NO_2)_2 \end{array}\right] \xrightarrow[(NO_2)_2C_6H_3NHN]{H_2SO_4} \underset{N-NHC_6H_3(NO_2)_2}{\overset{R-C-C-CFClH}{\parallel \ \parallel}}$$
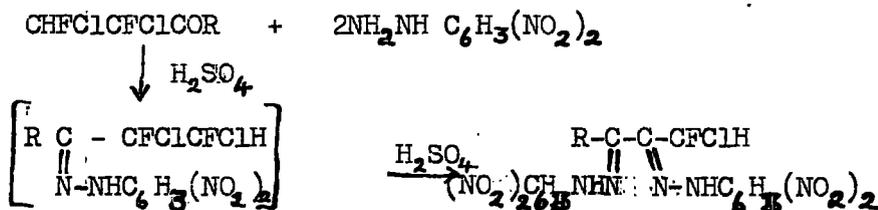
Reduction of fluoroketones to alcohols has been successfully carried out by catalytic hydrogenation [74] and with lithium aluminium hydride [147],

$$Rf \ COR \longrightarrow Rf \ CH(OH)R$$

while fluoro-acids have been obtained from permanganate oxidations [74].

$$RfCFHCF_2 COR \xrightarrow{KMnO_4 \ /acetone} RfCFHCF_2 COOH$$
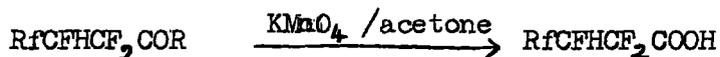
3. <u>Carboxylic acid derivative additions</u>   Although there have been a number of reported free radical additions of acids and their anhydrides, esters and nitriles to hydrocarbon olefins [118, 148 - 150], the only references to such reactions with fluoro-olefins occur in a number of patents by Hanford dealing with telomers of tetrafluoroethylene [65 - 67]. In general radical formation involves abstraction of an α-hydrogen atom from the acyl group,

$$RCH_2 CO_2 X \longrightarrow RCHCO_2 X + H\cdot \quad (X = H, R')$$

$$RCH_2 CN \longrightarrow RCHCN + H\cdot$$

although with esters some hydrogen abstraction from the alkyl group may also occur, giving a mixture of products [148].

e.g.

$$CH_3 CO_2 CH_2 CH_3 \begin{cases} \longrightarrow \cdot CH_2 CO_2 Et + H\cdot \quad (A) \\ \longrightarrow CH_3 CO_2 CHCH_3 + H\cdot \quad (B) \end{cases}$$

$$RCH:CH_2 + (A) \longrightarrow RCH_2 CH_2 CH_2 CO_2 Et$$

$$RCH:CH_2 + (B) \longrightarrow RCH_2 CH_2 CH(CH_3) OCOCH_3$$
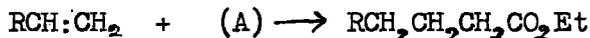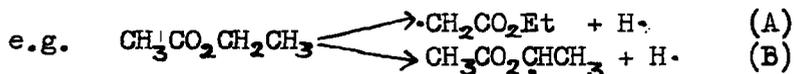
Most examples are of peroxide initiated reactions, and since competition from the olefin for the initiating radical is strong, obtention of good yields has been found to necessitate use of a high ratio of acid derivative to olefin [148, 118], or of an α-bromo derivative [149] (an α-Br being more susceptible to attack by the initiator

than either an α-H or the olefin.)

Hydrogen fluoride elimination

Reagents   Concentrated aqueous potassium hydroxide has been successfully used for dehydrofluorinating perfluorocyclohexanes [159 ÷ 163, 165 ÷ 172], cyclopentanes [173], and cyclobutanes [174 - 5], while 3,3,3-trifluoropropionic acid has been dehydrofluorinated by the addition of dilute sodium hydroxide solution at such a rate as to keep the reaction mixture only slightly basic [176].   Use of alcoholic alkali is complicated by ether formation, either by direct substitution of fluorine in the saturated molecule or by addition of alcohol to the unsaturated product; and this in fact predominates over elimination in the case of primary alkyl fluorides [179].

$$RCH_2CH_2F \xrightarrow{NaOEt} RCH_2CH_2OEt$$
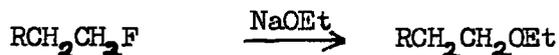
Other reagents which have been used include a potassium hydroxide slurry in mineral oil [177] and anion exchange resin [178], and for certain compounds containing fluorine activated by adjacent ether [180] or carbonyl groups [181], amides have proved effective dehydrofluorinating agents.

Mechanisms

The mechanisms of olefin-forming elimination reactions have recently been reviewed by Bunnett [182] and Ingold [183].   Three possible mechanisms have been distinguished for the reaction

$$B + H - \overset{\diagdown}{\underset{\diagup}{C}} - \overset{\diagup}{\underset{\diagdown}{C}} - X \rightarrow BH + \overset{\diagdown}{\underset{\diagup}{C}} = \overset{\diagup}{\underset{\diagdown}{C}} + X$$
$$\qquad\qquad\quad \beta \qquad \alpha$$
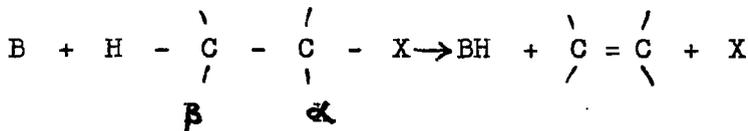
where B = base capable of removing a proton, and X = any group which can carry away its bond electrons e.g. halogen, which will leave as halide ion,

or R_3N+, R_2S+ which will leave as R_3N, R_2S. (While being primarily
concerned with the case where X = F, a greater understanding of the
factors influencing this type of reaction will be gained by considering
a wider field) The three mechanisms are:-

1. The E 1 mechanism in which the bonds C-H and C-X are broken in separate
steps, C-X rupture occurring first to give a carbonium ion intermediate
which then loses the β-proton.

$$H-C \;-\; C \;-\; X \rightleftharpoons H \;-\; C \;-\; C^+ \;+\; X$$

$$\downarrow B$$

$$\rangle C \;=\; C\langle \;+\; BH$$
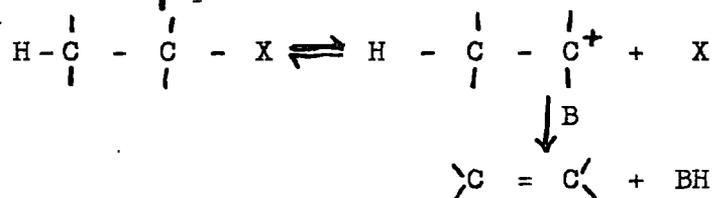
2. The E2 mechanism in which the C-H and C-X bonds are broken in a
single step.

$$B \;+\; H \;-\; C \;-\; C \;-\; X \rightarrow B\text{----}H\text{----}C\overline{\overline{}}C\text{----}X$$

Transition state

$$\rangle C \;=\; C\langle \;+\; BH \;+\; X$$
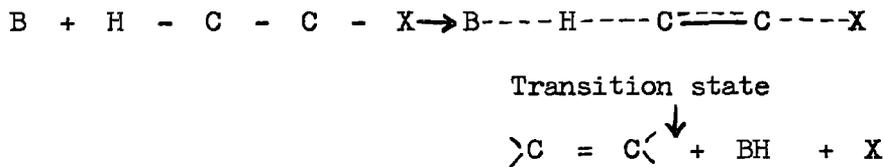
3. The E 1 cb or carbanion mechanism in which the C - H bond is broken
first.

$$H \;-\; C \;-\; C \;-\; X \;+\; B \rightleftharpoons {}^-C \;-\; C \;-\; X \;+\; BH$$

$$\rangle C \;=\; C\langle \;+\; X$$
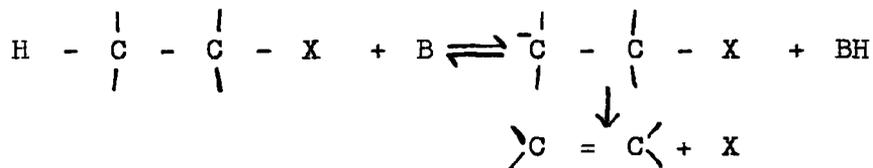
The latter two mechanisms both show second order kinetics, and
while they are therefore easily distinguished from the E 1 mechanism, it
is more difficult to determine by which of the two a given second order
elimination occurs. Positive proof of a El cb mechanism can be given

by some incorporation of deuterium in starting material recovered from

a reaction carried out in a deuterated solvent,

$$BD + B + H - C - C - X \rightleftharpoons {}^-C - C - X + BH + BD$$

$$D - C - C - X + BH + B$$

but absence of deuterated starting material does not rule out this

mechanism, since the rate of olefin formation by rupture of the carbanion

C-X bond might greatly exceed the rate of recombination of the

carbanion with hydrogen or deuterium.

It is now recognised that in the concerted E 2 mechanism the

breaking of the C - H and C - X bonds need not be entirely

synchronous, so that depending upon the relative extents of proton

transfer from the β-carbon and of electron transfer from the α-carbon,

the transition state may show a certain amount of carbanion or carbonium

ion character.

$$B\text{---}H\text{--------}\overset{\delta-}{C} \equiv\equiv C\text{---}X$$ Proton transfer more advanced than electron transfer

$$B\text{------}H \text{---}C \equiv\equiv C\text{---}X$$ Proton and electron transfer synchronous

$$B\text{-----}H\text{---} C \equiv\equiv \overset{\delta+}{C}\text{-------} X$$ Electron transfer more advanced than proton transfer

For synchronous E 2 eliminations the transition state of lowest

energy requires the four centres concerned to be in one plane [191].

In cyclohexane systems this requirement is satisfied by 1:2 - trans

diaxial substituents

(Dihedral ∠ between H and X = 180°)

A coplanar system in which substituents H and X are cis to one another may be involved in certain cis-eliminations from cyclopentane systems since in a five-membered ring such coplanarity is fairly easily attained [173, 190]. With six-membered rings however co planar cis-elimination would necessitate considerable ring deformation and is therefore far less likely to occur.
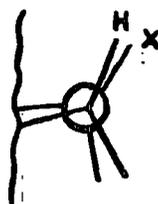
Cyclopentyl cis elimination.
(Dihedral ∠ between H and
X ≃ 0°)
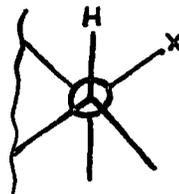
Cyclohexyl cis-elimination
(Dihedral ∠ between H and
X = 45°)

Studies of the dehydrochlorination of benzene hexachloride isomers [184 - 7] have shown that while trans-elimination occurs readily, the reaction rate shows a marked decrease in those cases in which only cis-elimination is possible. While Hughes et al [187] think that an E 2 mechanism still operates here, extra activation energy being necessary to force the relevant parts of the molecule more nearly into a coplanar configuration, Cristol suggests a carbanion mechanism, in support of which he reports the formation of a small amount of deuterated β-benzene hexachloride from a partial dehydrochlorination carried out in deuterated ethanol [186]. (There is similar evidence of a carbanion dehydrohalogenation mechanism in the case of some 2,2 - di halo - 1, 1, 1- trifluoroethanes [188 - 9]

substantiating that this mechanism, of which there are few proven

examples, does operate in certain cases)

The cis-eliminations from cyclohexanes which have been considered

so far occur only because trans-elimination is not possible,but there

are other examples known where cis-elimination is the energetically

favoured reaction. For instance some elimination of a cis-hydrogen

rather than of an alternative trans-hydrogen has been shown to take

place in cases where the acidity of the former is sufficiently

increased by a strongly electron attracting group (R) attached to

the same carbon.

(a)   (b)   in some cases.
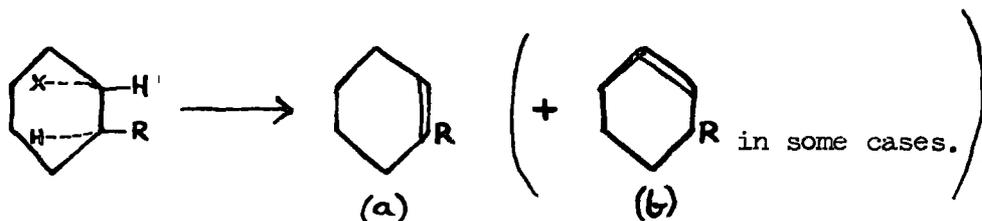
These groups, which also accelerate the more rapid trans-elimination

from the cis-isomer to give the same olefin(a),

include sulphonates [192,193], fluoroalkyl [128] and chlorine [196].

e.g.

15%   85%   [128]

40%   47%   [196]
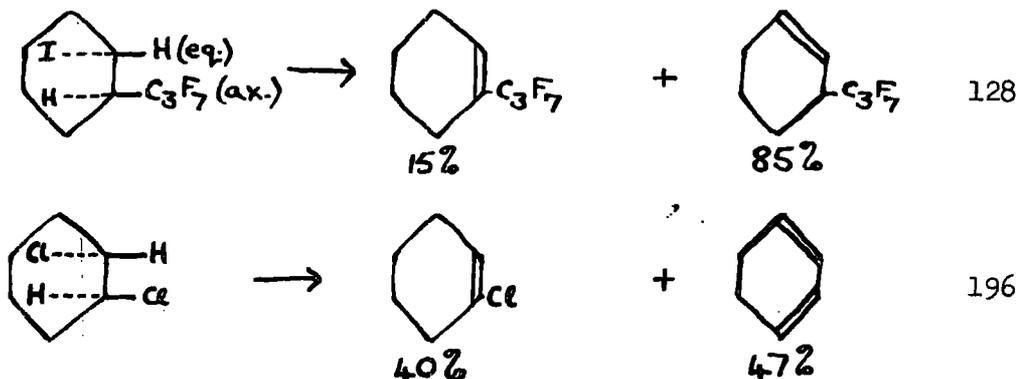
Phenyl, which can conjugate with the cyclohexene double bond in (a)

but not in (b) also favours cis-elimination [194 - 5, 197].

It is not certain however whether these eliminations proceed
by an Elcb or E2 mechanism. If the reaction does occur by the latter
path, the electron attracting β-substituent is likely to cause proton
release from the β-carbon to be considerably more advanced than
electron transfer from the α-carbon in the transition state. If
Bunnet's hypothesis [182], that the requirement for a coplanar conformation
should be less stringent the less synchronous the mechanism, is
correct, attainment of the conformation necessary for occurrence of
these cis-eliminations is more easily envisaged. It follows that
a lessening of stereochemical preference for trans-elimination should
result from any factors which favour a transition state showing a high
degree of either carbanion or carbonium ion character.

An E 2 mechanism appears to be the preferred process for dehydro-
fluorination of polyfluorinated cyclohexanes, rapid reaction occurring
when vicinal hydrogen and fluorine occupy axial positions, making
possible a planar four-centered transition state. Whereas with large
leaving groups such as ammonium, sulphonium or even larger halogens,
steric opposition to their occupation of the necessary axial position might
increase the activation energy of trans elimination [197], no such
effect is likely for the small fluorine atom.
Since fluoride ion is more easily removed from a CFH group than
from a CF_2 or CF_3 group, the reaction is further favoured by attachment
of hydrogen, or another activating substituent, to the carbon from which
the fluorine is to be eliminated, while hydrogen elimination is
encouraged by neighbouring fluorines which increase its acidity [163].

In the system (a), $- CF_2 CHF CF_2-$, the hydrogen is more acidic than in (b), $-CF_2 CHF CHF CF_2-$, but only in (b) is there a vicinal fluorine in a CFH group. Therefore on electronic grounds there should be little difference in the ease of hydrogen fluoride elimination from the two systems. In a rigid system however the two hydrogens in (b) may be trans to one another, in which case trans-elimination of hydrogen fluoride will only be able to occur in the less electronically favoured direction involving a fluorine from a CF_2 group as in (a). Under these circumstances comparison of the two types should show the effect of the increased acidity of the hydrogen in (a), and it has been found that undecafluorocyclohexane (systema) loses hydrogen fluoride at a faster rate than trans-1H,2H-decafluorocyclohexane (system b) [160].

Where the steric and electronic effects are in opposition trans-elimination does not however occur exclusively. Thus with trans-1H,2H-decafluorocyclohexane some of the electronically favoured 1H-nonafluorocyclohex-1-ene is formed in addition to the octafluorocyclohexa-1,3- diene which is favoured sterically (provided the hydrogens are in axial rather than equatorial positions) [160].

F [structure with H, H] $\xrightarrow{KOH}$ F [structure] + F [structure with H]
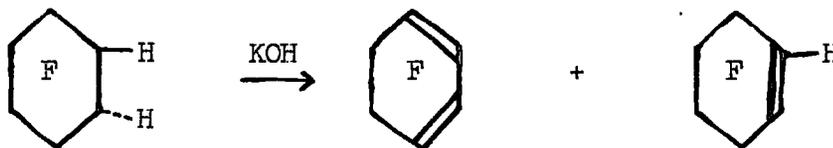
Rapid, exclusive formation of 1H-nonfluorocyclohex-1-ene occurs with the cis isomer, since this product is favoured by both steric and electronic factors.

F [structure with H, H] $\xrightarrow{KOH}$ F [structure with H]
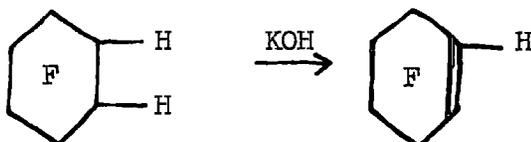
As in the cases considered earlier, these electronically favoured
cis-eliminations may occur by an E2 mechanism in which the transition
state shows strong carbanion character.

$$B\text{---}H\text{----------}C\underset{\beta}{====}C\text{----}F$$

(with substituents: F $\delta-$ and $-CF_2$ on β-carbon; H and $-CF_2$ on α-carbon)
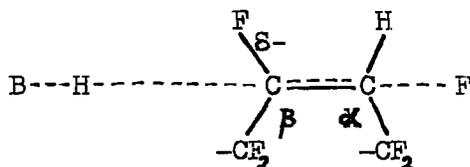
Proton release from the β-carbon will be favoured by the electron
withdrawing influence of the fluorine substituents on this and adjacent
carbon atoms, but present evidence is inconclusive as to whether or not
this is sufficiently strong for complete proton transfer to occur before
electron transfer from the α-carbon begins i.e. the El cb mechanism[165].
No deuterium exchange occurred when cis and trans-lH,2H- decafluorocyclo-
hexanes were partially dehydrofluorinated using potassium hydroxide
in heavy water[173], but as previously mentioned, this negative result
does not prove that no carbanion was formed.

The mechanism and direction of hydrogen fluoride elimination thus
depends upon the balance between steric factors which permit or
prohibit trans-elimination, and electronic factors which may work in
conjunction with or in opposition to the steric influences.

CHAPTER   2

DISCUSSION

DISCUSSION

Attempts have been made to add a variety of organic compounds to perfluoropropene and cyclic perfluoro-olefins by a free radical mechanism, but under the conditions used appreciable yields of adduct were obtained only with certain alcohols and esters, acetaldehyde and methanethiol. Additions were carried out in sealed, evacuated Carius tubes, using benzoyl peroxide (1% by weight) or γ-irradiation to initiate the reaction.

REACTION CONDITIONS AND YIELDS

1. Alcohol additions

Peroxide initiated additions

LaZerte and Koshar[74] found that maximum yields were obtained from the benzoyl peroxide initiated addition of methanol to perfluoropropene when a molar ratio of methanol to olefin of at least 5 : 1 and temperatures in the range 115 - 120° were used. Similar conditions were therefore used for a series of peroxide initiated additions of alcohols to perfluoropropene and perfluorocyclic olefins. LaZerte and Koshar found that addition was complete after 8 hrs. under these conditions, but a standard time of 24 hrs. was used for all the attempts to ensure maximum yields in all cases.

Percentage conversions of olefins to fluoroalcohols were
as follows (including LaZerte and Koshar's results with
perfluoropentene-1 for purposes of comparison) :-

Olefin Alcohol	C_3F_6	C_6F_{10}	$1,4-C_6F_8$	$C_5F_{10}-1$[74]
Methanol	66-84	87	90(68 1:1 adduct) (22 2:1 adduct)	89
Ethanol	44	43-75	56(1:1 adduct)	70
n-Propanol	41	5-17		20
i-Propanol	36	0		40
n-Butanol		7		< 5

No adducts were obtained with 2,2,2-trifluoroethyl,
allyl, crotonyl, benzyl and neopentyl alcohols and
ethylene glycol.

In all cases methanol clearly reacts to the greatest
extent, and the general trend towards reduced yields with
increasing molecular weight of the alcohol observed by
LaZerte and Koshar is discernible in the case of C_6F_{10}.

The expected increase in reactivity with increased
resonance stabilization, and consequent increased ease
of formation, of the α-hydroxyalkyl radical is seen on
comparing the yields of normal- and iso-propanol adducts
of C_5F_{10}-1. The limits of experimental accuracy do not
permit any definite conclusions to be drawn from the
C_3F_6 series, but with C_6F_{10} isopropanol failed to give any
adduct. This surprising result indicates that here, as
in the cases of certain chloro-fluoro-olefins[71], attack
by the $(CH_3)_2C.OH$ radical is sterically hindered.

γ-ray initiated additions

Benzoyl peroxide initiated additions are
complicated by side-reactions involving the initiator,
(see p. 30) leading to a reversal of the order of
reactivity found using other methods of initiation, so in
order to obtain a clearer picture of the factors influencing
the ease with which alcohols undergo free radical addition
to fluoro-olefins a series of reactions initiated by
γ-irradiation from a 100 curie Co^{60} source was carried out.

Alcohol	% conversion of C_3F_6 to adduct after 12 days	Moles alcohol / Moles C_3F_6
Methanol	16	4.8
Ethanol	88	5.8
n-Propanol	90	4.3
i-Propanol	85	4.5
n-Butanol	34	2.4
CF_3CH_2OH	-	1.2
Allyl alcohol	-	5.7
Crotonyl alcohol	- (76°)	2.0
Neopentyl alcohol	{ - - (42°)	4.9 3.6

The overall reactivity of the alcohols with the fluoro-olefins depends firstly on the ease of formation of the initial radical

(1) $RH \longrightarrow R\cdot + H\cdot$

and secondly on the tendency of that radical to attack the olefin to propagate the chain.

(2) $R\cdot + CF_3CF : CF_2 \longrightarrow CF_3\overset{\cdot}{C}F\ CF_2R$

Polar effects

Since fluorine substituents reduce the electron density at the double bond of the olefin, radicals of the electron-donor type react most readily with fluoro-olefins, and the high reactivity of alcohols as a class has been explained on these grounds (p./7). Electron donating substituents in the α-hydroxyalkyl radical ought therefore to lead to increased reactivity with fluoro-olefins. Ethanol, normal- and iso-propanol, which all have one or more α-alkyl substituent are noticeably more reactive than methanol. (The result of the n-butanol addition cannot be compared directly since a different ratio of reagents was used, but it appears to be more reactive than methanol.) However transfer constant measurements for additions of these alcohols to hydrocarbon olefins[114] show a similar order of reactivity, although these olefins should have no special affinity for electron donor radicals. Any influence exerted by the electron donating substituents in the alcohol must therefore be considered to affect the ease of radical formation (step 1) rather than the ease of radical attack on the olefin (step 2). However neopentanol, which bears the strongly electron donating t-butyl group, and might therefore be expected to form a radical very readily, gives no adduct.

While this could be due to steric hindrance of attack by this large radical (step 2), it also suggests that increasing the number of electron donating substituents in the alcohol does not have a significant effect upon the rate of step 1, and that other factors are probably more important in producing the trend observed for the lower alcohols.

Alcohols bearing α-substituent groups which should increase the electron acceptor properties of the radical, e.g. $-CF_3$, $-CH = CH_2$, $-CH = CHCH_3$, failed to react with C_3F_6. While this may be due to the decreased reactivity of this type of radical with olefins having electron withdrawing substituents, it can be explained on other grounds. In the case of CF_3CH_2OH it may be due to the difficulty of hydrogen abstraction, owing to the reduced electron density at the α-carbon caused by inductive electron withdrawal by the $-CF_3$ group; while the two unsaturated alcohols may form radicals which are too stable to propagate the chain (see below).

Resonance stabilization effects

The effect of resonance stabilization of the initial α-hydroxy alkyl radical upon overall reactivity will be both to favour radical formation (step 1) and to reduce its tendency to attack the olefin (step 2). Hyperconjugative resonance stabilization should increase with increase in the number of β-hydrogen atoms

$$\overset{\beta\quad\alpha}{R_2CH}\ \underset{\cdot}{\overset{}{C}}ROH \iff R_2C = CROH$$
$$\cdot H$$

It has been shown that secondary alcohols give higher yields of adduct than primary ones[71, 74, 114], (although this is not evident within the limits of experimental accuracy in the present series of results) and this has been interpreted as indicating that the increased ease of radical formation is more important than the accompanying retarding influence on the rate of chain propagation. Neopentyl alcohol is a primary alcohol with no β-hydrogen atoms, and radical formation will therefore be less favoured than in other primary alcohols, with the exception of methanol.

There must be some point however at which the retardation of the propagation step (2) begins to predominate, and the failures of allyl and crotonyl alcohols to give appreciable yields of adducts may well be due to the high stability of the radicals.

$$CH_2 : CH \overset{.}{C}HOH \longleftrightarrow \overset{.}{C}H_2CH : CHOH$$

$$CH_3CH : CH \overset{.}{C}HOH \longleftrightarrow CH_3\overset{.}{C}HCH : CHOH$$

$$\updownarrow$$

$$H. \ CH_2 : CHCH : CHOH$$

Steric and solubility effects

Other possible influences on reactivity to be considered are those of steric hindrance and of the degree of solubility of the olefin in the alcohol. Both of these are likely to result in lower yields of adduct with alcohols of higher molecular weight. The possibility of steric hindrance in the peroxide initiated reaction of isopropanol with C_6F_{10} has already been mentioned. Although in the majority of cases C_3F_6 formed a separate liquid layer when sealed with the alcohol in a Carius tube, the ease of conversion of olefin with ethanol, n- and i-propanol suggests that an equilibrium amount of olefin was dissolved in the alcohol layer, and as this reacted so more olefin dissolved until conversion was complete.

In certain cases where it was thought that immiscibility
of the reagents might be hindering reaction, steps were
taken to remedy this. Thus crotonyl alcohol was irradiated
with C_3F_6 at 76°, and the peroxide initiated reaction of
benzyl alcohol and C_6F_{10} was attempted with a mutual inert
solvent ($CF_2Cl\ CFCl_2$), but in neither case was there any
adduct formation.

While it is not possible, from the results obtained,
to attribute differences in alcohol reactivity in free
radical additions entirely to any one factor, the observed
order can be explained by considering a combination of
influences, of which the most important appears to be the
resonance stabilization of the radicals.

Ethylene glycol addition

The case of ethylene glycol deserves special mention.
Irradiation of a 5 : 1 mixture of the alcohol and C_3F_6 for
7 days at room temperature and then for 8 days at 76°
resulted in conversion of 74% of the olefin to a complex
mixture of compounds. The infrared spectrum of the mixture
shows strong absorption at C-H stretching frequencies but
none for O-H; whereas the spectra of all the other alcohol
adducts show strong O-H absorption bands.

It therefore seems that these adducts contain units of the type $-O-CH_2-CH_2-O-$ or $-(CH_2)_n$ but no $-CH(OH)CH_2OH$ or $-CH(OH)CHOH$ groups. Two compounds were isolated from the mixture by preparative scale V.P.C. and were found to have fluorine contents of (a) 25%, (b) 61%. Since a 1 : 1 adduct would contain 54% fluorine, the number of glycol molecules reacting with each molecule of perfluoropropene to give (a) must be considerably in excess of one, while (b) contains less than one molecule of glycol per C_3F_6 molecule. This is the only case where a reaction other than one involving radical formation by α-H abstraction appears to have occurred, but further investigation into the structures of the products is necessary before any suggestions may be made as to the actual nature of the reaction mechanism.

2. Aldehyde additions

Lazerte and Koshar[74] obtained 70% yields of ketones by heating equimolecular mixtures of aldehydes and fluoro-olefins with benzoyl peroxide for 15 hrs. at $100°$, while Muramatsu and Inutsai[72] report only 15 - 40% yields from chloro-fluoro-olefins using a 2 :1 excess of aldehyde.

Equimolar quantities of acetaldehyde and olefin were
therefore used in the present work, and heating of the
mixture with 1% benzoyl peroxide for 24 hrs. at 115 - 125°
resulted in over 90% conversion of perfluoropropene and
perfluorocyclohexene to the methyl fluoroalkyl ketones.
When a 10 : 1 excess of acetaldehyde was used with C_6F_{10}
the yield of 1 : 1 adduct was reduced to 63%, and its
isolation from the reaction mixture was complicated by the
presence of paraldehyde and another product with a tendency
to decompose. While the infrared spectrum of the 1 : 1
adduct shows a carbonyl absorption band at 1751 - 1736 cm^{-1},
that of the second product has a broad band at 1751 - 1597 cm^{-1},
indicating a greater degree of unsaturation. This probably
results from hydrogen fluoride loss involving the fluorine
atom α to the carbonyl group.
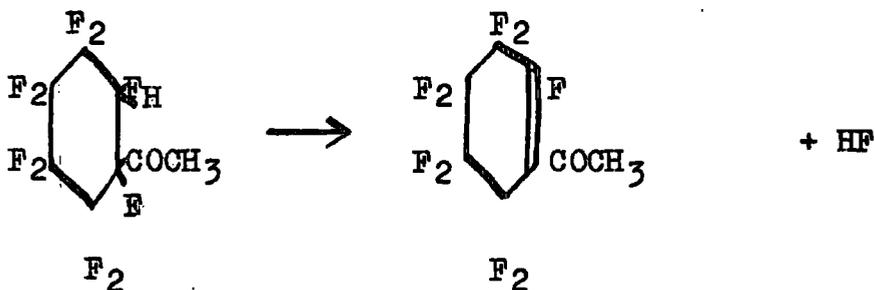
With octafluorocyclohexa-1,4-diene however, use of an equimolecular quantity of acetaldehyde under similar conditions gave only 25% conversion to the 1 : 1 adduct. Two higher boiling compounds were also obtained in low yields, probably resulting from addition of acetaldehyde across both double bonds of the diene.

No other low molecular weight aldehydes were used, but LaZerte and Koshar and Muramatsu and Inukai have found aldehydes up to n- and i-butyraldehyde to show reactivity of a similar order to that of acetaldehyde. No adduct was obtained from a 8.8 : 1 mixture of benzaldehyde and octafluorocyclohexa-1,4-diene, which is not surprising in view of the high expected stability of the benzoyl radical and observed low reactivity of the olefin towards aldehyde addition.

3. Ester additions

Peroxide initiated additions of esters have been found to require high ester to olefin ratios, to enable the ester to compete successfully with the olefin for the initiating radicals[148]. A number of ester additions to fluoro-olefins have been attempted using 1% benzoyl peroxide as initiator, under conditions found suitable for alcohol and aldehyde additions i.e. 24 hrs. at 110 - 125°.

A 48% yield of 1 : 1 adduct was obtained from an 11 : 1
molar mixture of ethyl acetate and perfluoropropene, and with
the same ester 28.5% conversion of octafluorocyclohexa-1,4-
diene resulted, although the molar ratio in this case was
only 6 : 1. Perfluorocyclohexene however gave only a trace
of product with a 5 times excess of ethyl acetate. Methyl
acetate (10 : 1) showed a similar lack of reactivity with
this olefin, but might give reasonable yields with the others.

        Diethyl malonate gave small yields of adduct with
perfluoropropene, no noticeable increase in yield occurring
when the molar ratio of ester to olefin was increased from
5 : 1 to 10 : 1. It is likely that a considerably greater
increase in the proportion of ester would be needed to give
an appreciable improvement. The product could not be
separated from the starting material by preparative scale
V.P.C. owing to extensive decomposition on the column at the
temperatures required. Prior hydrolysis and decarboxylation
of both product and unchanged diethyl malonate might have
yielded more easily separable derivatives, but the small
quantities of material available did not warrant such a
procedure. A 10 : 1 excess of diethyl malonate also gave
low yields of two products with perfluorocyclohexene.

Since γ-initiated additions should not be complicated by competition between olefin and ester for the initiator, it was considered that a lower ester to olefin ratio would be necessary, and that the chances of a radical formed from the ester attacking an olefin molecule would be favoured by a high proportion of olefin, although at the same time the rate of formation of these radicals would be reduced. However 12 days irradiation of a 1.5 : 1 molar mixture of ethyl acetate and perfluoropropene gave only a trace of 1 : 1 adduct and 89% of the olefin was recovered unchanged. Under the same conditions a 5 : 1 molar mixture of diethyl malonate and perfluoropropene gave a small yield of adduct and only 63% recovery of olefin. It seems from this that initial formation of a radical from the ester, rather than olefin attack by that radical, may be the limiting factor in these reactions; but further work to determine the optimum reaction conditions, both for γ and peroxide initiated additions, is needed before any definite conclusions may be drawn.

4. Thiol additions

The increased reactivity towards thiyl radicals
found for olefins with electron-supplying groups, as
compared with olefins with electron-withdrawing groups,
indicates that thiyl radicals act as electron acceptors[111,115].
It is therefore not surprising that thiols react much less
readily with fluoro-olefins than do alcohols and aldehydes
which form radicals showing electron-donor character.
Harris and Stacey[85] have obtained a mixture of isomeric
1 : 1 adducts from methanethiol and perfluoropropene in 11%
yield from an X-ray initiated reaction.   A similar mixture
was obtained by γ-irradiation of a 1.2 : 1 molar mixture
of thiol and olefin.   Five days' irradiation from a
500 curie Co^{60} source, plus one day with a 100 curie source,
produced 58% conversion.   Octafluorocyclohexa-1,4-diene
was much less reactive, only a small quantity of a mixture
of products resulting from prolonged irradiation.   Hydrogen
fluoride was eliminated during distillation of the reaction
mixture, so some of the observed products were in fact the
results of decomposition of the initial adducts.

Attempted benzoyl peroxide initiated additions of methanethiol to octafluorocyclohexa-1,4-diene and perfluoro-cyclohexene, using molar ratios of thiol to olefin of 1.5 : 1 and 11 : 1 respectively, were both unsuccessful. Crystals of benzoic acid were isolated from the former reaction, showing that the initiating benzoyl radicals had abstracted hydrogen either from thiol molecules or from other molecules of initiator. If thiyl radicals were formed they were apparently unable to propagate the chain to any significant extent, as is evidenced also by the low yields in the corresponding γ-initiated reaction.

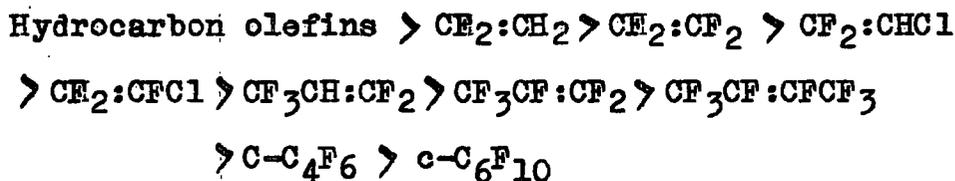## 5. Other attempted additions

No appreciable yields of adduct were obtained from the following peroxide initiated reactions under the conditions used (21 - 28 hrs. at 105 - 130°).

Addendum	Olefin	Moles addendum/Moles olefin
CH_3COOH	C_3F_6	21.4
CH_3COOH	$1,4-C_6F_8$	9.1
CH_3CN	C_3F_6	6.3
CH_3CN	$1,4-C_6F_8$	4.8
CH_3COCH_3	$1,4-C_6F_8$	8.6
$C_2H_5OC_2H_5$	C_6F_{10}	4.2
$C_6H_5OCH_3$	C_6F_{10}	6.4
$HCONH_2$	C_6F_{10}	5.7

Suitable modification of the conditions might lead to adduct formation, but these attempts are sufficient to show the great difference in reactivity between these compounds and low molecular weight alcohols and aldehydes, in free radical reactions with fluoro-olefins. This type of reaction is therefore unlikely to provide a practical route to fluorine-containing acids, nitriles, ethers and amides.
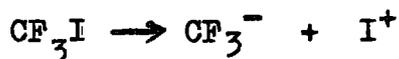
6. Iodide additions

Haszeldine[38] has compared the radical additions of trifluoromethyl iodide to a number of fluoro-olefins, and has found the following order of reactivity:-

Hydrocarbon olefins $>$ $CH_2:CH_2$ $>$ $CH_2:CF_2$ $>$ $CF_2:CHCl$

$>$ $CH_2:CFCl$ $>$ $CF_3CH:CF_2$ $>$ $CF_3CF:CF_2$ $>$ $CF_3CF:CFCF_3$

$>$ $c\text{-}C_4F_6$ $>$ $c\text{-}C_6F_{10}$

In order to compare the reactivities of octafluorocyclohexa-1,4- and 1,3-dienes with that of perfluorocyclohexene, the radical additions of trifluoromethyl iodide to these three olefins were carried out.

Thermal initiation of addition was found to be the most efficient, since ultraviolet initiation gave little or no conversion under the conditions used, while γ-irradiation appeared to cause some breakdown of the initial adducts as well as of trifluoromethyl iodide, resulting in mixtures of unsaturated products.

Thermally initiated reactions might proceed by an ionic mechanism,

$$CF_3I \longrightarrow CF_3^- + I^+$$

but the kinetics of the thermal addition of trifluoromethyl iodide to ethylene indicate a radical mechanism[151].
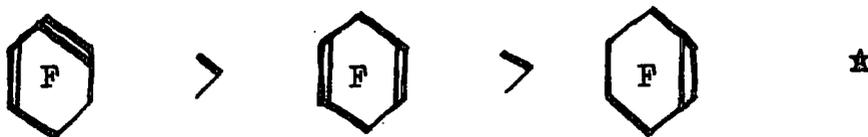
Heating of a 2-3 : 1 molar mixture of trifluoromethyl iodide and olefin at 205 - 210° for 4 days gave the following results:-

Olefin	% conversion of olefin
$1,3\text{-}C_6F_8$	26.3
$1,4\text{-}C_6F_8$	18.6
C_6F_{10}	7.3

This shows that ease of initial reaction of the olefin with the trifluoromethyl radical,

$$^\bullet CF_3 + olefin \longrightarrow CF_3 (olefin)^\bullet$$

lies in the order:

As in the case of hydrocarbon olefins the conjugated diene is the most reactive.

Examination of the reaction products showed that only 22% of the total product from the addition to the 1 , 3-diene was likely to be 1 : 1 adduct. (Although insufficient pure material was isolated for analytical purposes, comparison of its infrared spectrum with that of the 1 : 1 adduct from the 1,4-diene supports the supposition that it is the product of addition of trifluoro-methyl iodide across one double bond only, and the development of pink colouration on standing in the light shows the presence of iodine.) The remaining 78% of the product was identified by halogen analysis as a perfluoro-dimethylcyclohexene. An infrared absorption band at 1733 cm^{-1} proved the presence of a double bond; and n.m.r. spectroscopy favoured the structure

ɡ $\boxed{F}$ represents a compound in which all unindicated carbon substituents are fluorine atoms.

(A)   rather than   (B)
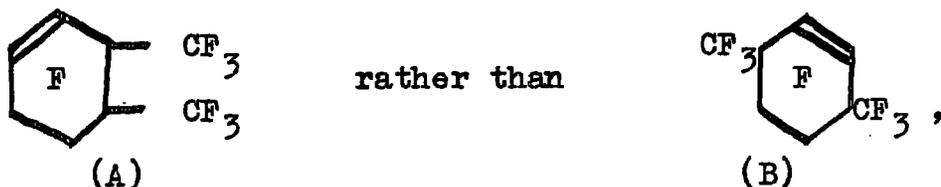
on the grounds of the presence of two CF_3 resonance peaks
(with chemical shifts of -4.03 and -3.33 p.p.m. relative to
CF_3COOH as external reference), although two CF_3 peaks could
arise from conformations of B.

The only previous report of addition of trifluoromethyl
groups at both ends of a double bond, rather than of a
trifluoromethyl group and iodine, is for the ultraviolet
initiated addition of trifluoromethyl iodide to perfluoro-
cyclohexene[38]. Haszeldine obtained a mixture comprising
86% of 1-iodo-2-trifluoromethyldecafluorocyclohexane and
14% of perfluoro-1,2-dimethylcyclohexane. In the present
case only 7.3% conversion to 1-iodo-2-trifluoromethyldeca-
fluorocyclohexane was found for perfluorocyclohexene, so
that only a minute amount of the bistrifluoromethyl derivative
would be formed if the two products were obtained in the same
ratio as before, and it might easily remain unnoticed when
the reaction mixture was worked up.

Only 4-iodo-5-trifluoromethyloctafluorocyclohexene was
isolated from the reaction with the 1,4-diene, though here
again the possible formation of traces of a bistrifluoromethyl
adduct cannot be ruled out.

Considering these products it is seen that the
initially formed CF_3 (olefin). radical may react in one of
three ways.

(i) CF_3 (olefin)· + $CF_3I \rightarrow CF_3$ (olefin) I + ·CF_3
(chain transfer)

(ii) CF_3 (olefin)· + $CF_3I \rightarrow CF_3$ (olefin)CF_3 + I· (chain transfer)

(iii) CF_3 (olefin)· + ·$CF_3 \rightarrow CF_3$ (olefin)CF_3 (chain termination)

Radical displacements on carbon atoms of the type (ii)
are rare and therefore (iii) is more likely to be the step
involved in formation of the bistrifluoromethyl derivatives.
Since trifluoromethyl iodide molecules are greatly in excess
of trifluoromethyl radicals in the reaction mixture,
collisions resulting in chain transfer (i) are statistically
the more probable, and only radicals with a low reactivity
in this step will exist long enough for collision with a
trifluoromethyl radical, leading to step (iii), to occur.
Comparison of the percentages of iodo derivative in the total
product gives a measure of the relative ease with which the
respective CF_3 (olefin)· radicals undergo the transfer step (i).
The order of reactivity of the radicals is found to be:-

(100%??)   (86% - u.v. reaction[38]) (22%)
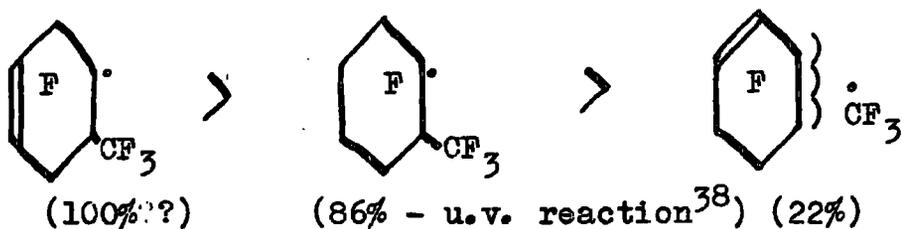
Since steric hindrance of step (i) should not differ markedly for these three radicals, there must be some other reason for the low reactivity of the radical obtained from the 1,3-diene.   If it has the structure , this low reactivity (and its ease of formation), can be easily explained on the grounds of resonance stabilisation involving canonical forms such as .
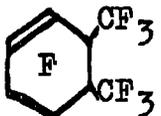
An attempt to add heptafluoroisopropyl iodide to octafluorocyclohexa-1,3-diene, using the thermal initiation conditions which proved suitable for the trifluoromethyl iodide additions, gave only trace amounts of three products. This reduced yield, with an iodide which should be a better chain transfer agent than trifluoromethyl iodide, is probably due to steric hindrance of attack by the perfluoro-isopropyl radical, as in the case of perfluorocyclohexene and the radical from isopropanol.

Relative reactivities of cyclic fluoro-olefins

It has been seen in the preceding section that the three olefins under consideration show the order of reactivity towards the trifluoromethyl radical:-

$$1,3-C_6F_8 > 1,4-C_6F_8 > C_6F_{10}$$
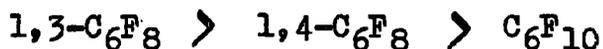
and Haszeldine[38] has shown that perfluorocyclobutene is also more reactive than perfluorocyclohexene. Comparison of the yields of adducts from peroxide induced additions of methanol to cyclic perfluoro-olefins gives the following order, which is the reverse of the one expected.

| Olefin	% Conversion
C_6F_{10}	87
$1,4-C_6F_8$	90
C_4F_6	60
$1,3-C_6F_8$,	0

This order does however resemble the one found for conversion of the olefins to CF_3 (olefin)I adducts. This order has been attributed to the relative ease with which the radicals derived from the olefins undergo chain transfer, and a similar explanation seems likely in this case.

In the trifluoromethyl iodide additions the overall yield
of products depended on the rate of the propagation step,
since those radicals which failed to undergo chain transfer
(step i) could combine with trifluoromethyl radicals (step iii).
In the case of methanol there is no evidence of the formation
of a product of the type CH_2OH (olefin)CH_2OH by a step
analogous to step (iii).   Therefore provided the rate of
the propagation step

$$\cdot CH_2OH \ + \ \text{olefin} \longrightarrow \cdot(\text{olefin})CH_2OH$$

is high, the total yield of adduct will depend on the rate
of the transfer step,

$$\cdot(\text{olefin})CH_2OH \ + \ CH_3OH \longrightarrow H(\text{olefin})CH_2OH \ + \ \cdot CH_2OH.$$

If the 1,3-diene forms the radical ,
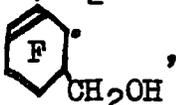
resonance stabilisation, as postulated in the case of ,
could reduce chain transfer efficiency, resulting in the
observed low yields.   The radicals ,

and on the other hand would be expected to undergo

chain transfer fairly readily to give reasonable yields of
H(olefin)CH_2OH adducts, and this too is the observed result.

Perfluoro-3,4-dimethylcyclohexene, formed by the reaction of the 1,3-diene with trifluoromethyl iodide, does not appear to undergo any further reaction with the iodide in the reaction mixture. This suggests that the rate of formation of the $(CF_3)_3 C_6F_8 \cdot$ radical is very low or that such a radical fails to react by either step (i) or step (iii), and the lack of reactivity with methanol may similarly be due to a slow rate for either the propagation or the transfer step.

STRUCTURE AND PROPERTIES OF ADDUCTS

1. Alcohol and acetaldehyde adducts

Infrared Spectra

The infrared spectra of all the alcohol adducts in the liquid state show a broad, strong absorption band in the region 3333 - 3448 cm^{-1} and a sharper, weaker band between 3597 and 3631 cm^{-1}. These are the stretching frequencies characteristic of hydrogen bonded and 'free' OH groups respectively. The increased intensity of the 'free' OH absorption, as compared with that in non-fluorine-containing alcohols, is attributed to weakening of the hydrogen bond because of the reduced basicity of the oxygen atom in fluorinated alcohols[130, 131].

This effect apparently overrides the opposing effect of the increased acidity of the hydrogen atom. Spectra of alcohols in the solid state show only a band at 3333 cm^{-1}, as the hydrogen bonded form is favoured by the reduced intermolecular distances.

The spectra of the acetaldehyde adducts show bands in the region 1733 - 1754 cm^{-1} which are attributable to C=O stretching. Such a shift to higher frequencies from the region 1705 - 1725 cm^{-1} (hydrocarbon ketones) is characteristic of halogen substituted ketones.

Saturated alcohol adducts have no absorption in the C=C stretching region, but products of addition across one double bond only of octafluorocyclohexa-1,4-diene have a band between 1748 and 1754 cm^{-1} (CF=CF).

Isomers

Studies of the analytical chromatograms and n.m.r. spectra of the adducts have shown that most free radical alcohol additions give mixtures of geometric and/or optical isomers.

(i) Perfluoropropene adducts

Taking first the perfluoropropene adducts, the analytical chromatograms (obtained using a Perkin Elmer fractomer, with di-n-decylphthalate as stationary phase, at temperatures from 23 to 50° below the boiling point of the adduct) gave the following picture:-

C_3F_6 + MeOH   One major component plus a trace of compound of shorter retention time.

C_3F_6 + EtOH   A single broad peak (could not be resolved into two by lowering column temperature).

C_3F_6 + Pr^nOH   2 overlapping peaks in the ratio 1 : 1.25.

C_3F_6 + Bu^nOH   2 overlapping peaks in the ratio 1 : 1.5.

C_3F_6 + Pr^iOH   Single narrow peak.

C_3F_6 + CH_3CHO Single narrow peak.

Isomer formation could arise from:

a) Occurrence of both possible orientations of addition
   i.e. CF_3CFHCF_2R and CF_3CFRCF_2H.

b) Some radical formation involving abstraction of a
β, γ or δ hydrogen instead of the usual α hydrogen
(except in the case of methanol).

c) Optical isomerism involving the asymmetric α-carbon atom
(not applicable to methanol and i-propanol).

LaZerte and Koshar[74] found that addition occurred
exclusively by radical attack at the $=CF_2$ end of the double
bond of perfluoropropene and similar terminal fluoro-olefins,
giving products of the type Rf $CFHCF_2R$. Confirmation that
a similar orientation of addition exists in the present
examples comes from n.m.r. spectroscopy, which has shown
that where two isomers have been formed (in the adducts with
ethanol, n-propanol and n-butanol) both contain a CF_2R and
a CFH group (see p. 96). The only possible examples of
addition in the opposite direction to give CF_3CFRCF_2H are
the small quantities of unidentified material obtained from
the methanol, n-propanol and n-butanol additions. In the
latter two cases these compounds showed longer retention
times than the major adducts and are more likely to be of
higher molecular weight. The proportion of unidentified
material in the methanol adduct mixture was too low for any
peaks arising from its presence to be discernible in the
n.m.r. spectrum.

There have been no reports of radical formation
from alcohols involving abstraction of other than
α-hydrogen atoms. While abstraction of hydrogens attached
to the secondary β-carbon in n-propanol and to secondary
β- and γ-carbons in n-butanol should occur fairly easily,

in the cases of ethanol and isopropanol all the β-hydrogens are attached to primary carbon atoms and are therefore unlikely to be abstracted in preference to α-hydrogens. Thus while the isomerism of the n-propanol and n-butanol adducts could be accounted for by theory (b), it does not offer an adequate explanation of the appearance of two isomers in the n.m.r. spectrum of the ethanol adduct.

The only theory which accords with all the facts is (c). Two isomers are observed for adducts having $R = CH(OH)CH_3$, $CH(OH)C_2H_5$, $CH(OH)C_3H_7$ (and $CH(CH_3)OCOCH_3$, which will be discussed later), but not for those in which $R = CH_2OH$, $(CH_3)_2COH$ and $COCH_3$. While all the adducts have one asymmetric carbon ($CF_3\overset{*}{C}FHCF_2R$), isomers which show two groups of peaks in the CFH and CF_2R regions of the ^{19}F spectra, and are in most cases distinguishable by analytical V.P.C., are limited to those with a second asymmetric carbon in the group R.

(ii) Adducts of cyclic perfluoro-olefins

In the case of perfluorocyclohexene-alcohol adducts only addition of methanol gives two components which are distinguishable by V.P.C., and even here the peaks overlap to a great extent. However the n.m.r. spectra of the adducts give clear evidence of the presence of at least two components in each case. The ^{19}F spectra of the adducts

with ethanol and higher alcohols i.e. those alcohols containing an asymmetric carbon, show three chemically shifted peaks attributable to CFH groups. This suggests that while two optical isomers should occur for each component, only in one case is the difference in environmental conditions of the CFH fluorines of the two isomers such as to give rise to two chemically shifted peaks (see p. 99).

Two components, one greatly in excess of the other can be distinguished by V.P.C. in the perfluorocyclohexene-acetaldehyde adduct. N.M.R. studies indicate that the major component has both hydrogen and acetyl substituents in equatorial positions, while the minor one is the cis isomer with an equatorial hydrogen and axial acetyl group.

Since the alcohol adducts show similar chemically shifted groups, they too are believed to be mixtures of trans, e,e and cis e(H), a(R) isomers. The reasons for these assignments are discussed in the section on n.m.r. spectra, P. 100-105

The chromatograms of the octafluorocyclohexa-1,4-diene adducts show two peaks in the ratio 1 : 2 for the methanol adduct and three in the ratio 1 : 3 : 6.5 for the ethanol adduct. The number of distinguishable isomers corresponds to the number of CFH peaks in the respective

[19]F n.m.r. spectra. The similarity of these spectra to those of the corresponding perfluorocyclohexene adducts indicates that these two are cis e(H), a(R) and trans e,e isomers. The n.m.r. spectrum of the 1,4-diene-acetaldehyde adduct suggests that this also exists in two such isomeric forms, in contrast to the perfluorocyclohexene adduct, which is predominantly the trans isomer.

Steric course of addition

Current theories relating to the stereochemistry of radical, additions to cyclohexene derivatives have been outlined on pages 24 - 29. If these are accepted, attack by the radical R• upon perfluorocyclohexene should give the initial radical (a), which may undergo ring inversion to (b) or inversion at the trigonal carbon to form (c), which may itself undergo ring inversion to (d).

(a)

(b)

(c)

(d)
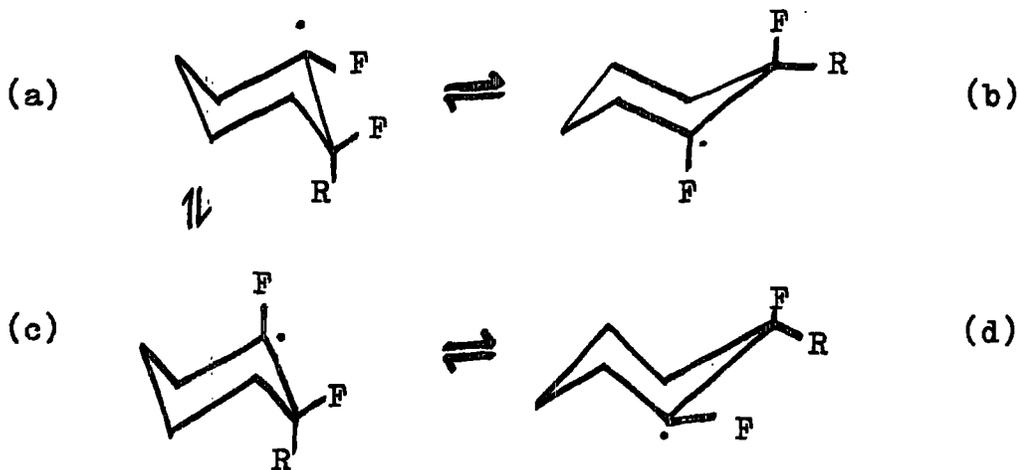
If inversion to (c) occurs before the chain transfer step, $RC_6F_{10} \cdot + HR \rightarrow RC_6F_{10}H + R\cdot$, the product will be the observed cis e(H), a (R) adduct. It is of interest to note that a slight decrease in the proportion of cis isomer formed can be traced on passing from the addition of methanol to perfluorocyclohexene and octafluorocyclohexa-1,4-diene to the addition of the more efficient transfer agent, ethanol (see table on p. 84).

The trans adduct which is obtained is the sterically more favoured e,e conformer; and while it may be derived from radical (b) following ring inversion of radical (a), there is also the possibility that it arises after chain transfer by inversion of the less stable a, a conformer.

It is difficult to suggest why almost exclusive trans addition of acetaldehyde to perfluorocyclohexene should occur, since factors such as chain transfer efficiency and intramolecular electrostatic attractions which might favour trans addition, would be expected to have a similar effect upon addition to octafluorocyclohexa-1,4-diene, instead of which this olefin undergoes both cis and trans addition.

Physical properties

Most of the alcohol and acetaldehyde adducts are colourless liquids of fairly high viscosity, and a few isomers which have been isolated in the pure state have been found to be solids.

e.g. (ring with F) CH_2OH , (ring with F) $CH(CH_3)OH$, (ring with F) $COCH_3$.
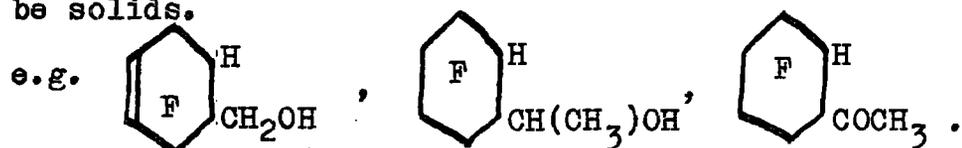
Comparison of the physical properties of these α, α, γ - trihydrofluoro-compounds with those of the corresponding α, α -dihydro- ones shows an increase in boiling point of about 20° as well as a higher refractive index, resulting from intermolecular H---F bonding involving the γ -hydrogen.

e.g.

Compound	B.p. $^{\circ}$c. (X = H)	B.p. $^{\circ}$c. (X = F)
$CF_3CFXCF_2 CH_2OH$	115	96.5 (Ref. 152)
$CF_3CFXCF_2CH(OH)CH_3$	120	101 (")
$CF_3CFXCF_2CH(OH)C_2H_5$	132	114 (Ref. 147)
$CF_3CFXCF_2CH(OH)C_3H_7$	150	128 (")
$CF_3CFXCF_2C(CH_3)_2OH$	129	108 (")
$CF_3CFXCF_2COCH_3$	78	58 (")

2. Ester adducts

Most information about the structures of the adducts obtained from octafluorocyclohexa-1,4-diene and perfluoropropene with ethyl acetate has been derived from their ^{19}F and ^{1}H n.m.r. spectra.

The presence of a =C$\underline{F}$ resonance peak (ϕ = 155 ppm) in the ^{19}F spectrum of the 1,4-diene adduct confirms that addition has occurred across one double bond only; and six groups of peaks in the high field region are attributable to the C$\underline{F}$H and C$\underline{F}$R resonances of the three stereoisomers which are distinguishable by analytical V.P.C. These may be optical isomers or three of the four conformers possible for

i.e. having H(a), R(a); H(e), R(e); H(e), R(a) or H(a), R(e).

The ^{19}F spectrum of the perfluoropropene adduct shows that it is a mixture of two isomers, each of which has a CFH and a CF$_2$R group. The direction of addition is therefore CF$_3$CFHCF$_2$R, as in the examples considered earlier, and here too the two products are believed to be optical isomers involving an asymmetric carbon in the group R.

This group appears to have the structure $-CH(CH_3)OCOCH_3$ rather than $-CH_2COOCH_2CH_3$ or $-CH_2CH_2OCOCH_3$ i.e. radical formation has occurred exclusively by abstraction of hydrogen from the α-carbon of the ethyl group rather than from the β-carbon or from the acetyl group. This conclusion is drawn from a study of the ^1H spectra of the adducts, which contain two peaks of intensity 1, attributable to C$\underline{H}$F and C$\underline{H}$CH$_3$, and two of intensity 3, attributable to the two CH$_3$ groups, one showing doublet structure from coupling with vicinal hydrogen. Although the expected quartet structure of the C$\underline{H}$CH$_3$ peak (resulting from coupling with the methyl group) is lacking, the observed spectra are otherwise in good agreement with the structure $-CH(CH_3)OCOCH_3$, but give no evidence for the presence of ethyl or $-CH_2CH_2-$ groups as required for the other possible structures.
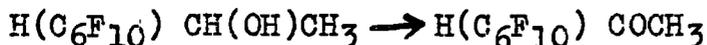
REACTIONS OF ADDUCTS

1. <u>Esterification.</u> 2, 2, 3, 4, 4, 4-hexafluorobutanol formed a 3,5-dinitrobenzoate when refluxed with the acid chloride in benzene with a trace of pyridine.

$$(NO_2)_2C_6H_3COCl + CF_3CFHCF_2CH_2OH \longrightarrow (NO_2)_2C_6H_3COOCH_2CF_2CFHCF_3$$
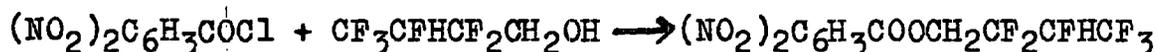
2. <u>2,4-dinitrophenylhydrazone formation.</u>   Rapid hydrazone

formation occurred when 1,1,1,2,3,3 hexafluoropentanone-4

was added to a solution of 2,4-dinitrophenylhydrazine in
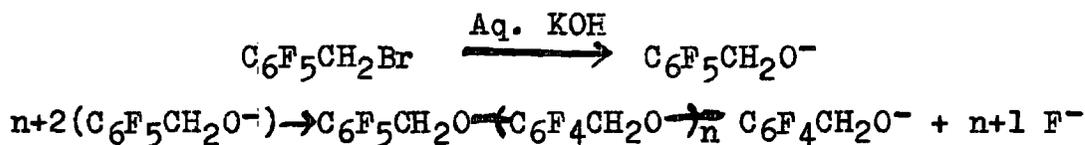
methanol with sulphuric acid.

$$CF_3CFHCF_2COCH_3 + (NO_2)_2C_6H_3NHNH_2 \rightarrow CF_3CFHCF_2C(CH_3)NNHC_6H_3(NO_2)_2$$
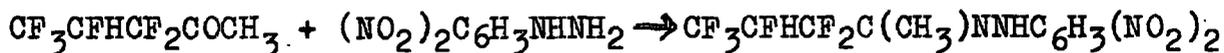
3. <u>Oxidation.</u>   The cis isomer of methyl (2H - deca-

fluorocyclohexyl) methanol was oxidised to the corresponding

ketone, the cis form of 2H-deca-fluorocyclohexyl methyl ketone,

by heating with potassium dichromate in sulphuric acid.

$$H(C_6F_{10}) \ CH(OH)CH_3 \rightarrow H(C_6F_{10}) \ COCH_3$$

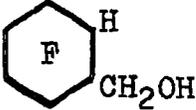Even after 27 hrs. at 95° only a 49% yield of ketone was

obtained.

4. <u>Dehydrofluorination.</u>   <u>Reaction conditions.</u>   In attempts

to find the optimum dehydrofluorination conditions for cyclic

fluoro-olefin alcohol adducts, 2H-octafluorocyclohex-4-enyl

methanol was treated with potassium hydroxide in mineral oil

at temperatures of up to 130°;   anion exchange resin at $20 - 55^O$;

and aqueous potassium hydroxide.   The first two methods

yielded mixtures of liquid products (Fig. 2a, Page /4/)

accompanied by formation of dark brown polymeric material.

Excess 2N potassium hydroxide solution at room temperature

gave a slightly simpler product mixture (Fig. 2b) from which

an impure sample of the major component (iii) was isolated by

preparative scale V.P.C. and was found to show strong

absorption in the infrared at 1786, 1757, 1724 and 1639 cm^{-1},

indicating a high degree of unsaturation.   The accompanying

orange solid product had a molecular weight in the region

500 - 750; and the infrared spectrum showed, in addition to

considerable absorption in the C = C stretching region

1776 - 1620 cm^{-1}, a decrease in the intensity of the OH

relative to the CH stretching bands as compared with the

starting material.   This suggests the occurrence of polymer

formation involving ether linkages of the type $\boxed{F}$-CH$_2$O-$\boxed{F}$.

Haszeldine[153] has reported a similar type of polymer from

the reaction of $C_6F_5CH_2Br$ with aqueous potassium hydroxide.

$$C_6F_5CH_2Br \xrightarrow{\text{Aq. KOH}} C_6F_5CH_2O^-$$

$$n+2(C_6F_5CH_2O^-) \rightarrow C_6F_5CH_2O\text{---}(C_6F_4CH_2O)_n\ C_6F_4CH_2O^- + n+1\ F^-$$

Since use of ion exchange resin or of potassium

hydroxide in mineral oil resulted in too vigorous a reaction,

a series of reactions using aqueous potassium hydroxide were

carried out with 2H-decafluorocyclohexyl methanol to determine

the concentration, temperature and time necessary for

elimination of one molecule of hydrogen fluoride per alcohol

molecule.   The best results were obtained by prolonged

treatment of the alcohol with 1N potassium hydroxide solution

at room temperature.   After 7 hrs. analytical V.P.C. showed

a slight excess of olefin over unchanged starting material,
and while a similar extent of reaction was found after only
$2\frac{1}{2}$ hrs. at 55°, this was at the expense of more polymer
formation. (The latter reaction predominated when the
potassium hydroxide concentration was increased to 4.5N, only
high molecular weight products being obtained). Addition of
one equivalent of dilute alkali over a period of some hours,
so that the alkali concentration in the reaction mixture
remained low, gave the least by-product formation. After
30 hrs. the 2H-decafluorocyclohexylmethanol reaction mixture
contained unchanged starting material and a single product
of shorter retention time in the ratio 1 : 3, and a further
13 hrs. reaction time brought about no significant increase
in the proportion of product. Using similar conditions for
a number of cyclic fluoro-alcohols, the following results
were obtained:-

Alcohol	Ratio olefin to unchanged starting material	Ratio trans : cis isomers in starting material
(ring) F, H, CH_2OH	3 : 1	~1.5 : 1
(ring) F, H, $CH(OH)CH_3$	1.7 : 1 [*]	
(ring) F, H, CH_2OH	2 : 1 [*]	2 : 1
(ring) F, H, $CH(OH)CH_3$	3 : 1 [⊕]	2.5 : 1
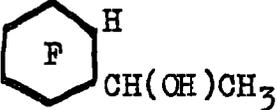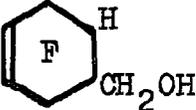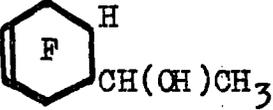
[*] Shown to be pure isomer by n.m.r.

[⊕] Shown to be pure isomer by V.P.C.

Samples of unchanged starting material were examined by V.P.C. and n.m.r. spectroscopy and were found to be pure geometric isomers or enriched in one isomer at the expense of the other. Correlation of the chemically shifted peaks of the alcohols with those of the C_6F_{10} - CH_3CHO adducts, indicates that the isomers which eliminate hydrogen fluoride to the greatest extent are the trans ones having both H and CH(OH)R groups in equatorial positions. The ethanol adduct mixtures show three CFH peaks in the ^{19}F spectrum, but only one occurs in the spectrum of the isomer which was recovered unchanged, and analytical V.P.C. confirms that of the three

distinguishable $H(C_6F_8)CH(OH)CH_3$ isomers, two undergo 100%
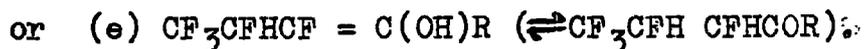conversion to olefin. Comparison of the ratios of product
to unchanged alcohol with those of the two starting material
isomers shows that in most cases little dehydrofluorination
of the cis isomer can have occurred. (Two and three peaks
are distinguishable by V.P.C. in the olefins from $H(C_6F_{10})CH_2OH$
and $H(C_6F_8)CH(OH)CH_3$ respectively, but the nature of this
isomerism is not certain.)

It was not possible to obtain a keto-olefin from
2H-decafluorocyclohexyl methyl ketone since with dilute alkali
dehydrofluorination was accompanied by haloform cleavage.
The infrared spectrum of the product mixture suggested that
1H-nonafluorocyclohexene was the chief component, probably
resulting from the reaction sequence
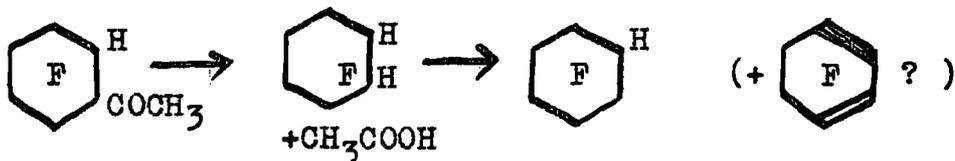
Little dehydrofluorination of the perfluoropropene
alcohol adducts occurred under the mild reaction conditions
used for the cyclic alcohols, but 2.5N potassium hydroxide at
100° gave the following results with the propanol adducts:-

-86-

Alcohol	Reaction time	No. of Products	% unchanged starting material
$CF_3CFHCF_2CH(OH)C_2H_5$	$2\frac{1}{2}$ hrs.	2 (ratio nearly 1:1)	0
$CF_3CFHCF_2C(OH)(CH_3)_2$	6 hrs.	2 (ratio 14:1)	20

Although fairly high percentage conversion of
$CF_3CFH\ CF_2CH_2OH$ occurred when the alcohol was stirred with
2.5N potassium hydroxide solution at 75° for $\frac{1}{2}$ hr., production
of two olefins was accompanied by considerable decomposition
and formation of polymeric by-products. At 50° however
nearly 50% conversion to the olefin mixture with little by-
product formation resulted after $9\frac{1}{2}$ hrs. stirring with 2N
potassium hydroxide.

Structures of dehydrofluorinated products

The positions of the double bonds in the olefins
obtained in the above dehydrofluorinations were assigned by
studying the infrared and n.m.r. spectra. Two products are
possible for the cyclic fluoroalcohols, e.g.

(a)   (b)

while the perfluoropropene adducts, $CF_3CFHCF_2CH(OH)R$,
could give:

(c) $CF_3CF = CFCH(OH)R$,

(d) $CF_2 = CFCF_2CH(OH)R$

or (e) $CF_3CFHCF = C(OH)R$ ($\rightleftharpoons CF_3CFH \ CFHCOR$);

(Possibility(e) does not apply in the case of the isopropanol adduct.)

Structure (e) is ruled out since the infrared spectra of the olefins and the corresponding saturated alcohols are identical in the 2.5 to 3.5 μ region.   (c) and (d) can be distinguished by the position of the C = C absorption which occurs at the following frequencies.

Saturated compound	C = C absorption in olefin (cm^{-1})
$CF_3CFHCF_2CH_2OH$	1733
$CF_3CFHCF_2CH(OH)C_2H_5$	1724
$CF_3CFHCF_2C(OH)(CH_3)_2$	1712

For comparison the C = C stretching frequencies in a number of terminal and internal fluoro-olefins (measured mostly in the gaseous state) are listed below.

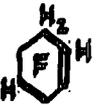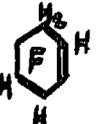|	Compound	$\nu\ (cm^{-1})$	Reference
$CF = CF_2$	$c-C_4F_8-CF=CF_2$	1785	155
	$C_2F_5CF=CF_2$	(1792 (1799	154 41
	$CF_3CF=CF_2$	(1798 (1799	52 41
$CF = CF$	$C_2F_5CF=CFC_2F_5$	1713	52
	$-(-CF_2CF=CFCH_2-)-_n$	1724	156
	$RfCF=CFR$	1730	157
	$CF_3CF=CFCF_3$	1733	154, 41
	$CF_3CF=CFH$	1742	52

It is clear that in all the alcohols the double bond is
internal rather than terminal i.e. the correct structure is
(c) rather than (d).   This is to be expected since bond
strength differences suggest that a 'secondary' fluorine atom
on the β carbon will be more easily removed than a 'primary'
fluorine on the δ carbon in $\overset{\delta}{C}F_3\ \overset{\gamma}{C}FH\ \overset{\beta}{C}F_2\ \overset{\alpha}{C}H(OH)R$.   (The terms
primary, secondary, etc., refer to the number of substituents
other than fluorine attached to the same carbon as the
fluorine atom in question.)

N.M.R. studies confirm this position of the double bond, and show that $CF_3CF = CF\ CH(OH)C_2H_5$ is a mixture of cis and trans-geometric isomers, while $CF_3CF = CFC(OH)(CH_3)_2$, which will suffer greater steric interaction in the cis form, exists predominantly as the trans isomer. (P. *106*). By analogy the two forms of $CF_3CF = CFCH_2OH$ are believed to be cis and trans-isomers.

Dehydrofluorination of methyl, 1,1,2,3,3,3,-hexafluoro-propyl sulphide also gives two products, which are probably geometric isomers of $CF_3CF = CF\ SCH_3$. The $C = C$ infrared absorption occurs at 1692 cm^{-1}, indicating an internal $CF = CF$ double bond, shifted to lower frequencies because of the attached sulphide group.

The infrared spectra of a number of fluorine containing cyclohexenes and cyclohexadienes have been examined, and some of the observed $C = C$ frequencies are listed below.

Compound Cyclohexenes	$C = C$ bond	ν (cm^{-1})	Reference
	CH=CCl	1660	204
	CH=CH	1695	157
	CH=CH	1682	157,163
	CH=CH	1690	204

Compound Cyclohexenes	C = C bond	ν (cm^{-1})	Reference
(structure)	CF=CH	(1714 (1710 (1707	157 160 165
(structure)	CF=CH	1710	204
(structure)	CF=CH	1717	157,163
(structure)	CF=CH	1713	157,163
(structure)	CF=CH	1715	161
Trans (structure) Cis	CF=CH CF=CH	1722 1720	}157
(structure)	CF=CH	1711	162
(structure)	CF=CH	1710	162
(structure)	CF=CH	1710	162
(structure)	CF=CF	(1745(liq.) (1754(gas) (1739(C Cl4)	* 158 159
(structure)	CF=CF	1752	157

Compound Cyclohexenes	C = C bond	ν (cm^{-1})	Reference
H〔F〕	CF=CF	1747	157
Trans H〔F〕 Cis H〔F〕H	CF=CF CF=CF	1750 1745	}157,163
Trans H〔F〕H Cis	CF=CF CF=CF	1755 1746	}157,163
Cis+trans. H〔F〕 Cis CH₂OH	CF=CF CF=CF	1748 1742	* *
Cis+trans. H〔F〕 Cis HOHC CH₃	CF=CF CF=CF	1754 1751	* *
Br〔F〕Br	CF=CF	1754	159
CF₃〔F〕I	CF=CF	1761	*
CF₃〔F〕CF₃	CF=CF	1733	*

Cyclohexa-1,4-dienes

〔F〕	CF=CF	(1745(liq.) (1739(gas) (1739(C CCl₄)	* 157 159
H〔F〕H	(CF=CF) (CH=CH)	1770,1688	163
H〔F〕H	CF=CH	1744,1711	161

Cyclohexa-1,4-dienes

 CF=CH   1737(weaker)   161
                              1707

 (CF=CH)   1729,1676   16**2**
                     (CH=CH)

 (CF=CF)   1789,1718   164
                     (CF=C Cl)

Cyclohexa-1,3-dienes

 CF=CF   (1751,1709(liq)   *
                              (1754,1721(gas)   Durham-
                              (workers
                              (1753,1713(C Cl$_4$) 159

 (CF=CF)   1734,1635   161,163
   (CH=CH)
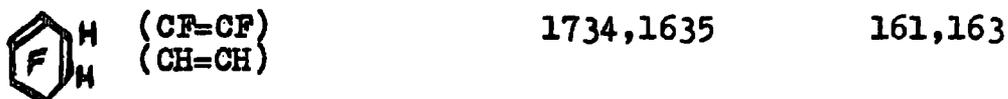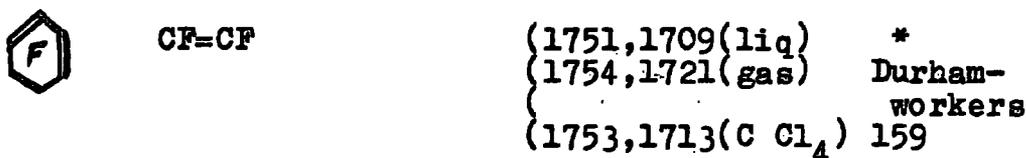
* = present work

       These examples show that for cyclohexenes
CF=CF absorption generally occurs at 1739-1755 cm^{-1}, regardless
of substituents at other positions in the ring, CF=CH at 1710-1722
cm^{-1}, and CH=CH at 1682-1695 cm^{-1}.   All the cyclohexadienes,
apart from octafluorocyclohexa-1,4-diene, show two C=C absorption
bands (at frequencies which are often slightly shifted from those
shown by the component double bonds when they occur singly).

The new cyclic olefins were found to have C=C bands at the following frequencies:-

Compound	ν (cm^{-1})
(ring) $^H_{CH_2OH}$ - HF	1712
(ring) $^H_{CH(OH)CH_3}$ - HF	1692
(ring) $^H_{CH_2OH}$ - HF	1776, 1721
(ring) $^H_{CH(OH)CH_3}$ - HF	1773, 1715
(ring) $^H_{CH_2OH}$ - HF (vigorous reaction conditions)	1786, 1757, 1724, (1639)

In passing from $CF_3CF=CFH$ to $CF_3CF=CF\ CH_2OH$ the C=C absorption shifts from 1742 to 1733 cm^{-1}, and if a shift of similar magnitude occurs in cyclic olefins, (ring)CH_2OH should absorb in the region 1701-1713 cm^{-1}, while increasing alkyl substitution in the alcohol side chain should shift the band to even lower frequencies. The observed positions for the cyclohex-enyl alcohols are therefore consistent with structure (a), (ring)$CH(OH)R$, rather than with (b), (ring)$CH(OH)R$, which would be expected to absorb in the 1739-1755 cm^{-1} region. This direction of hydrogen fluoride elimination is confirmed by N.M.R. spectroscopy (P. 105), and while no conclusions as to the

position of the new double bond in the cyclohexadienyl alcohols
can be drawn from the infrared data, n.m.r. studies indicate
that here too it is the more easily removed "tertiary" fluorine
that is eliminated, giving a 1,4 - rather than a 1,3-diene.

F—CH(OH)R $\xrightarrow{-HF}$ F—CH(OH)R
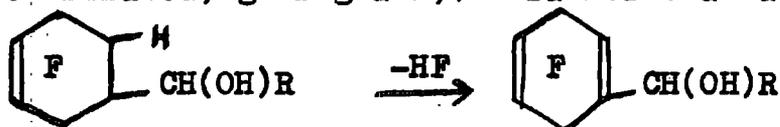
Only when vigorous reaction conditions were used was there any
sign that some hydrogen fluoride elimination might have
occurred in the alternative direction to that favoured by
electronic factors.

In both cis and trans isomers the hydrogen atom is
believed to be equatorially situated, which means that in neither
case can the requirement for a di-axial coplanar transition
state for trans-elimination be met.   It is therefore not
surprising that the rate of dehydrofluorination is slow, and that
in fact little or no elimination occurs from the cis isomer in
which both hydrogen and the CFR fluorine occupy equatorial
positions.   Cis-elimination of equatorial hydrogen and axial
fluorine from the trans isomer does occur, possibly by a
carbanion mechanism but more probably by an E2 mechanism in
which the transition state shows strong carbanion character
(see P.44).   It is not clear why a similar mechanism does not
operate in the case of the cis isomer, since here too the
inductive effect of fluorine substituents should favour proton
release.   One possible explanation could be the failure of the

cyclohexene rings to exist in a true chair-conformation, so that an "equatorial" hydrogen might be able to form a more nearly coplanar transition state with an "axial" fluorine than with an "equatorial" fluorine,

F "equatorial"

H

F "axial"
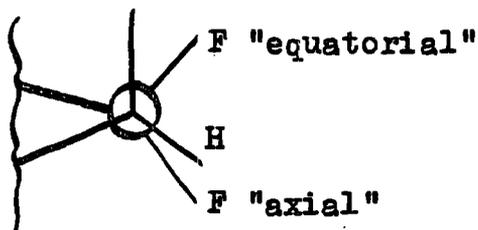
In the extreme case of a boat conformation a cis-coplanar transition state would be possible, and Tatlow and co-workers[204] have suggested that cis-eliminations from cyclohexanes may involve boat transition states. The activation energy for cis-eliminations from hexachlorocyclohexanes has been found to be 12 k.cal/mole higher than for trans eliminations[185]; and while the energy differences between boat and chair forms, have not been measured for substituted cyclohexanes, the value of 5.5 k.cal/mole for cyclohexane itself[205] suggests that formation of a boat transition state may well be energetically reasonable in these other cases. This must however remain mere speculation until more conformational and kinetic data are available.

Interpretations of N.M.R. Spectra

1. Perfluoropropene adducts

There are two possible structures for the product obtained on addition of RH to perfluoropropene, namely

CF_3CFHCF_2R(I) and CF_3CFRCF_2H(II). In either case the ^{19}F spectrum should show four chemically shifted groups of peaks arising from the CF_3, CF and the two non-equivalent CF_2 fluorine nuclei. In structure I the CFH fluorine would give rise to a group of peaks in the chemical shift range ϕ = 200-250 p.p.m. from $CFCl_3$,[201] with a geminal FH coupling constant of the order of 40-50c/s[202]; while in Structure II the CFR fluorine peak would be in the region ϕ=100 p.p.m. and would not contain such a large coupling constant. The two non-equivalent geminal fluorines in the CF_2H group of II would give an AB quartet which would be further split by geminal FH coupling with J_{FH}=40-50 c/s.

The ^{19}F spectra of the adducts in which R=CH_2OH, $CH(OH)CH_3$, $CH(OH)C_2H_5$, $CH(OH)C_3H_7$, $CH(CH_3)_2OH$, $COCH_3$ and $CH(CH_3)OCOCH_3$, all show peaks in the CFH range ϕ=207-217 p.p.m., with J_{FH} coupling constants from 43-48 c/s, while CF_2R fluorine nuclei resonate in the region ϕ=113-135 p.p.m. The spectra clearly indicate that the true structure is I; and further confirmation comes from the ^1H spectra of these adducts, since there is no 1:2:1 triplet with J_{FH} splitting of 40-50 c/s as expected for the CF_2H group of structure II.

Where R contains an asymmetric carbon atom i.e. when R=$CH(OH)CH_3$, $CH(OH)C_2H_5$, $CH(OH)C_3H_7$ and $CH(CH_3)OCOCH_3$, the ^{19}F spectrum of the adduct shows two groups of peaks of equal intensity in the CFH region, each with geminal FH coupling,

while the CF_2R region shows two overlapping AB quartets, also of equal overall intensity.   The most satisfactory explanation is that these spectra occur as a result of the existence of structure I in two optically isomeric forms.
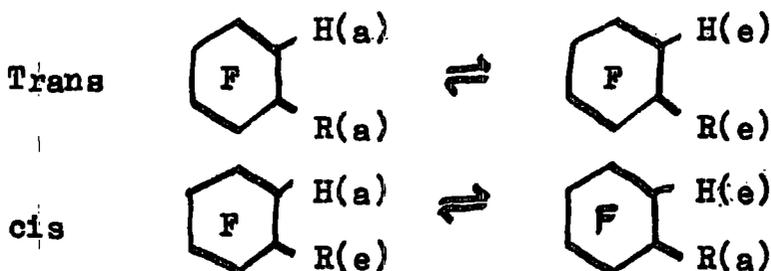
2. Cyclic perfluoro-olefin adducts

The ^{19}F spectra of the adducts ⬡(F)(H)(R)   (where $R=CH_2OH$, $CH(OH)CH_3$, $CH(OH)C_2H_5$, $CH(OH)C_3H_7$ and $COCH_3$) all show a number of peaks with chemical shifts in the range $\emptyset=116$–149 p.p.m. which are assigned to the ring CF_2 fluorine nuclei.   In compounds of the type ⬡(F)(H)(R)   ($R=CH_2OH$, $CH(OH)CH_3$, $COCH_3$ and $CH(CH_3)OCOCH_3$), peaks arising from the resonances of the CF_2 fluorines occur in the range $\emptyset=98$–127 p.p.m, while an intense peak at 155 p.p.m. is assigned to the two $CF=CF$ fluorines.

The methanol adduct mixtures obtained from perfluoro-cyclohexene and octafluorocyclohexa-1,4-diene show four peaks in the high field region (Fig.(i)). On treatment with potassium hydroxide, hydrogen fluoride is eliminated preferentially from component A, and examination of the unreacted alcohols, now greatly enriched in component B, shows that peaks 1 and 3 belong to B, and 2 and 4 to A.   A fifth high field peak which appears in the spectra of the adduct mixtures when $R=CH(OH)CH_3$, $CH(OH)C_2H_5$ and $CH(OH)C_3H_7$, is assigned to component A on similar grounds.

Molecules of the type [cyclohexane ring with F, H and R] and [cyclohexene ring with F, H and R] can exist in both cis and trans forms, and for each geometric isomer there are two possible conformations, i.e. in the transform both substituents may be either axially or equatorially situated, while the cis form may have H axial and R equatorial or vice versa.

Trans [ring structure with F, H(a), R(a)] ⇌ [ring structure with F, H(e), R(e)]

cis [ring structure with F, H(a), R(e)] ⇌ [ring structure with F, H(e), R(a)]

A sample containing cis and trans isomers, both of which were only slowly interconverting between the two conformations, would therefore show eight chemically shifted peaks in the high field region (4 $C\underline{F}R$ and 4 $C\underline{F}H$). If the rate of interconversion of the conformers was rapid or if each isomer existed in a single conformation, only two peaks would arise from each isomer. The presence of four peaks in the spectra of the methanol adduct mixture indicates that each component is either a mixture of rapidly interconverting conformers or a single conformer. In the latter case A and B could be two conformers of the same isomer or single conformers of different isomers.

When the group R contains an asymmetric carbon two

High Field Region of ^{19}F Spectra   Fig. (i)

(60 Mc/s)
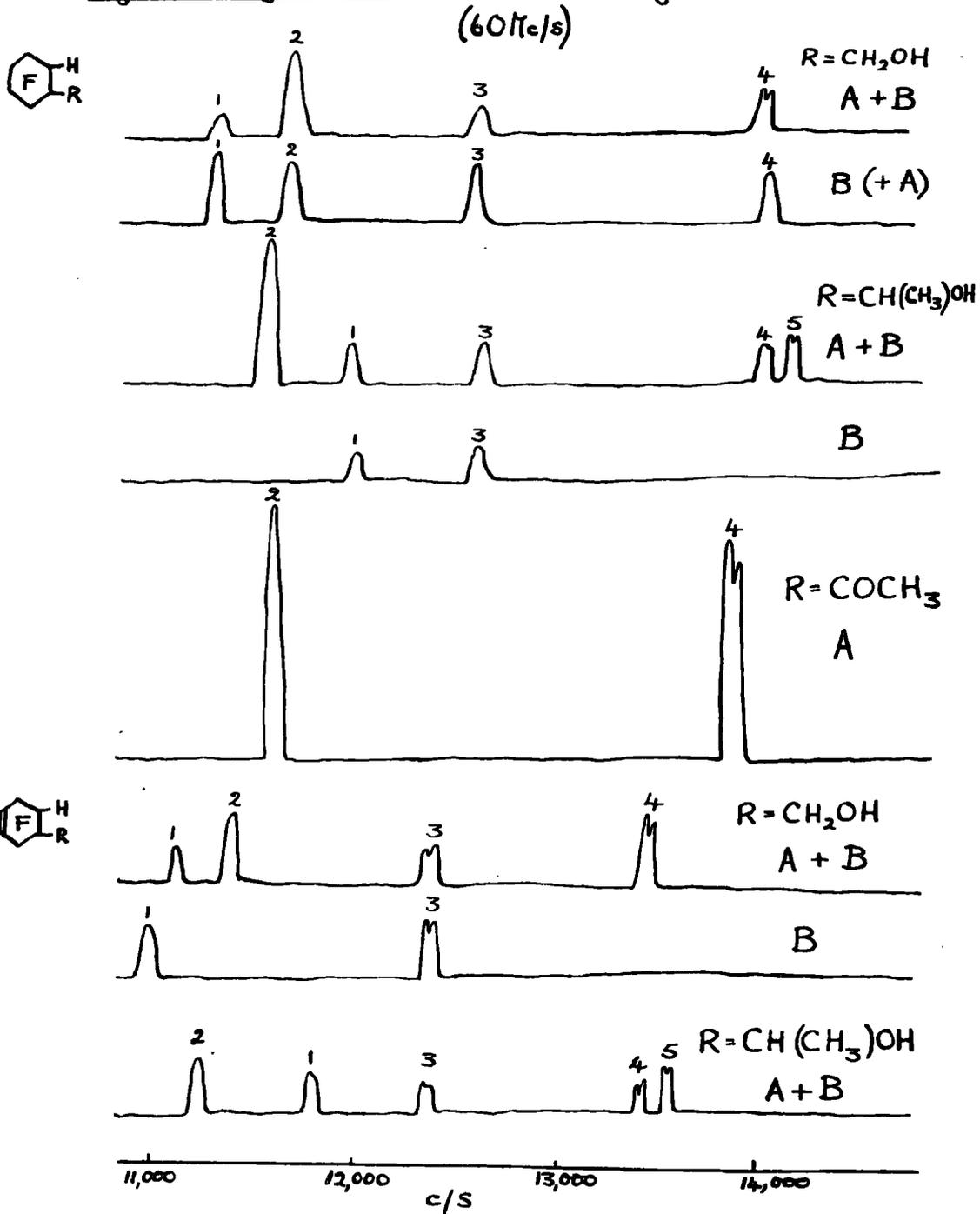
optical isomers are possible for each conformer (or mixture of interconverting conformers), and this is the explanation suggested for the appearance of a third CFH peak in the spectra of the higher alcohol adducts.   The number of CFR peaks remains unchanged, indicating that while the CFH fluorine nuclei have different environments in the two optical isomers, both CFR fluorines have similar environments.   Each optical isomer has three possible configurations about the C-C bond, which may be represented schematically (for the case where R=CH(OH)CH$_3$) as:
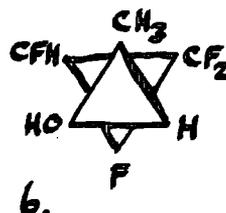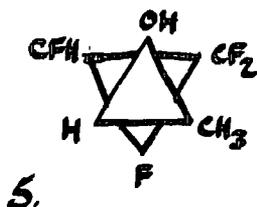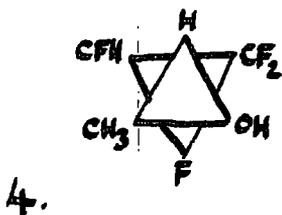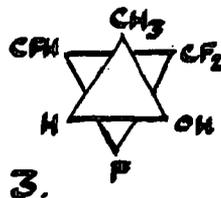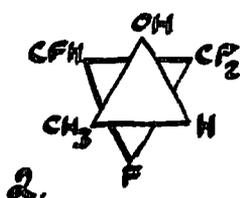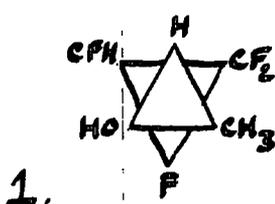
The requirement for similar environments for the CFR fluorines only would be met if steric hindrance or electrostatic attractions caused the isomers to exist predominantly in one pair of configurations i.e. 1 and 4, 2 and 5 or 3 and 6. Complete rotational freedom would result in equivalent environments for both CFH and CFR fluorines in the two optical isomers.   The fact that only A shows two CFH peaks may therefore

mean that only in this component is the energy barrier to free rotation high enough to cause the predominance of one pair of configurations.
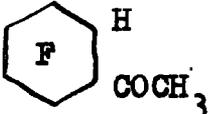
The chemical shifts of the two high field peaks of the major adduct of perfluorcyclohexene and aceteldehyde are so close to those of peaks 2 and 4 of the alcohol adducts that it is reasonable to conclude that this compound has the same conformation as the alcohols of type A.   The sharpness of the ketone spectrum makes it a particularly suitable example for closer study.

<u>Configuration A</u>

In order to interpret the spectrum of (A) a number of assumptions are made, based on observations of the spectra of perfluorocyclohexane[198] and dihydrodecafluoro-cyclohexanes[199,200].

While the ^{19}F spectrum of perfluorocyclohexane consists of a single broad line at room temperature, at $-66^{\circ}C$ this is resolved into four peaks typical of an AB system.


The molecule is thought to exist in the chair configuration, and the room temperature spectrum is interpreted as arising because the molecule is interconverting at a rate faster than the chemical shift difference, $\Delta \nu$, between axial and

equatorial fluorines.   By reducing the temperature to $-66^{\circ}C$
the rate of interconversion is brought below the value of $\Delta \nu$
so that the spectrum of a fixed conformer can be observed.
The chemical shift, $\Delta \nu$, between axial and equatorial
fluorine is found to be 18.2 p.p.m., and the coupling constant
between geminal fluorines Jgem=284 c/s.

Studies of 1,2-dihydrodecafluorocyclohexanes[200]
indicate that this value for the chemical shift between axial
and equatorial fluorine (18.2 p.p.m.) occurs only when each
fluorine nucleus in a CF_2 group has only fluorine neighbours
both through bonds and through space.   When a CF_2 group has
all fluorine neighbours except for an equatorial hydrogen
on an adjacent carbon, the axial and equatorial fluorines are
equally shielded and give rise to a single peak.   Thus
in [structure] , when both hydrogens are equatorial the two
equivalent F_2 groups at positions 3 and 6 give a single peak,
while the fluorine nuclei at positions 4 and 5 are hardly
affected and give an AB quartet with $\Delta \nu$ = 18.2. p.p.m.
and Jgem=280-290 c/s.   In compounds with two axial hydrogens
the chemical shift of 18.2 p.p.m. is absent from the spectrum
since no pair of geminal fluorine atoms has only fluorine
neighbours.

The ^{19}F spectrum at 60 Mc/s of   [structure] $COCH_3$ (isomer A)
shows twelve peaks in the range 7000-9000 c/s arising from the
resonances of the CF_2 groups (Fig.(11)a).   Peak 7 can be
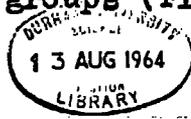
attributed to two equivalent geminal fluorine nuclei, and the
other eleven peaks comprise three AB quartets with two peaks
overlapping to give peak 11.   Peaks 1 and 4, 2 and 5, and 3
and 6 form the low field halves of the quartets and peaks 8 and
9, 10 and 11, and 11 and 12 the high field halves.   The
relative intensities suggest that the chemical shifts, δ AB,
of the three quartets are all similar, so that the most
probable combinations are:-

	Peak nos.	J_{AB}(c/s)	δ AB(c/s)
(i)	1,4,8,9	293± 6	930
(ii)	2,5,10,11	290± 2	1016
(iii)	3,6,11,12	298± 8	1261

Comparison of these values with the chemical shift of 1095 c/s
(18.2 p.p.m.) between axial and equatorial fluorine nuclei in
perfluorocyclohexane suggests that these quartets arise from
three pairs of different geminal fluorine atoms.   If the
principles derived from study of the dihydro compounds are
valid in this case, only the conformation with both substituents
(H and COCH$_3$) in equatorial positions can give the observed
single peak for one F$_2$ group and three geminal F$_2$ groups
with chemical shifts of the order 1095 c/s.

This assignment of conformation is confirmed by closer
examination of the CFH group resonances.   A slower sweep rate
shows that the ^{19}F resonance (peak 14) actually consists of

Fig.(ii)   N.M.R. Spectra of (F) $\overset{H}{\underset{COCH_3}{|}}$ (A)

(a) ^{19}F spectrum (60 Mc/s)

7

11

13 (C$\underline{F}$COCH$_3$)

14 (C$\underline{F}$H)

8

10

5 6

4

2

1 3

9

12

7000   8000   9000 // 11000   12000   13000   14000
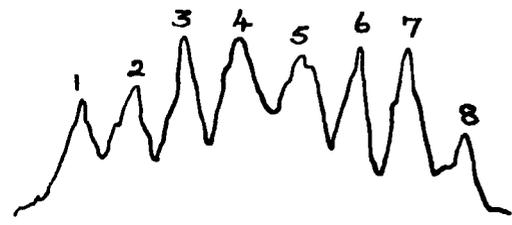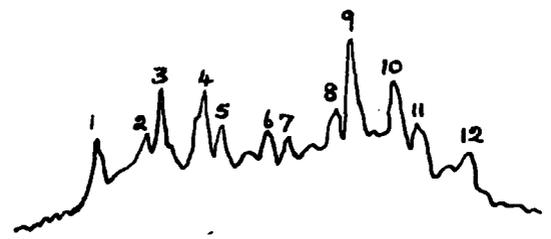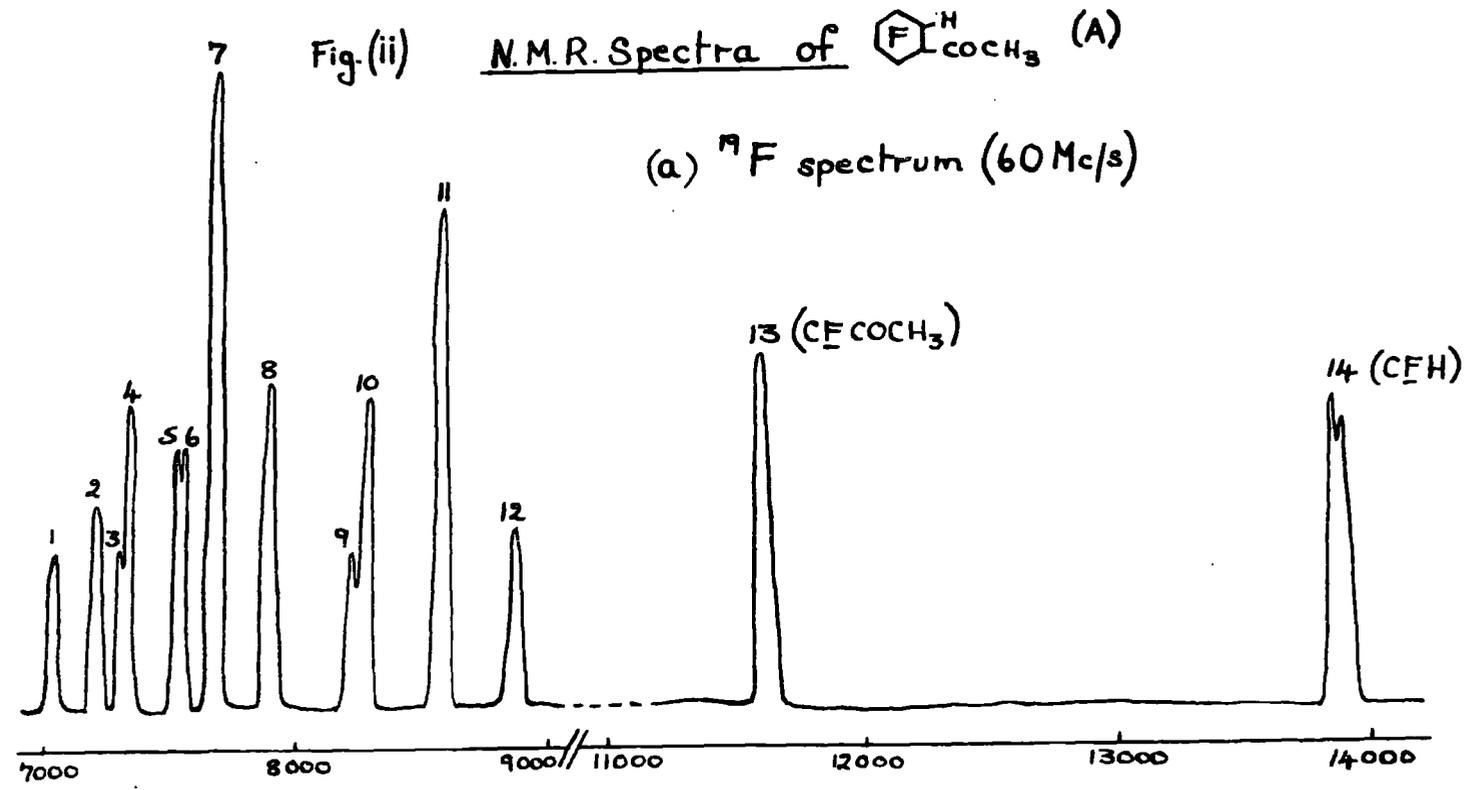
(b) ^{19}F spectrum C$\underline{F}$H fluorine nucleus.   (c) ^1H spectrum CF$\underline{H}$ hydrogen nucleus.

twelve peaks (Fig.(ii)b).   These are interpreted as a pair of
triplets with a large doublet spacing of 52.3± 0.8 c/s arising
from F-H geminal coupling, with each component further split
into two peaks.

If the CFH fluorine were in an equatorial position,
in addition to coupling with the geminal H it would couple
equally with each of the three vicinal fluorine nuclei, giving
a pair of quartets..   If however both R and H occupy equatorial
positions, the axial CFH fluorine will have two axial and one
equatorial fluorine neighbours.   Provided the $COCH_3$ group has
no effect upon the geminal fluorine, the CFH fluorine will
couple equally with the two axial fluorine neighbours, and
the resulting pair of triplets will be further split by
coupling with the equatorial vicinal fluorine.   The observed
triplet spacing of 17.7 ± 0.9 c/s can therefore be attributed
to trans F-F vicinal coupling, and the smaller doublet spacing
of 12.5 ± 0.9 c/s to gauche F-F vicinal coupling.

A group of eight peaks arising from the CFH hydrogen
nucleus occurs in the low field region of the 'H spectrum.
These peaks can be interpreted as two 1:3:3:1 quartets resulting
from geminal H-F coupling and from the equal coupling of the
three neighbouring fluorine nuclei with the hydrogen, for which
J_{HF} (gauche) = 12.3 ± 1.0 c/s.   This is further evidence
that hydrogen occupies an equatorial position, since an axial
hydrogen could not couple equally with all three vicinal
fluorines.

It is on the above grounds that all the compounds of configuration A are believed to be trans isomers in which both H and R occupy equatorial positions.

Configuration B

Only a trace of adduct thought to have the same conformation as the alcohols of type B was obtained by addition of acetaldehyde to perfluorocyclohexene. However it was possible to obtain sufficient of this ketone for study of its n.m.r. spectrum by oxidation of a sample of the pure B isomer of [hexagon ring with F and H substituents] CH(OH)CH$_3$.
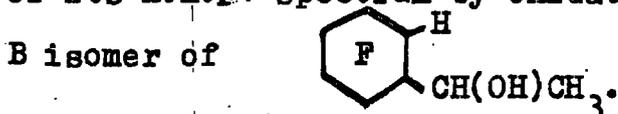
The ^{19}F spectrum of the ketone contains nine peaks in the CF$_2$ region (ϕ=116 - 141 p.p.m.), a CFR fluorine resonance at 176.53 p.p.m. and a broad peak at 212.917 p.p.m. which can be assigned to the CFH fluorine, although there is no resolved F-H coupling. This spectrum is less easy to interpret than that of the trans e,e isomer, and most structural information has been derived from the hydrogen spectrum. This shows a pair of quartets for the CFH hydrogen, arising from a geminal F-H coupling of 43.2 c/s and an equal coupling with three vicinal fluorine nuclei, suggesting that the hydrogen is in an equatorial position as in the trans isomer A. However, the F-H coupling constant is only 5.5± 0.2 c/s, whereas in the case of isomer A the corresponding hydrogen spectrum showed a gauche F-H coupling constant of 12.3 c/s. The relatively small

coupling constant for the B isomer may well be an indication of rapid interconversion between the two conformers of the cis isomer. This would give rise to an averaged F-H vicinal coupling constant, and if $J_{FH(gauche)}$ and $J_{FH(trans)}$ are of opposite signs, then the averaged value, (J.vic)av., could be of the order of 5.5 c/s.

If Isomer B is interconverting the form of the spectrum should be temperature dependent, and until tests have been carried out along these lines, it cannot be definitely stated whether B exists as the single e(H),a(R) conformer or as a mixture of the conformers of the cis isomer.

3. Products of dehydrofluorination reactions

(i) Cyclic olefins. Dehydrofluorination of compounds of the type [F, H, R ring] and [F, H, R ring] (where R=CH_2OH,etc) could give either (a) [F, R ring] and [F, R ring] or (b) [F, R ring] and [F, R ring]. The n.m.r. spectra of the olefinic products show clearly that in both cases it is alternative (a) that is formed, since neither the monoene nor the diene contains CFR peaks in the region of $\emptyset=200$ p.p.m. The intensities and positions of the five peaks in the ^{19}F spectrum of [F, CH_2OH ring] are consistent with a structure containing three CF=groups ($\emptyset=132$–160 p.p m.) and two CF_2 groups ($\emptyset=106$–115 p.p.m.), while [F, CH_2OH ring] has the four expected CF_2 peaks ($\emptyset=112$–136 p.p.m.).

and one CF=peak ($\emptyset$=127 p.p.m.).

(ii) <u>Straight chain olefins.</u> Dehydrofluorination of perfluoropropene-alcohol adducts yielded olefins of the formula $CF_3CF=CFR$. The ^{19}F spectra of the compounds in which R=$CH(OH)C_2H_5$ and $CH(CH_3)_2OH$ all show two groups of peaks in the region $\emptyset$=143-175 p.p.m. and one group in the region $\emptyset$=66-69 p.p.m, which can be assigned to CF= and CF_3 fluorine nuclei respectively.

These olefins may exist in either the cis or the trans form, and it should be possible to identify each isomer by its ^{19}F spectrum since McConnell et al[203] have found that for fluorinated olefins coupling constants usually lie in the following distinct ranges:-

J_{F-F}	trans	115-130 c/s
	cis	30-60 c/s
J_{CF_3-F}	trans	8-12 c/s
	cis	20-22 c/s

The spectra of the single isomer of $CF_3CF=CFCH(CH_3)_2OH$ and of one isomer of $CF_3CF=CFCH(OH)C_2H_5$ both contain a coupling constant of the order 134 c/s, typical of trans F-F coupling. Their other coupling constants can be assigned to cis CF_3-F coupling (22.5 and 21.8 c/s respectively) and geminal CF_3-F coupling (9.5 and 10.3 c/s). This is clear evidence that these are trans isomers,

$$\begin{array}{ccc} CF_3 & & F \\ \diagdown & & \diagup \\ & C \; = \; C & \\ \diagup & & \diagdown \\ F & & R \end{array}$$
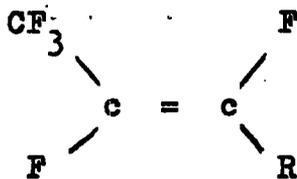
The spectrum of the other isomer of $CF_3CF{=}CF$ $CH(OH)C_2H_5$ contains coupling constants assigned to cis F-F coupling (27.7 c/s), trans CF_3-F coupling (12.1 c/s) and geminal CF_3-F coupling (8.6 c/s), which is adequate proof that this is the cis isomer,

$$\begin{array}{ccc} CF_3 & & R \\ \diagdown & & \diagup \\ & C \; = \; C & \\ \diagup & & \diagdown \\ F & & F \end{array}$$
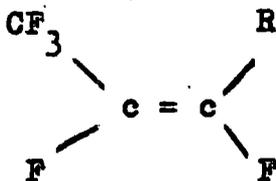
CHAPTER 3.

EXPERIMENTAL WORK

EXPERIMENTAL WORK

Most addition reactions were carried out in sealed Carius tubes, which were charged by vacuum transfer of weighed samples of volatile reagents using a conventional vacuum system with mercury diffusion and oil pumps. High boiling liquids were weighed directly into the tube, which was then cooled to -183° and evacuated. Air trapped in the frozen sample was removed by closing the tap connecting the tube to the vacuum system, allowing the contents to reach room temperature, then cooling again to -183° and pumping off any liberated gas. Reagents used were purified by distillation.

Volatile products and unchanged starting material were separated by fractionation under vacuum using the system shown in Fig.1. The Carius tube, cooled in liquid air, was connected to the system at A and taps 1-5 were left open until a "sticking" vacuum was obtained. With tap 1 closed and traps B and C cooled to selected temperatures (C at -183° and B usually at -78°), the Carius tube was allowed to warm up to room temperature, the volatile contents condensing in either trap B or C. One or two repetitions of this fractionating procedure were usually sufficient for efficient separation of e.g. C_3F_6 from alcohols, the olefin being collected in trap C and the less volatile alcohol in trap B.

Products were purified by distillation and by preparative scale vapour phase chromatography. New compounds
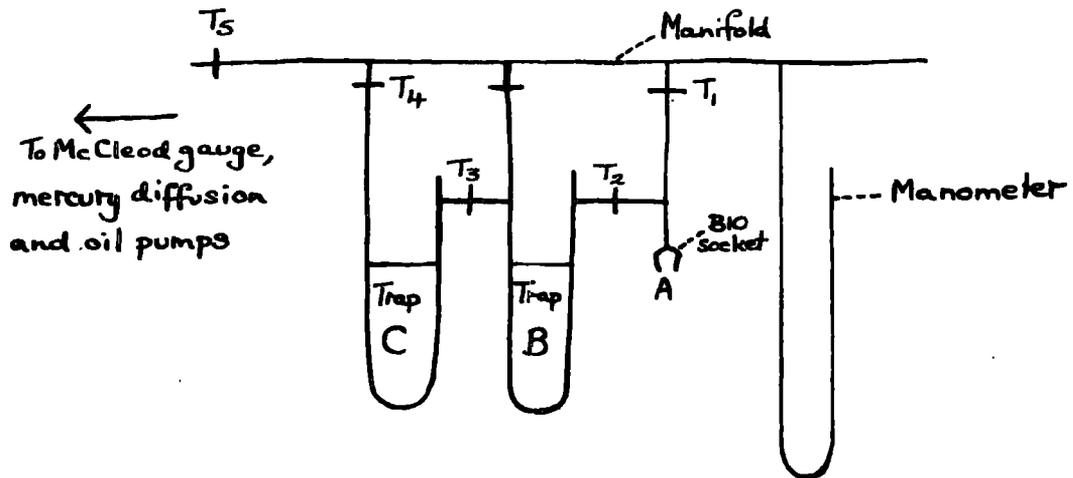
Fig. 1   Vacuum Fractionating System.

were identified by analysis for fluorine content (decomposition
using diphenyl-sodium-dimethoxyethane) and by study of their
infrared and nuclear magnetic resonance spectra.

Infrared spectroscopy.   Spectra were recorded using a Grubb-
Parsons type G.S.2A double beam grating infrared spectrometer.
Liquid and low-melting solid samples were in the form of thin
films between potassium bromide discs. (See P. /60).

Nuclear magnetic resonance (n.m.r.) spectroscopy.

Spectra were recorded using an A.E.I. R.S.2 spectrometer
operated at 60 Mc/s. (See P. /55).

Vapour phase chromatography (V.P.C.)

Analytical work was done using:-

a)   A Griffin and George Mark IIB model with two U-shaped
glass columns (3 ft. x ¼ in) containing kieselguhr as inert
support, with 40% of silicone elastomer or tricresylphosphate
as stationary phase. Nitrogen was used as the carrier gas.

b) A Perkin-Elmer Fractometer Model 451 with a double U-shaped
stainless steel column (2 m. x ¼ in) containing G.C.22 Super-
support as inert support, with 20% of di-n-decylphthalate as
stationary phase. The instrument was operated using a hot wire
detector, with hydrogen as carrier gas.

The greater sensitivity of the latter instrument made
possible detection of isomers in a mixture which gave a single
peak when the other instrument was used.

The apparatus for preparative scale work comprised a

horizontal aluminium oven containing a preheater and a glass
U-shaped column (8 ft. x $\frac{7}{8}$ in), a thermistor detector with by-
pass and a trapping system (U-shaped traps connected to a
manifold by ball and socket or B10 ground glass joints, and
cooled in liquid air).   The carrier gas, nitrogen, was passed
through the apparatus by suction.   Column packings were as
described for the analytical scale.

ADDITIONS TO PERFLUOROPROPENE

a) Peroxide initiation

Methanol.   A Carius tube charged with perfluoropropene
(8.2g, 0.055 moles), methanol (8.0g, 0.250 moles) and benzoyl
peroxide (0.3g) was heated for 24 hrs. at 117°.   Unchanged
C_3F_6 (1.2g) was vented into a cooled trap (-183°), and the
liquid mixture left after distillation of some unchanged CH_3OH
was separated by preparative scale V.P.C. (Silicone elastomer
at 93°; N_2 flow rate 100 ml./min; p.d. 24 cm). into its components
CH_3OH and 2,2,3,4,4,4.-hexafluorobutan-1-ol (6.6g, 66.3%) b.p.
115°/775mm, n_D^{21} 1.3135 (LaZerte and Koshar[74] report b.p. 114.5^o/
740 mm, n_D^{25} 1.3115).   Infrared spectrum No.1.   The analytical
chromatogram (di-n-decylphthalate at 90°) showed a small
quantity of an inseparable unidentified component (possibly an
isomer) of shorter retention time than the major product.

Ethanol.   A Carius tube charged with perfluoropropene
(5.8g, 0.039 moles), ethanol (8.9g, 0.194 moles) and benzoyl

peroxide (0.1g) was heated for 24 hrs at 115°. The contents
of the tube were fractionated under vacuum, unchanged C_3F_6(1.3g)
being condensed in a trap at -183°, while unchanged C_2H_5OH and
adduct (12.4g) were retained in a trap at -78°. Some C_2H_5OH
was distilled from the mixture (b.p. $76-9^\circ$/760mm) and the
residue separated by preparative scale V.P.C. (Silicone elastomer
at 95°; N_2 flow rate 150ml/min; p.d. 36 cm) into its components,
C_2H_5OH and 3,3,4,5,5,5 -hexafluoropentan-2-ol (3.0g., 43.5%)
b.p. 120°/775mm, n_D^{21} 1.3249. Found: F,58.7%, $C_5H_6F_6O$ requires
F,58.2%.

Infrared spectrum No.2.

<u>n-Propanol</u>. A Carius tube charged with perfluoropropene (3.9g.,
0.026 moles), n-propanol (7.5g., 0.125 moles) and benzoyl
peroxide (o.1g) was heated for 24 hrs at 110°. The more
volatile contents of the tube were fractionated under vacuum,
giving (i) C_3F_6 at -183° (1.5g), (ii) $n-C_3H_7OH$ plus adduct at
-78° (0.8g). Distillation of the liquid left in the Carius tube
gave (iii) $n-C_3H_7OH$, b.p. $97-100^\circ$/760mm. (3.5g), (iv) $n-C_3H_7OH$
plus adduct, distilled at 50°/0.001mm (4.8g), (v) white solid
(0.4g). Fractions (ii) and (iv) were combined for preparative
scale V.P.C. separation (silicone elastomer at 103°; N_2 flow
rate 150 ml./min; p.d. 36cm) of the adduct, 4,4,5,6,6,6-hexa-
fluorohexan-3- ol (2.25g, 41.2%). Analytical V.P.C. (Silicone
elastomer at 135°) showed the presence of a trace of material

of slightly longer retention time. Further purification by
V.P.C. yielded a pure sample of the major product b.p. 132°/
750 mm., n_D^{21} 1.3379. Found: F, 54.6%, $C_6H_8F_6O$ requires
F, 54.3%. Infrared spectrum No.3. The analytical chroma-
togram of the pure adduct (di-n-declyphthalate at 106°)
showed two overlapping peaks in the ratio 1:1.25.

Isopropanol. A Carius tube charged with perfluoropropene
(5.3g, 0.035 moles), isopropanol (10.4g., 0.173 moles) and
benzoyl peroxide (0.15g) was heated for 24 hrs. at 110°. The
contents of the tube were fractionated under vacuum, giving
unchanged C_3F_6 (2.2g) and a mixture of i-C_3H_7OH and adduct
(13.3g) some i-C_3H_7OH was distilled from the mixture and the
residue was separated by preparative scale V.P.C. (Silicone
elastomer at 84°; N_2 flow rate 150 ml./min., p.d. 37 cm) into
its components, i-C_3H_7OH and 2-methyl-3,3,4,5,5,5-hexafluoro-
pentan-2-ol (2.7g, 36.4%) b.p. 129°/750mm., n_D^{21} 1.3372.
Found: F, 54.1%, $C_6H_8F_6O$ requires F, 54.3%. Infrared spectrum
No.4. The analytical chromatogram of the pure product
(di-n-decylphthalate at 106°) showed only one component.

2,2,2-trifluroethanol. No adduct was obtained when a 6.2:1
molar mixture of 2,2,2-trifluoroethanol and perfluoropropene
was heated with benzoyl peroxide for 24 hrs. at 112°.

Allyl alcohol

(1) No adduct was obtained when a 6.4:1 molar mixture of
allyl alcohol and perfluoropropene was heated with benzoyl

peroxide for 24hrs. at 120°.

(2) Perfluoropropene (3.0g., 0.02 moles) and allyl alcohol (29.6g, 0.510 moles) (Molar ratio: 1:25.5) were heated with benzoyl peroxide (0.5g) for 24 hrs at 112°. Fractionation of the reaction mixture under vacuum led to the recovery of C_3F_6(2.4g) and allyl alcohol (29.4g) leaving a clear brown solid (o.7g).

Crotonyl alcohol. No adduct was obtained when a 4.7:1 molar mixture of crotonyl alcohol and perfluoropropene was heated with benzoyl peroxide for 24 hrs. at 120°.

Benzyl alcohol. No adduct was obtained when a 3.2:1 molar mixture of benzyl alcohol and perfluoropropene was heated with benzoyl peroxide for 25 hrs. at 123°. The reagents were miscible at this temperature, although immiscible at room temperature.

Ethylene glycol. No adduct was obtained when a 6.7:1 molar mixture of ethylene glycol and perfluoropropene was heated with benzoyl peroxide for 24 hrs. at 123°.

Neopentyl alcohol. Perfluoropropene (4.0g., 0.027 moles), neopentyl alcohol (11.8g., 0.134 moles) and benzoyl peroxide (0.2g) were heated for 24 hrs. at 110°. Vacuum fractionation of the reaction mixture gave (i) C_3F_6 at -183° (3.5g., 87.5%), (ii) mainly Me_3CCH_2OH at -78° (5.4g). Some Me_3CCH_2OH (6.8g) was left in the Carius tube. Analytical V.P.C. (Silicone elastomer at 116°) showed only a trace of material of longer

retention time than neopentyl alcohol in fraction (ii).

Acetaldehyde.   A Carius tube charged with perfluoropropene
(14.5g, 0.097 moles), acetaldehyde (5.2g, 0.118 moles) and
benzoyl peroxide (0.2g) was heated for 24 hrs. at 115°.   A
yellow liquid (19.7g) was distilled from the tube under vacuum,
leaving 0.1g solid. Atmospheric pressure distillation gave
the following fractions:- (i) b.p. 67-74° (3.7g), (ii)b.p.
75-80° (13.8g), (iii) yellow liquid residue (1.3g).   All three
fractions were shown by analytical V.P.C. to contain a single
product (retention time 2 min. on silicone elastomer at 98°;
N_2 flow rate 1.41/hr), while (i) also contained a little
CH_3CHO.   The product was identified as 1,1,1,2,3,3-hexa-
fluoropentanone-4 (18.8g)(99.9%) b.p. 78°/755mm., n_D^{20} 1.3047.
Found: F, 60.6%, $C_5H_4F_6O$ requires F, 58.8%.   Infrared spectrum
No.7.

Acetic acid.   No adduct was obtained when a 21.4:1 molar
mixture of acetic acid and perfluoropropene was heated with
benzoyl peroxide for 24 hrs. at 110°.

Acetonitrile. No adduct was obtained when a 6.3:1 molar mixture
of acetonitrile and perfluoropropene was heated with benzoyl
peroxide for 24 hrs. at 118°.

Ethyl acetate.   A Carius tube charged with perfluoropropene
(3.4g., 0.023 moles), ethyl acetate (21.9g., 0.249 moles) and
benzoyl peroxide (0.3g) was heated for 24 hrs. at 120°.

Fractionation under vacuum gave (i) C_3F_6 at $-183°$ (0.4g);
(ii) a mixture of ethyl acetate and adduct at $-78°$ (24.3g).
Some ethyl acetate was distilled (b.p. 76-79°/760mm) and the
residue was separated by preparative scale V.P.C. (Silicone
elastomer at 100°; N_2 flow rate 125 ml/min.; p.d. 10 cm) into
its components, ethyl acetate and adduct (2.0g)   The liquid
left in the Carius tube (0.7g) was distilled at 100°/0.01 mm
to give a colourless liquid (0.35g), shown by analytical V.P.C.
(Silicone elastomer at 98°; N_2 flow rate 1.4 l/hr) to consist
mainly of the 1:1 adduct (retention time $8\frac{1}{2}$ min) plus small
amounts of two compounds of retention times $5\frac{1}{2}$ and 14 min.
Therefore the total weight of the major product, identified
from its ^{19}F and ^1H n.m.r. spectra as 1-methyl-2,2,3,4,4,4-
hexafluorobutyl acetate, was 2.3g(42%) b.p. 142°/755mm, n_D^{25}
1.3356.   Found: F,49.7% $C_7H_8F_6O_2$ requires F,47.8%.

Diethyl malonate.   A Carius tube charged with perfluoropropene
(3.0g, 0.02 moles) diethyl malonate (17.0g., 0.106 moles) and
benzoyl peroxide (0.2g) was heated for 24 hrs. at 110°.
Distillation at 0.001mm yielded the following fractions:-
(i) C_3F_6 distilled at 20° (1.1g); (ii) diethyl malonate,
distilled with bath at 55° (17.5g); (iii) distilled with bath
at 55-100° (0.95g); (iv) orange residue (0.15g).   Analytical
V.P.C. (Silicone elastomer at 224°; N_2 flow rate 1.4 l/hr)
showed that (iii) consisted mainly of diethyl malonate
(retention time 4 min.) plus a small amount of a second compound

(retention time 5 min.)   Attempts to separate the two
components by preparative scale V.P.C. (Silicone elastomer at 210°
were unsuccessful owing to extensive decomposition of the
compounds on the column, giving complex mixtures.   No noticeable
improvement in yield of product resulted from using a 10:1
molar ratio of ester to olefin instead of 5:1.

b) X-Ray initiation using a Co^{60} 100 curie source.

In all cases the products had infrared spectra and
retention times on silicone elastomer or di-n-decylphthalate
identical with those of the products of the corresponding
peroxide initiated additions.

Methanol.   A Carius tube charged with perfluoropropene
(3.1g., 0.021 moles) and methanol (3.2g., 0.100 moles) was
irradiated for 12 days.   Fractionation under vacuum gave
C_3F_6 (2.0g) and a mixture of methanol and adduct (4.0g).
Methanol was removed by distillation and preparative scale V.P.C.
separation, giving a pure sample of 2,2,3,4,4,4-hexafluorobutan-
1-ol (0.6g., 16.0%).

Ethanol. Perfluoropropene (3.9g, 0.026 moles) and ethanol
(7.0g, 0.152 moles) were irradiated for 12 days.   No unchanged
C_3F_6 was recovered from the reaction mixture, and removal of
ethanol left 3,3,4,5,5,5-hexafluoropentan-2-ol (4.5g, 88.2%).

n-Propanol. Perfluoropropene (5.1g, 0.034 moles) and n-propanol
(8.7g, 0.145 moles) were irradiated for 12 days. No unchanged

C_3F_6 was recovered and excess n-propanol was removed to give 4,4,5,6,6,6-hexafluorohexan-3-ol (6.4g, 89.6%), contaminated with a trace of material of slightly longer retention time on silicone elastomer at 122°.

Isopropanol. Perfluoropropene (4.05g, 0.027 moles) and isopropanol (7.3g, 0.122 moles) were irradiated for 11 days 19 hrs. No unchanged C_3F_6 was recovered, and removal of isopropanol left 2-methyl-3,3,4,5,5,5-hexafluoropentan-2-ol (4.5g, 84.8%).

n-Butanol. Perfluoropropene (5.4g., 0.036 moles) and n-butanol (6.3g., 0.085 moles) were irradiated for 13 days. Fractionation under vacuum gave (i) C_3F_6 at -183° (3.4g), (ii) n-butanol at -78°(3.6g). The liquid residue was separated by preparative scale V.P.C. (Silicone elastomer at 135°; N_2 flow rate 150 ml/min; p.d. 19cm) into its components, n-butanol (3.0g) and 1,1,1,2,3,3,-hexafluoroheptan-4-ol (1.0g., 33.5%) b.p. 150-1°, n_D^{25} 1.3470. Found: F,50.3%. $C_7H_{10}F_6O$ requires F, 50.9%. Infrared spectrum No.5. The analytical chromatogram of the pure product (di-n-decylphthalate at 101°) showed two peaks in the ratio 1:1.5. A compound of considerably longer retention time (0.1g) was also isolated during the V.P.C. separation, and showed an infrared spectrum similar to that of $CF_3CFHCF_2CH(OH)C_3H_7$ but with additional bands at 1736(m) and 1701(w) cm^{-1}.

2,2,2-Trifluoroethanol. No adduct was obtained when a 1.2:1 molar mixture of 2,2,2-trifluoroethenol and perfluoropropene was irradiated for 12 days.

<u>Allyl alcohol.</u>   Perfluoropropene (3.8g., 0.025 moles) and
allyl alcohol (8.4g., 0.145 moles) were irradiated for 12 days,
giving only a little viscous liquid (0.3g).

<u>Crotonyl alcohol.</u>   Only a trace of product was obtained when a
2:1 molar mixture of crotonyl alcohol and perfluoropropene was
irradiated for 14 days at room temperature, followed by 8 days
at 76°.

<u>Ethylene glycol.</u>   Perfluoropropene (5.1g., 0.034 moles) and
ethylene glycol (9.5g., 0.154 moles) were irradiated for 7 days
at room temperature, followed by 8 days at 76°.   Unchanged
C_3F_6 (1.4g) was recovered by fractionation under vacuum, and
excess glycol (8.4g) was separated from an immiscible lower
layer (4.4g) which was shown by analytical V.P.C.   (Silicone
elastomer at 146°) to contain at least 5 compounds.   The infra-
red spectrum of the mixture showed only weak absorption in the
3450 cm^{-1} region (OH stretching), but strong bands at 2985 and
2899 cm^{-1} (CH stretching).

Preparative scale V.P.C. (Silicone elastomer at 112°; N_2 flow
rate 150 ml/min., p.d. 23cm) was used to isolate the two most
volatile components (0.1g) which had an aldehydic smell.   The
column temperature was then lowered to 95° and the remaining
material reinjected in order to isolate samples of two of the
major constituents (retention times (a) 28 min., (b) 48 min.).
The infrared spectra of both compounds showed no absorption
in the OH and C:C stretching regions, but absorption at 2985

and $2899 cm^{-1}$ was strong in (a) and of medium intensity in (b).
Found: (a) F,25.0%; (b) F,60.6%.   Calc. for $C_8H_6F_{12}O_2$
(i.e. $1(CH_2OH)_2:2C_3F_6$):F,63.0%.

Neopentyl alcohol.   No adduct was obtained when a 4.9:1 molar
mixture of neopentyl alcohol and perfluoropropene was irradiated
for 12 days at room temperature.   Since most of the alcohol
was in the solid state under the conditions used, a repeat
reaction was carried out at a higher temperature.   A 3.6:1 molar
mixture of neopentyl alcohol and perfluoropropene was irradiated
for 12 days at 42° (a homogenous liquid being obtained at this
temperature), but again no addition took place.

Methanethiol.   Perfluoropropene (9.2g., 0.061 moles) and
methanethiol (3.4g., 0.071 moles) were irradiated for 1 day
using a 100 curie Co^{60} source and for 5 days $4\frac{1}{2}$ hrs. using a
500 curie Co^{60} source.   Unchanged starting materials (5.7g)
were vented from the Carius tube into a trap at -78°, and
distillation of the remaining liquid (7.6g) gave a fraction of
b.p. $82-85^o$(7.0g).   Analytical V.P.C. (tricresyl phosphate at
68°; N_2 flow rate 0.9 1/hr) showed two components of retention
times (a) 31 min., (b) 41 min.   Separation by preparative scale
V.P.C. (tricresyl phosphate at 85°; N_2 flow rate 150 ml/min)
gave only 53% recovery, (a) forming 6% and (b) 94% of the
recovered material.   (b) had b.p. 87°, n_D^{20} 1.3352.   (Harris and
Stacey[85] report for a mixture of 91% $CH_3SCF_2CFHCF_3$ and 9%
$CH_3SCF(CF_3)CF_2H$, b.p. $84.5-86^o$, n_D^{25} 1.3400-1.3393).   Crude yield

of mixture 57.6%.

Ethyl acetate. Perfluoropropene (3.7g., 0.025 moles) and ethyl acetate (3.3g., 0.038 moles) were irradiated for 12 days. Fractionation under vacuum gave (i) C_3F_6 at $-183°$ (3.3g., 89% recovery), (ii) ethyl acetate plus a trace of product at $-78°$ (3.6g); (iii) residue (0.1g). The product was not isolated, but had a retention time on di-n-decylphthalate at $98°$ identical to that of the peroxide-iniated adduct.

Diethyl malonate. Perfluoropropene (2.4g., 0.016 moles) and diethyl malonate (12.7g., 0.079 moles) were irradiated for 12 days. Fractionation under vacuum gave (i) C_3F_6 at $-183°$ (1.5g); (ii) diethyl malonate at $-78°$ (0.3g). The liquid left in the Carius tube (13.3g) was shown by analytical V.P.C. (Silicone elastomer at $198°$; N_2 flow rate 1.2 l/hr). to consist mainly of diethyl malonate plus a small amount of adduct (retention times 6 and 8 min. respectively).

ADDITIONS TO PERFLUOROCYCLOHEXENE

Methanol (1). A Carius tube charged with perfluorocyclohexene (8.8g., 0.034 moles), methanol (11.9g, 0.372 moles) and benzoyl peroxide (0.2g) was heated for 26 hrs. at $125°$. The mixture was distilled at 0.001 mm giving the following fractions:-
(a) distilled at $20°$(11.6g); (b) distilled with bath at $50°$(8.6g); (c) orange solid residue (0.2g). Unchanged starting materials were removed from (a) by distillation at atmospheric pressure, and the residue (2.0g) was combined with (b). Preparative scale

V.P.C. (Silicone elastomer at 143°; N_2 flow rate 100 ml/min; p.d. 21cm) was used to separate remaining traces of starting materials from the adduct, (2H-decafluorocyclohexyl)methanol (8.7g., 87%) b.p. 149.5°, n_D^{21} 1.3402. Found: F,64.7%. $C_7H_4F_{10}O$ requires F, 64.7%. Infrared spectrum No.8. The analytical chromatogram of the pure product (di-n-decylphthalate at 154°) showed two overlapping peaks in the ratio 1:1.5.

(2) A 10:1 molar mixture of methanol and perfluorocyclohexene was treated with benzoyl peroxide for 41 hrs. at 125° giving 82.4% conversion to (2H-decafluorocyclohexyl)methanol.

Ethanol. Perfluorocyclohexene (15.1g., 0.058 moles) and ethanol (13.7g., 0.298 moles) were heated with benzoyl peroxide (0.35g) for 24 hrs. at 113°. Unchanged C_6F_{10} (3.0g) and C_2H_5OH (10.8g) were distilled off, and the residue heated to 50° at 0.001mm, giving a colourless distillate. This gave a single peak on di-n-decylpthalate at 154° and was identified as methyl(2H-decafluorocyclohexyl)methanol (13.4g), 75.0%; b.p. $168-9^{\circ}/745mm$; n_D^{21} 1.3479. Found: F,61.9%. $C_8H_6F_{10}O$ requires F,61.7%. Infrared spectrum No.9a.

n-Propanol. Perfluorocyclohexene (11.0g, 0.073 moles) and n-propanol (19.0g., 0.317 moles) were heated with benzoyl peroxide (0.5g) for 24 hrs. at 119°. Unchanged starting materials and adduct were distilled at $20^{\circ}/0.01mm$, leaving a yellow solid (1.5g). C_6F_{10}(4.0g) and $n-C_3H_7OH$ (9.2g) were distilled from the mixture at atmospheric pressure, and

preparative scale V.P.C. (Silicone elastomer at 160°; N_2 flow rate 100 ml/min., p.d. 17cm) was used to separate the rest of the mixture into its components, n-C_3H_7OH(7.0g) and ethyl (2H-decafluorocyclohexyl)methanol (4.0g., 17.0%) b.p. 182°, n_D^{21} 1.3556. Found: F,58.8% $C_9H_8F_{10}O$ requires F,59.0%. Infrared spectrum No.10.

<u>Isopropanol.</u> Perfluorocyclohexene (7.1g., 0.027 moles) and isopropanol (9.5g., 0.158 moles) were heated with benzoyl peroxide (0.2g) for 45 hrs at 135°. Although the two liquids were immiscible at room temperature they were miscible at the reaction temperature. Most of the unchanged starting materials was removed by distillation at atmospheric pressure. Further distillation at 20°/0.05 mm yielded a mixture (1.5g) shown by analytical V.P.C. (di-n-decylphthalate at 153°) to consist mainly of isopropanol with trace amounts only of two components of longer retention time.

<u>n-Butanol.</u> Perfluorocyclohexene (9.2g., 0.035 moles) and n-butanol (16.0g., 0.216 moles) were heated with benzoyl peroxide (0.2g) for 24 hrs. at 130°. A lower layer of unchanged C_6F_{10} (4.7g) was separated from a yellow upper layer (19.1g) which was distilled, giving C_6F_{10} (0.6g), n-C_4H_9OH (14.8g), a mixture of n-C_4H_9OH and adduct (1.7g), and a yellow oily residue (0.4g). Preparative scale V.P.C. (Silicone elastomer at 170°; N_2 flow rate 100 ml/min; p.d. 28 cm) was used to purify the adduct, n-propyl (2H-decafluorocyclohexyl)methanol

(0.8g, 6.8%) b.p.192°, n$_{D}^{21}$ 1.3621. Found: F,56.0% C$_{10}$H$_{10}$F$_{10}$O requires F,56.6%. Infrared spectrum No.11.

2,2,2-Trifluoroethanol. No adduct was obtained when a 6.4:1 molar mixture of 2,2,2-trifluoroethanol and perfluorocyclohexene was heated with benzoyl peroxide for 24 hrs. at 130°.

Benzyl alcohol. (1) A Carius tube charged with perfluoro-cyclohexene (5.1g., 0.019 moles), benzyl alcohol (14.2g, 0.132 moles) and benzoyl peroxide (0.2g) was heated for 24 hrs. at 130°, followed by 18 hrs at 167°. (The reagents were miscible only at the higher temperature). No adduct was obtained.

(2) With solvent. A Carius tube charged with perfluorocyclohexene (2.0g., 0.008 moles), benzyl alcohol (1.5g, 0.014 moles), benzoyl peroxide (0.05g) and 1,1,2-trifluoro-1,2,2-trichloroethane (20.3g) was heated for 39 hrs. at 104°. Distillation of unchanged starting material (20-50°/0.01mm) left only a yellow oil (0.04g).

Ethylene glycol. No adduct was obtained when a 5.9:1 molar mixture of ethylene glycol and perfluorocyclohexene was heated with benzoyl peroxide for 47 hrs. at 135-145°. The two reagents were immiscible under these conditions, but no inert mutual solvent could be found.

Acetaldehyde. A Carius tube charged with perfluorocyclohexene (5.5g, 0.021 moles), acetaldehyde (10.4g, 0.236 moles) and benzoyl peroxide (0.25g) was heated for 24 hrs. at 125°. A yellow liquid mixture (14.8g) which distilled at 20°/0.01 mm, was shown

by analytical V.P.C. (Silicone elastomer at 92°; N_2 flow rate
1.1 1/hr) to consist of three products of retention times
(a) 12 min., (b) 14 min., (c) 19 min., in addition to unchanged
acetaldehyde (3 min) and paraldehyde (26 min). Preparative
scale V.P.C. (Silicone elastomer at 102°; N_2 flow rate 150 ml/min
p.d. 25 cm) was used to separate a pure sample of the major
product (b), (2H-decafluorocyclohexyl)methyl ketone (4.0g, 62.3%)
b.p. 121°, n_D^{25} 1.3247. Found: F,62.7% $C_8H_4F_{10}O$ requires F,62.1%
Infrared spectrum No.12

The retention time of the minor product (c) was
identical with that of the product of oxidation of a single
isomer of methyl (2H-decafluorocyclohexyl)methanol (P. *134*).
The n.m.r. spectra have been studied and as a result (b) has
been assigned the structure in which both acyl and hydrogen
substitutes are in equatorial positions, while (c) has hydrogen
equatorial but the acyl group axial.

The infrared spectrum of an impure sample of (a), which
showed a tendency to decompose, had strong absorption bands at
1751-1597 and 1439-935 cm^{-1}.

Repetition of the reaction with equimolar quantities
of perfluorocyclohexene and acetaldehyde gave a 90% yield of
(b) plus a trace of (c).

Methanethiol. No adduct was obtained when a 11:1 molar
mixture of methanethiol and perfluorocyclohexene was heated with
benzoyl peroxide for 24 hrs. at 128°.

<u>Diethyl ether</u>. Perfluorocyclohexene (5.1g, 0.019 moles) and diethyl ether (6.1g, 0.082 moles) were heated with benzoyl peroxide (0.1g) for 26 hrs at 105°. Unchanged starting materials were distilled off, leaving a yellow liquid (0.6g) shown by analytical V.P.C. (Silicone elastomer at 220°; N_2 flow rate 0.9 l/hr) to consist of C_6F_{10} and roughly equal quantities of four components with retention times of 2, $3\frac{1}{2}$, 7 and 8 min. respectively.

<u>Anisole</u>. No adduct was obtained when a 6.4:1 molar mixture of anisole and perfluorocyclohexene was heated with benzoyl peroxide for 28 hrs. at 130°.

<u>Formamide</u>. No adduct was obtained when a 5.7:1 molar mixture of formamide and perfluorocyclohexene was heated with benzoyl peroxide for 25 hrs. at 105°. The reagents were immiscible, but no suitable solvent could be found.

<u>Methyl acetate</u>. Perfluorocyclohexene (3.6g, 0.014 moles) and methyl acetate (6.2g., 0.107 moles) were heated with benzoyl peroxide (0.1g) for 25 hrs. at 123°. Unchanged starting materials were removed by distillation at $20^\circ/0.01$mm. The residue (0.2g) was shown by analytical V.P.C. (Silicone elastomer at 150°; N_2 flow rate 1.2 l/hr) to consist of two components of retention times $9\frac{1}{2}$ and $10\frac{1}{2}$ min.

<u>Ethyl acetate</u>. Only a trace of product (retention time $7\frac{1}{2}$ min. on silicone elastomer at 170°; N_2 flow rate 1.2 l/hr) was

obtained when a 5:1 molar mixture of ethyl acetate and perfluoro-cyclohexene was heated with benzoyl peroxide for 25 hrs. at 125°.

Diethyl malonate.   Perfluorocyclohexene (6.2g., 0.024 moles) and diethylmalonate (35.1g, 0.219 moles) were heated with benzoyl peroxide (0.3g) for 38 hrs. at 127°.   After separation of a layer of unchanged C_6F_{10} (2.5g) the upper layer (37.6g) was distilled at 100°/0.01mm.   The orange liquid residue (0.9g) contained two components (retention times 14 and 16 min. on silicone elastomer at 211°; N_2 flow rate 1 1/hr).

ADDITIONS TO OCTAFLUOROCYCLOHEXA-1,3-diene

Methanol.   A Carius tube charged with octafluorocyclohexa-1,3-diene (2.6g, 0.012 moles), methanol (4.3g., 0.134 moles) and benzoyl peroxide (0.1g) was heated for 25 hrs. at 125°.   Unchanged starting materials were distilled at 20°/0.01 mm, leaving only a yellow oil and solid (0.3g) which had a strong smell of hydrogen fluoride.

Ethyl acetate.   A Carius tube charged with octafluorocyclohexa-1,3-diene (4.7g, 0.021 moles), ethyl acetate (9.7g, 0.110 moles) and benzoyl peroxide (0.1g) was heated for 25 hrs at 125°. Unchanged starting materials were distilled at 20°/0.01 mm, leaving a yellow oil (0.5g).   The infrared spectrum of this showed strong absorption at 1739-1698, 1449, 1372-952, 763, 746 and 694cm^{-1}.

ADDITIONS TO OCTAFLUOROCYCLOHEXA-1,4-DIENE

Methanol.   A 500 ml. stainless steel autoclave charged with

octafluorocyclohexa-1,4-diene (44.8g, 0.200 moles), methanol
(64.0g, 2.000 moles) and benzoyl peroxide (1.0g) was rotated at
150° for 24 hrs. Distillation at 20°/0-10mm gave (i) methanol
(54.4g); (ii) (2H-octafluorocyclohex-4-enyl)methanol (34.8g, 68%).
A sample purified by preparative scale V.P.C. (Silicone elastomer
at 150°; N_2 flow rate 175 ml./min; p.d. 47 cm) had b.p. 164°,
n_D^{21} 1.3679. Found: F,59.0%. Calc.for $C_7H_4F_8O$:F,59.4%. Infrared
spectrum No.14a. The analytical chromatogram of the pure
product (di-n-decylphthalate at 154°; H_2 flow rate 65 ml/min)
showed two peaks of retention times 10.4 and 13.2 min. in the
ratio 1:2.

A very viscous colourless distillate was obtained from
the residue (12.5g) at 185°/0.01 mm, and was identified as a
2:1 methanol-octafluorocyclohexa-1,4-diene adduct (crude yield
21.7%) m.p. 96-97° (recrystallised from pet.ether). Found:
F,53.3%, m.wt. (ebullioscopy)292. Calc.for $C_8H_8F_8O$:F,52.8%
m.wt.288. The infrared spectrum shows absorption in the
regions 3610-3300(OH), 2959 and 2890 (CH) and 1460-1000cm^{-1}(CF),
but none in the region 1780-1690cm^{-1}(C=C).

Ethanol. A Carius tube charged with octafluorocyclohexa-1,4-
diene (5.0g, 0.022 moles), ethanol (5.0g, 0.109 moles) and
benzoyl peroxide (o.1g) was heated for 24 hrs. at 125°. The
mixture was distilled at 0.001 mm giving the following fractions:-
(a) distilled at 20° (6.2g), (b) distilled with bath at 100°
(2.7g), (c) yellow solid residue (0.6g). Unchanged starting

materials were removed from (a) by distillation at atmospheric pressure, and the residue (4.2g) was combined with (b). Preparative scale V.P.C. (Silicone elastomer at 155°; N_2 flow rate 200ml/min., p.d. 51 cm) was used to separate remaining traces of starting materials from the adduct, methyl (2H-octafluorocyclohex-4-enyl)methanol (3.35g, 55.6%) b.p. 177°, n_D^{21} 1.3760. Found: F,56.1% $C_8H_6F_8O$ requires F,56.3%. Infrared spectrum No. 15. The analytical chromatogram of the pure product (di-n-decylphthalate at 153°; H_2 flow rate 60 ml/min), showed three peaks of retention times 13.0, 14.8 and 17.2 min. in the ratio 1:3:6.5 (Fig.3, page 146).

Acetaldehyde. A Carius tube charged with octafluorocyclohexa-1,4-diene (3.3g, 0.015 moles), acetaldehyde (0.7g, 0.016 moles) and benzoyl peroxide (0.1g) was heated for 25 hours at 120°. Fractionation under vacuum gave (i) CH_3CHO at -183° (0.2g), (ii) a little CH_3CHO plus products (A) and (B) at -78° (2.4g). The residue in the Carius tube was filtered, and the filtrate (0.7g) was shown by V.P.C. to contain products (C) and (D) of much longer retention times than (A) and (B). Preparative scale V.P.C. separation (Silicone elastomer at 95°; N_2 flow rate 150 ml/min.; p.d. 14cm) gave (A) (0.4g), the infrared spectrum of which indicated that it was a non-fluorocarbon by-product, and (B) (2H-octafluorocyclohex-4-enyl)methyl ketone (1.0g, 24.9%) b.p. 134-5°/755 mm, n_D^{23} 1.3547. Found: F,58.1%. $C_8H_4F_8O$ requires F,56.7%. Infrared spectrum No.13.

<u>Benzaldehyde.</u>   No adduct was obtained when a 8.8:1 molar mixture of benzaldehyde and octafluorocyclohexa-1,4-diene was heated with benzoyl peroxide for 18 hrs. at 125°.

<u>Acetone.</u>   Octafluorocyclohexa-1,4-diene (4.2g, 0.019 moles) and acetone (9.5g, 0.164 moles) were heated with benzoyl peroxide (0.2g) for $21\frac{1}{2}$ hrs. at 125°.   The residue (0.4g) from the distillation of unchanged starting materials was distilled at $100^{\circ}/0.01$mm, giving a yellow liquid which eliminated hydrogen fluoride and darkened on standing. Analytical V.P.C. (Silicone elastomer at 225°; N_2 flow rate 0.9 l/hr) showed two components of retention times 4 and 7 min. The infrared spectrum of the mixture included bands at 3448, 3086, 3003, 2941, 1760-1700, 1631, 1464-909, 855 and 526 cm^{-1}.

<u>Methanethiol</u>

1; <u>Peroxide initiation.</u>   No adduct was obtained when a 1.5:1 molar mixture of methanethiol and octafluorocyclohexa-1,4-diene was heated with benzoyl peroxide for 24 hrs at $100-120^{\circ}$. Crystals of benzoic acid were filtered off from the reaction mixture, and distillation of unchanged starting material left only a small amount of orange gum.

2; <u>γ-Ray Initiation.</u>   A Carius tube charged with octafluoro-cyclohexa-1,4-diene (17.5g, 0.078 moles) and methanethiol (7.9g, 0.165 moles) was subjected to irradiation for 20 days from a 100 curie Co^{60} source and then for 9 days 15 hrs. from a 500 curie Co^{60} source. Unchanged CH_3SH was vented into a trap at -78°, and unchanged $1,4-C_6F_8$ (b.p.59°) distilled off. Etching

of the receiving vessel indicated HF elimination during the
distillation. Further distillation of the residual dark
brown liquid (4.0g) at $130^{\circ}/3$ mm gave a yellow distillate (2.7g)
Analytical V.P.C. (Tricresyl phosphate at 146°; N_2 flow rate
1 l/hr) showed it to be a mixture of at least eight components
with retention times ranging from 5 to 37 min.

Acetic acid. Only an orange oil (0.5g) was obtained when
octafluorocyclohexa-1,4-diene (5.0g, 0.022 moles) and acetic
acid (12.0g, 0.200 moles) were heated with benzoyl peroxide
(0.2g) for 22 hrs. at 130°.

Acetonitrile. Octafluorocyclohexa-1,4-diene (5.0g, 0.022 moles)
and acetonitrile (4.3g, 0.105 moles) were heated with benzoyl
peroxide (0.15g) for 21 hrs. at 125°. The reaction mixture
was distilled at $20^{\circ}/0.001$ mm., leaving a dark brown oil (0.3g).
The distillate (8.4g) was redistilled at atmospheric pressure
and the residue of b.p. $> 78^{\circ}$ (0.3g) was shown by analytical
V.P.C. (Silicone elastomer at 205°; N_2 flow rate 1 l/hr) to
consist of CH_3CN and a trace of a compound of retention time
9 min.

Ethyl acetate. Octafluorocyclohexa-1,4-diene (8.1g, 0.036 moles)
and ethyl acetate (16.1g, 0.183 moles) were heated with benzoyl
peroxide (0.2g) for 24 hrs. at 120°. Unchanged starting materials
(16.2g) were distilled at atmospheric pressure. The higher
boiling material was distilled at $20-90^{\circ}/0.0\frac{1}{2}$mm, leaving a yellow
oil (0.8g). The reduced pressure distillate was separated by

preparative scale V.P.C. (Silicone elastomer at 148°; N_2 flow rate 150 ml/min., p.d. 19cm) into its components, ethyl acetate (2.4g) and 1-(2H-octafluorocyclohex-4-enyl)ethylacetate (3.2g, 28.5%). b.p. 186°, n_D^{23} 1.3774. Found: F,48.3%. $C_{10}H_8F_8O_2$ requires F,48.7%. Infrared spectrum No.16. The analytical chromatogram of the pure product (di-n-decylphthalate at 153°; H_2 flow rate 50 ml/min) shows three peaks of retention times 8.4, 10.8 and 12.0 min. in the ratio 1.2:2:1.

ADDITIONS TO OTHER CYCLIC PERFLUORO-OLEFINS

Perfluoro(3,4-dimethylcyclohexene) plus methanol

No addition took place when a 9.4:1 mixture of methanol and perfluoro (3,4-dimethylcyclohexene) (P. 135) was heated with benzoyl peroxide for 23 hrs. at 120°. Since the reagents were immiscible at this temperature the reaction was repeated using 1,1,2-trifluoro-1,2,2,-trichloroethane as solvent, but again no adduct was obtained.

Perfluorocyclobutene plus methanol

Perfluorocyclobutene (8.0g, 0.049 moles) and methanol (7.4g, 0.231 moles) were heated with benzoyl peroxide (0.1g) for 24 hrs. at 115°. Fractionation of the reaction mixture under vacuum gave (i) C_4F_6 at -183° (0.2g), (ii) C_4F_6, CH_3OH and some product at -78° (9.7g). The material left in the Carius tube was distilled at 20°/0.01mm. The distillate (5.0g) consisted of two compounds with retention times identical to those of the products obtained by 𝛾-ray initiated addition[75], to which were

assigned the structures (a) (2H-hexafluorocyclobutyl)methanol and (b) pentafluorocyclobut-1-enyl methanol. A further 2.6g of (a) and (b) were recovered from trap (ii) after distillation of unchanged starting materials. Preparative scale V.P.C. (Silicone elastomer at 95°; N_2 flow rate 100 ml/min., p.d.32 cm) was used to separate the product mixture (7.6g) into its components (a) (5.1g; 53.7%), b.p. $129^O/750$ mm., n_D^{21} 1.3410. Found: F,57.8% Calc. for $C_5H_4F_6O$, F,58.7%; and an impure sample of (b) (0.5g, 6.1%).

PREPARATION OF DERIVATIVES OF ADDUCTS

Esterification of 2,2,3,4,4,4-hexafluorobutan-1-ol.

A solution of $CF_3CFHCF_2CH_2OH$ (2.0g, 0.011 moles) and 3,5-dinitrobenzoyl chloride (2.7g, 0.012 moles) in benzene (15 ml) containing a few drops of pyridine was refluxed for 1 hr. The reaction mixture was allowed to cool, then diluted with ether (15 ml) and washed with dilute hydrochloric acid, dilute sodium hydroxide solution and water. Distillation of the organic solvents under reduced pressure left an oily residue. Recrystall-isation from aqueous methanol yielded colourless crystals of the 3,5-dinitrobenzoate of 2,2,3,4,4,4-hexafluorobutan-1-ol (1.55g, 37.5%) m.p. 56°. Found: F,30.4; C,36.2; H,1.9%. $C_{11}H_6F_6N_2O_6$ requires F,30.3; C,35.1; H,1.6%.

Preparation of 2,4-dinitrophenylhydrazone of 1,1,1,2,3,3-hexa-fluoropentanone-4.

A solution of $CF_3CFHCF_2COCH_3$ (0.5g., 0.0026 moles) in a few ml.methanol was added to a filtered solution

of 2,4-dinitrophenylhydrazine (0.25g, 0.0013 moles) in methanol
(4 ml) with concentrated sulphuric acid ($\frac{1}{2}$ ml).   After a few
minutes at room temperature the 2,4-dinitrophenylhydrazone of
1,1,1,2,3,3-hexafluoropentanone-4 was precipitated as an orange
yellow solid.   Yellow crystals, m.p. 128°, were recrystallised
from ethanol.   Found: F,31.6%. $C_{11}H_8F_6N_4O_4$ requires F,30.5%.

Oxidation of methyl (2H-decafluorocyclohexyl)methanol

The starting material was the single isomer recovered
unchanged after treatment of the mixture of $H(C_6F_{10})CH(OH)CH_3$
isomers with aqueous potassium hydroxide (P. *150*).
Methyl (2H-decafluorocyclohexyl)methanol (0.7g, 0.002 moles),
potassium dichromate (0.7g, 0.002 moles), concentrated
sulphuric acid (0.5g) and water (3 mls) were stirred together
at 95° for 27 hrs.   The ether extract of the mixture was
neutralised by washing with aqueous potassium hydroxide, and
was then washed with water, dried ($MgSO_4$), filtered, and the
ether distilled off.   Analytical V.P.C. (di-n-decylphthalate at
137°) showed the mixture to consist of (i) a product having the
same retention time as the minor product of the addition of CH_3CHO
to C_6F_{10} (P. *125*.); (ii) unchanged starting material.   Absorption
at 1754 cm^{-1} in the infrared spectrum of the mixture is
attributable to (i) since (ii) shows no absorption in this region.
The components (i) 0.3g (49.1%) m.p. 38° and (ii) 0.2g, were
separated by preparative scale V.P.C. (Silicone elastomer at 120°,
N_2 flow rate 250 ml/min., p.d. 13cm).   The product (i) was

identified from its n.m.r. spectrum as the cis isomer of
(2H-decafluorocyclohexyl)methyl ketone, having an equatorial
hydrogen and an axial acyl group.

ADDITION OF TRIFLUOROMETHYL IODIDE TO CYCLIC PERFLUORO-OLEFINS

1. Thermal Initiation

Trial reactions showed at least 4 days at 205° to be
necessary for any appreciable addition to occur.

Octafluorocyclohexa-1,3-diene

A Carius tube charged with octafluorocyclohexa-1,3-diene
(9.3g, 0.042 moles) and trifluoromethyl iodide (19.0g, 0.097
moles) was heated for 5 days at 210°. The tube was opened
under vacuum and the more volatile material condensed in a trap
at -183°. Unchanged CF_3I (b.p. -20°) was distilled off, and
preparative scale V.P.C. separation of the higher boiling
components (Silicone elastomer at 120°; N_2 flow rate 150 ml/min;
p.d. 32 cm) yielded:- (i) $1,3-C_6F_8$(2.2g)., (ii) Compound (a)
(1.0g) of retention time 19 min., contaminated with a trace of
compound (b) of retention time 22 min. Solid iodine (2.8g) was
removed by centrifuging from the liquid left in the Carius tube
(3.1g), which was identified by analytical V.P.C. as compound (b).
Analysis and infrared and n.m.r. spectroscopy showed that (b)
was perfluoro-3,4-dimethylcyclohexene. Conversion 20.6%, b.p.
$198^O/745$ mm., n_D^{21} 1.3438. Found: F,73.1% C_8F_4 requires F,73.5%
Infrared spectrum No.23.

Compound (a)- insufficient pure material was obtained for
analysis, but a sample slightly contaminated with $1,3-C_6F_8$ had
b.p. 128-134° (with decomposition), and the infrared spectrum
showed strong absorption bands at 1745, 1333-917, 870, 775,
730, 637 and 610cm^{-1}.   The band at 1745cm^{-1} (C = C stretching)
indicates addition across one double bond only of $1,3-C_6F_8$.

Octafluorocyclohexa-1,4-diene

A Carius tube charged with octafluorocyclohexa-1,4-diene
(5.3g, 0.024 moles) and trifluoromethyliodide (13.0g, 0.066
moles) was heated for 4 days at 205°.   On opening the tube
gaseous material (shown by analytical V.P.C. (Tricresyl phosphate
at 38°) to consist of CF_3I plus a little material of shorter
retention time) was vented into a cooled trap(-183°), and
the liquid left (5.9g) was separated from solid iodine (0.25g).
Distillation at 20°/0.01mm gave a distillate (3.9g) shown by
analytical V.P.C. to consist mainly of $1,4-C_6F_8$, and a residue
consisting mainly of 4-iodo-5-trifluoromethyloctafluorocyclo-
hexene (1.75g, 17.4%). A sample of this, purified by preparative
scale V.P.C. (Silicone elastomer at 125°; N_2 flow rate 150 ml/min;
p.d. 35 cm) had b.p. 135°. Found: F,49.9; I,31.1%.$C_7F_{11}I$
requires F,49.8; I,30.2%. Infrared spectrum No.24.

Perfluorocyclohexene

A Carius tube charged with perfluorocyclohexene (6.3g.,
0.028 moles) and trifluoromethyl iodide (15.0g, 0.077 moles)
was heated for 4 days at 205°.   Recovered material consisted of

CF_3I (15.9g), C_6F_{10}(4.5g), iodine (0.1g) and 1-iodo-2-trifluoro-methyldecafluorocyclohexane (0.8g, 7.3%). A sample purified by preparative scale V.P.C. (Silicone elastomer at 125°; N_2 flow rate 125 ml/min., p.d. 15cm) had b.p. 132-3°. (Haseeldine and Osborne[38] report b.p. 132°). Infrared spectrum No.25.

II. γ-Ray Initiation

The following reactions were initiated by γ-Rays from a 500 curie Co^{60} source.

Octafluorocyclohexa-1,3-diene

A Carius tube charged with octafluorocyclohexa-1,3-diene (6.0g., 0.027 moles) and trifluoromethyl iodide (20.0g., 0.102 moles) was irradiated for 17 days. Gaseous material (19.0g) was vented into a cooled trap (-183°) and was shown by analytical V.P.C. (Tricresyl phosphate at 38°) to consist of CF_3I with a trace of material of shorter retention time. The liquid (6.6g) left after separation of solid iodine (0.4g) was distilled at 20°/0.01mm to remove 1,3-C_6F_8. The residue (0.5g), a brown liquid with a tendency to decompose on standing, was shown by analytical V.P.C. (Silicone elastomer at 133°) to consist of at least three components. Strong absorption bands in the infrared spectrum of the mixture occurred at 1724, 1397-935, 820 and 781cm^{-1}.

Octafluorocyclohexa-1,4-diene

Octafluorocyclohexa-1,4-diene (4.3g, 0.019 moles) and

trifluoromethyl iodide (11.4g, 0.058 moles) were irradiated
for 17 days. Recovered material consisted of CF_3I (11.3g), 1,4-
C_6F_8 (3.0g), iodine (0.3g), and a brown liquid (0.1g),
containing at least 2 components. Strong absorption bands
in the infrared spectrum of the mixture occurred at 1730, 1399-
926, 820 and 794cm^{-1}.

Perfluorocyclohexene

Perfluorocyclohexene (6.8g., 0.026 moles) and trifluoro-
methyliodide (24.3g, 0.124 moles) were irradiated for 17 days.
Recovered material consisted of CF_3I (24.2g)., C_6F_{10} (3.9g),
iodine (0.4g) and a mixture of two products (1.2g). Strong
absorption bands in the infrared spectrum of the mixture
occurred at 1730 and 1355-970cm^{-1}.

III. Ultraviolet initiation using Hanovia 1 k.w. and $\frac{1}{2}$ k.w. lamps.

Octafluorocyclohexa-1,4-diene

A pyrex Carius tube charged with octafluorocyclohexa-1,4-
diene (5.5g, 0.025 moles) and trifluoromethyliodide (17.5g.,
0.089 moles) was irradiated for 6 days 18 hrs (1 k.w. lamp)
followed by 2 days 12 hrs (500 w lamp). Recovered material
consisted of CF_3I (15.5g), 1,4-C_6F_8 (4.95g), iodine (0.15g) and
a single product (0.6g) of retention time coincident with that
of 4-iodo-5-trifluoromethyloctafluorocyclohexene obtained
by thermal addition.

Perfluorocyclohexene

No product was obtained when a pyrex Carius tube charged

with perfluorocyclohexene (5.0g, 0.019 moles) and trifluoro-
methyliodide (10.4g, 0.053 moles) was irradiated for 8 days
(1 k.w. lamp).

Attempted Addition of Heptafluoroisopropyl Iodide to Octafluor-ocyclohexa-1,3-diene.

A Carius tube charged with octafluorocyclohexa-1,3-diene
(4.3g., 0.019 moles) and heptafluoroisopropyl iodide (13.3g,
0.045 moles) was heated for 4 days at 200°. Distillation under
nitrogen gave the following fractions:- (i) b.p.40-41°, 9.25g;
(ii) b.p. 46-50°, 0.95g, (b.p. i-C_3F_7I, 39.5°; b.p. 1,3-C_6F_8,
63-64°); (iii) b.p. $> 50^{\circ}$, 3.0g. Analytical V.P.C. (Silicone
elastomer at 130°) showed (iii) to consist mainly of unchanged
starting material plus traces of three compounds of longer
retention time.

DEHYDROFLUORINATION OF ALCOHOL ADDUCTS

The starting materials were the mixtures of isomers obtained by free radical addition of alcohols to the appropriate perfluoro-olefins.

I.   (2H-octafluorocyclohex-4-enyl) methanol

(a)   Potassium hydroxide in mineral oil

(2H-octafluorocyclohex-4-enyl) methanol (4.8g., 0.019 moles) was added dropwise to a stirred suspension of powdered potassium hydroxide (4.5g., 0.080 moles) in heavy white oil (10 ml) in a three-necked flask fitted with a mercury-seal stirrer and reflux condenser.   A vigorous reaction ensued accompanied by darkening of the reaction mixture.   Stirring was continued at room temperature for 1 hr., then at 90-130° for 4$\frac{1}{2}$ hrs.   Distillation, firstly at atmospheric pressure with the oil bath at 160°, then at 10mm/70°, yielded a clear yellow distillate (0.7g.) with a tendency to liberate hydrogen fluoride on standing, and a dark brown solid residue.   Analytical V.P.C. (Silicone elastomer at 142°) showed the distillate to consist of a mixture of compounds of shorter retention time than the starting material, plus a small proportion of unchanged starting material.   Fig. 2a.
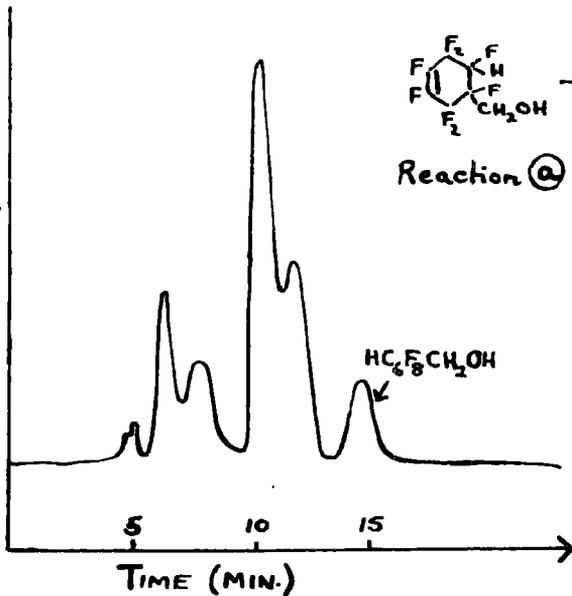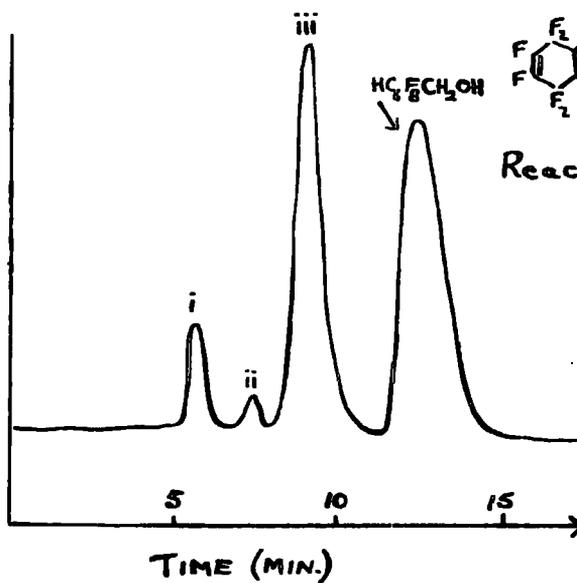
FIG. 2a

Reaction (a)

Stationary phase: Silicone elastomer

Temp. : 142°

Flow rate : 1 ℓ N₂ /hr.

HC₆F₈CH₂OH

FIG. 2b

Reaction (c)

Stationary phase: Silicone elastomer

Temp. : 125°

Flow rate : 1·5 ℓ N₂ /hr.

HC₆F₈CH₂OH

(b)   Anion exchange resin

Preparation of resin.   Amberlite IRA 400 (OH) resin was prepared
in its basic form by washing a column full of resin (50g) with
4% sodium hydroxide solution (1 litre), followed by distilled
water (1 litre).   The resin was then transferred to a Buchner
funnel, washed with methylated spirits (3 x 30 ml.), ether
(3 x 30 ml.) and dried in a drying pistil at 36°.

Dehydrofluorination.   (2H-octafluorocyclohex-4-enyl) methanol
(4.6g., 0.018 moles) and Amberlite IRA 400 (OH) resin (18g.,
i.e. 23% excess) were stirred for 1 hr. at room temperature,
during which time an exothermic reaction was observed, then
at 55° for a further hour.   The resin was washed well with
ether, evaporation of which left 2.3g organic material.   On
attempting to distill this at atmospheric pressure, decomposition,
involving liberation of HF, began when the temperature reached
110°, so the resulting deep red solution was distilled at 60°/
0.01mm. yielding a colourless distillate (1.1g.) and a dark red
residue (0.9g.).   The analytical chromatogram of the distillate
strongly resembled that of the mixture obtained from reaction (a).

(c)   Concentrated aqueous potassium hydroxide
(2H-octafluorocyclohex-4-enyl) methanol (5.3g., 0.095 moles)
was added dropwise over a period of 10 minutes to a 2N solution
of potassium hydroxide (2.2g, 0.04 moles, in 20 ml. water) in

a 250 ml. three-necked flask fitted with stirrer and reflux condenser. Stirring was continued at room temperature for 2 hrs., during which time a red organic layer formed beneath a yellow-brown aqueous layer. The reaction mixture was made slightly acid by addition of dilute HCl (3.5 ml.) to liberate any acidic alcohol present as the potassium alkoxide, and was extracted with ether, giving a viscous orange liquid (3.3g.). Distillation at $100^{\circ}/0.01$mm. yielded a yellow distillate (1.5g.), and a solid orange residue, shown by ebullioscopic measurements to have a molecular weight in the region 500-750. Analytical V.P.C. (Silicone elastomer at 125°) showed three major components in addition to starting material. Fig. 2b.

The infrared spectrum of an impure sample of component (iii), separated by preparative scale V.P.C. (Silicone elastomer at 125°; N_2 flow rate 175 ml./min; p.d. 25 cm) showed strong absorption bands in the C=C stretching frequency region at 1786, 1757, 1724 and 1639 cm^{-1}.

(d) Dilute aqueous potassium hydroxide

1N potassium hydroxide (2.8g., 0.05 moles, in 50 mls. water) was added dropwise over $2\frac{1}{2}$ hrs. to (2H-octafluorocyclohex-4-enyl)methanol (13.7g., 0.054 moles) with stirring at room temperature. Stirring was continued for a further $21\frac{1}{2}$ hrs. The ether extract of the reaction mixture (8.9g.) was shown by

analytical V.P.C. (Silicone elastomer at 150°) to consist of
(a) a single product and (b) unchanged starting material,
estimated from the peak areas on the chromatogram (assuming
equal response) to be in the molar ratio of approximately 2:1.
Preparative scale V.P.C. (Silicone elastomer at 112°; N_2
flow rate 120 ml./min; p.d. 29cm.) was used to obtain pure
samples of the two components, which had retention times of
(a) 35 min., (b) 50 min. (a) was identified by studies of
its infrared and n.m.r. spectra as (heptafluorocyclohexa-1,4-
dienyl) methanol. b.p. 158-9°/765mm.; n_D^{21} 1.3766.
Found ≠ F, 56.2%. $C_7H_3F_7O$ requires F, 56.4%.
Infrared Spectrum No.19.

(b) was identified from its n.m.r. spectrum as a single
geometric isomer of (2H-octafluorocyclohex-4-enyl) methanol
m.p. 50° (colourless needles recrystallised from pet.ether
60 - 80°).
Infrared Spectrum No. 14b.

II. <u>Methyl (2H-octafluorocyclohex-4-enyl) methanol</u>
1N potassium hydroxide (0.4g., 0.007 moles, in 7 ml. water)
was added dropwise over a period of 15 min. to methyl (2H-
octafluorocyclohex-4-enyl) methanol (1.6g., 0.006 moles), in
a 25 ml. three-necked flask fitted with stirrer and reflux
condenser, and stirring was continued at room temperature for
a further 5 hrs. The colourless distillate (1.3g) obtained

from the organic layer at $50^{\circ}/0.01$mm. was shown by analytical V.P.C. (di-n-decylphthalate at 153°; H_2 flow rate 60 ml./min.) to contain three product compenents (retention times 4.4, 7.4 and 8.6 min.) in the ratio 1:4.3:1 and a single starting material component, B, (retention time 14.8 min.). Starting material peaks A and C of retention times 13.0 and 17.2 min. were no longer present, but the proportions of B present in the reaction mixture and in the starting material were very similar, (Figs. 3 and 4). The infrared spectrum of the reaction mixture showed in addition to a band at 1751 cm^{-1} attributable to starting material, further C=C absorption bands of similar intensity at 1773 and 1715 cm^{-1}, which must belong to the products.
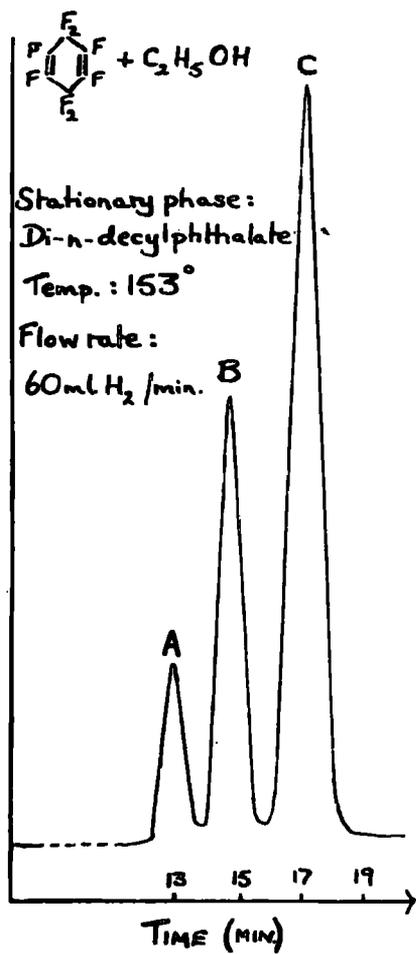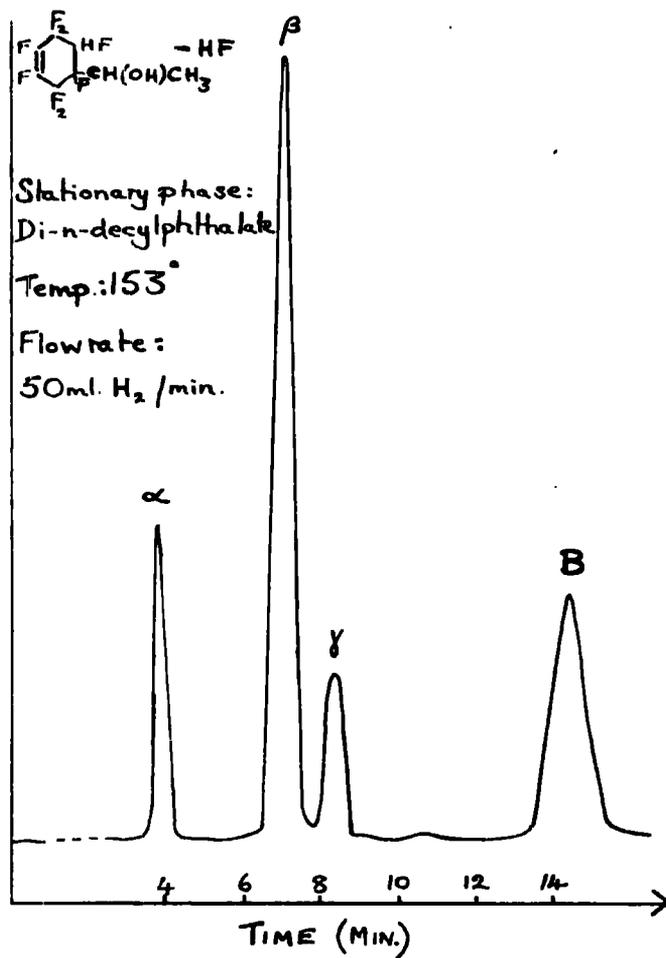
Fig.3

Fig. 4

III.   (2H-decafluorocyclohexyl) methanol

1.   1N KOH at 21°

(2H-decafluorocyclohexyl) methanol (2.4g., 0.008 moles) was
added dropwise over a period of 20 min. to a stirred solution
of potassium hydroxide (1.0g., 0.018 moles, in 20 ml. water)
and stirring was continued at room temperature for a further
20 min.   After acidification of the reaction mixture with
dilute HCl, ether extraction yielded a yellow liquid (1.85g.).
A colourless distillate (1.25g.) and an orange residue (0.6g.)
were obtained at 100°/0.01 mm.   Analytical V.P.C. (Silicone
elastomer at 138°) showed the distillate to consist of a
single product and unchanged starting material, estimated
from the chromatogram to be in the molar ratio 1:2.

2.   1N KOH at 21°

(2H-decafluorocyclohexyl) methanol (7.65g., 0.026 moles) was
added to a stirred solution of potassium hydroxide (2.2g.,
0.04 moles, in 40 ml. water) and stirring was continued at
room temperature for 7 hrs.   Ether extraction of the
acidified reaction mixture, followed by distillation at 100°/
0.01mm., gave an orange residue (0.5g.) and a colourless
distillate (6.05g.).   Analytical V.P.C. showed a slight
excess of product over unchanged starting material.

3.   1N. KOH at 55°

(2H-decafluorocyclohexyl) methanol (8.2g., 0.028 moles) was

added to a stirred solution of potassium hydroxide (2.2g., 0.04 moles, in 40 ml. water) and stirring was continued at 55° for $2\frac{1}{2}$ hrs. The acidified reaction mixture was continuously extracted with ether, and the extract distilled, giving a brown residue (1.2g.) and a colourless distillate (4.75g.). Analytical V.P.C. showed a slight excess of unchanged starting material over product.

4. **4.5N KOH at 65°**

(2H-decafluorocyclohexyl) methanol (7.9g., 0.027 moles) was added to a stirred solution of potassium hydroxide (10.0g., 0.179 moles, in 40 ml. water) and stirring continued at 65° for $3\frac{1}{2}$ hrs., during which time the reaction mixture became dark brown. Ether extraction of the acidified mixture, followed by distillation at $80^{\circ}/0.01$ mm. gave a dark brown gummy residue (4.8g.), and a distillate (1.2g. including some ether) which was shown by analytical V.P.C. (Silicone elastomer at 149°; N_2 flow rate 1.1 l/hr.) to contain two compounds of retention times 17 min. and 19 min. and a trace of starting material (retention time 9 min) but none of the product obtained in reactions (1) to (3) (retention time $6\frac{1}{2}$ min.).

5. **Addition of 0.9N KOH at 21°**

Aqueous potassium hydroxide (1.2g., 0.021 moles, in 25 ml. water) was added dropwise over a period of 27 hrs. to (2H-

decafluorocyclohexyl) methanol (6.0g., 0.020 moles) which was being stirred at room temperature, and stirring was continued for a further 16 hrs. (Comparison of the analytical chromatograms of samples taken from the mixture 3 hrs. and 16 hrs. after completion of KOH addition showed that little change in the ratio of product to starting material was brought about during the last 13 hrs.). Ether extraction of the reaction mixture gave a mixture of product and starting material (2.55g.), estimated from the analytical chromatogram to be in the molar ratio of 3:1.

Preparative scale V.P.C. separation of product from starting material

Complete separation of product and starting material could not be attained, but pure samples of each were obtained using Silicone elastomer at 105°; N2 flow rate 100 ml/min.; p.d. 28 cm. Retention times were:- product, 23 min; starting material 35 min. The product was identified by studies of its infrared and n.m.r. spectra as (nonafluorocyclohex-1-enyl) methanol. b.p. 143-4°/755 mm., n_D^{21} 1.3507. Found: F, 62.4%. $C_7H_3F_9O$ requires F, 62.4%. Infrared Spectrum No.17.

IV. Methyl (2H-decafluorocyclohexyl) methanol

0.9N potassium hydroxide (2.5g., 0.045 moles, in 50 ml.water)

was added dropwise over a period of 4 hrs. to methyl (2H-decafluorocyclohexyl) methanol (13.2g., 0.044 moles) which was being stirred at room temperature, and stirring was continued for a further 17 hrs. The lower organic layer (11.5g.) was combined with the ether extract of the upper aqueous layer (0.9g.) and distilled at $50^{\circ}/0.01$mm. Analytical V.P.C. (Silicone elastomer at 136°) showed a single product and unchanged starting material, estimated from the chromatogram to be in the approximate molar ratio of 1.7:1. Pure samples of each were obtained using preparative scale V.P.C. (Silicone elastomer at 112°; N_2 flow rate 200 ml/min.; p.d. 48 cm.), the retention times of product and starting material being 30 min. and 50 min. respectively.

The product was identified from its infrared spectrum as methyl (nonafluorocyclohex-1-enyl) methanol. m.p. 44° (colourless needles recrystallised from pet. ether $60-80^{\circ}$). Found: F, 59.3%. $C_8H_5F_9O$ requires F, 59.4%. Infrared spectrum No.18.

The unchanged methyl (2H-decafluorocyclohexyl) methanol was shown by its n.m.r. spectrum to consist of only one stereo-isomer. m.p. 57° (colourless needles recrystallised from pet. ether $60-80^{\circ}$). Found: F, 61.2%. Calc. for $C_8H_6F_{10}O$: F, 61.7%. Infrared spectrum No. 9b.

V.   4, 4, 5, 6, 6, 6-hexafluorohexan-3-ol

(i)   No dehydrofluorination occurred when $CF_3CFHCF_2CH(OH)C_2H_5$
was stirred with 0.74N potassium hydroxide solution at room
temperature for 5 hrs.

(ii)   2.6N potassium hydroxide (0.7g., 0.013 moles in 5 ml.
water) was added to CF_3CFH CF_2 $CH(OH)C_2H_5$ (0.8g., 0.004 moles)
and the mixture was stirred at 100° for $2\frac{1}{2}$ hrs.   The ether
extract of the reaction mixture was distilled at $20^o/0.01$ mm,
and the distillate (0.5g) was shown by analytical V.P.C.
(di-n-decylphthalate at 98°; H_2 flow rate 70 ml./min) to
contain two components of retention times 19.6 and 22.8 min., the
latter slightly in excess of the former, but no starting material
peaks (retention times 29.2 and 31.6 min.).   The products were
identified from the infrared and N.M.R. spectra of the mixture
as geometric isomers of 1,1,1,2,3-pentafluorohex-2-en-4-ol. b.p.
$121^o/745$ mm; n_D^{23} 1.3540.   Found: F, 49.3%. $C_6H_7F_5O$ requires
F, 50.0%.   Infrared spectrum No.21.

VI.   2-methyl-3,3,4,5,5,5-hexafluoropentan-2-ol.

2.4N potassium hydroxide (2.0g., 0.036 moles in 15 ml.
water) was added to $CF_3CFHCF_2C(OH)(CH_3)_2$ (4.0g., 0.013 moles)
and the mixture was stirred at 100° for 6 hrs.   The recovered
organic material (2.4g) was shown by analytical V.P.C. (di-n-
decylphthalate at 98°; H_2 flow rate 60 ml./min) to consist of
compounds of retention times 11 min. and 14 min. in the ratio
14:1, plus about 20% unchanged starting material (retention time

23 min.). A sample of product was obtained pure by preparative scale V.P.C. (Silicone elastomer at 93°; N_2 flow rate 100 ml./min; p.d. 10 cm.) and identified from its infrared and n.m.r. spectra as predominantly the trans isomer of 1,1,1,2,3-pentafluoro-4-methylpent-2-en-4-ol. b.p. 117°; n_D^{23} 1.3533. Found: F,50.2%. $C_6H_7F_5O$ requires F,50.0%. Infrared spectrum No.22.

VII.   2,2,3,4,4,4-hexafluorobutan-1-ol.

(i)   2N potassium hydroxide (1.2g., 0.021 moles in 11 ml. water) was added to $CF_3CFHCF_2CH_2OH$ (4.0g., 0.022 moles) and the mixture was stirred at room temperature for $43\frac{1}{2}$ hrs. and then extracted with ether. Analytical V.P.C. (di-n-decylphthalate at 112°; H_2 flow rate 100 ml./min.) showed only very small amounts of two products, X and Y, of retention times 4.4 min and 5.2 min. (Retention time of starting material, 7.2 min.)

(ii)   2.5N potassium hydroxide (3.0g., 0.053 moles in 20 ml. water) was added to $CF_3CFHCF_2CH_2OH$ (4.7g., 0.026 moles) and the mixture was stirred for $\frac{1}{2}$ hr. at 75°, during which time both aqueous and organic layers became dark brown. The ether extract was distilled at 50°/0.01 mm to give a colourless liquid mixture (1.7g), shown by analytical V.P.C. (di-n-decylphthalate at 112°; H_2 flow rate 100 ml./min.) to

contain a high proportion of X and Y, a small amount of
unchanged starting material, and a number of components
(peaks A-D) in the retention time range 11.5 to 20 min.
Preparative scale V.P.C. (3m. x 1 in. column with di-n-
decylphthalate at 90°; N_2 flow rate 200 ml./min.) was used
to isolate sufficient of product X (plus a trace of Y) for
an infrared spectrum (No.20), which showed a strong absorption
band at 1733 cm^{-1}. The spectrum of the rest of the reaction
mixture (starting material, Y, a little X, and A-D) showed
bands at 1733(s), 1700(w) and 1623(m) cm^{-1}.

(iii) Treatment of $CF_3CFHCF_2CH_2OH$ with 2N potassium hydroxide
at 50° for 2 hrs. gave only slight conversion to X and Y,
and none of compounds A to D. After a further $7\frac{1}{2}$ hrs. about
50% conversion to X and Y, plus formation of small amounts
of A to D, was observed. Samples consisting predominantly
of X and Y which were isolated by preparative scale V.P.C.
(3m. x 1 in. column with Apiezon 'L' grease at 70°; N_2
flow rate 150 ml./min; p.d. 25cm) showed infrared absorption
bands at 1733cm^{-1}.

Dehydrofluorination of methane thiol adduct of perfluoro-propene

Methyl 1,1,2,3,3,3-hexafluoropropyl sulphide, containing
a trace of methyl 1,2,2-trifluoro-1-(trifluoromethyl) ethyl

sulphide (2.3g., 0.013 moles) and potassium hydroxide (0.5g., 0.009 moles in a few ml. water) were heated together at 120-130° for 6 hrs. The organic layer (1.1g) was separated from the aqueous layer and distilled at atmospheric pressure. The fraction boiling at 82-85° (1.0g) was shown by analytical V.P.C. (Silicone elastomer at 80°) to consist largely of unchanged starting material, plus two products of shorter retention times in the ratio 8:7. The infrared spectrum of the mixture showed a band at 1692 cm^{-1} which is absent from the spectrum of the saturated material, indicating that the products are geometric isomers of $CH_3SCF:CFCF_3$.

Reaction of 2H-decafluorocyclohexyl methyl ketone with aqueous alkali

1N potassium hydroxide (1.2g., 0.021 moles in 25 ml. water) was added to 2H-decafluorocyclohexyl methyl ketone (7.1g., 0.023 moles) and the mixture was stirred at room temperature for 8 hrs. The analytical chromatogram (di-n-decylphthalate at 112°) of the lower organic layer (6.0g.) showed it to consist mainly of unchanged starting material plus two products of shorter retention time. Ether extraction of the aqueous layer yielded a further 0.1g organic material (mainly products). Preparative scale V.P.C. (Silicone elastomer at 95°; N_2 flow rate 150 ml./min.; p.d. 14 cm.)

was used to separate the products (0.9g) from the starting

material.   The infrared spectrum of the product mixture

included the following bands:- 3093(w), 3058(w), 1831(w),

1748(w), 1709(s), 1370-940 Cm^{-1}.

N.M.R. Data

Peak positions of ^{19}F resonances relative to $CFCl_3$
as an internal reference are given in the following tables:-

1. $\underline{CF_3CFHCF_2R}$

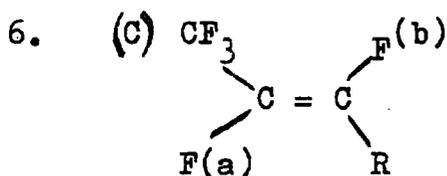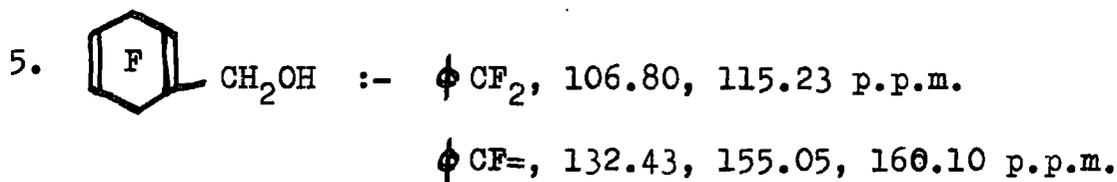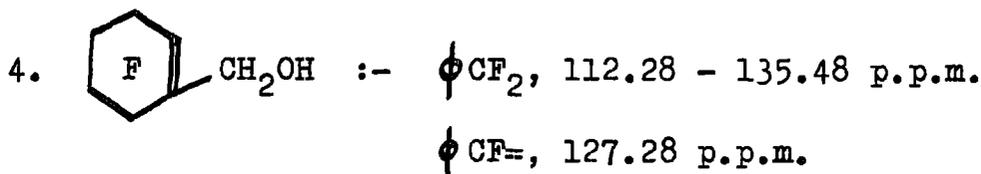| R	ϕCF_3 p.p.m.	ϕCF_2 p.p.m.	ϕ CFH ppm.
CH_2OH	75.0	115.43, 119.78, 121.57, 126.08	214.28
$CH(OH)CH_3$	74.91	118.65, 122.54, 123.19, 124.43, 127.00, 128.97, 130.10, 134.68	213.72 215.45
$CH(OH)C_2H_5$	74.71	117.37, 121.97, 123.25, 126.90, 128.38, 132.97	213.57 215.35
$CH(OH)C_3H_7$	74.78	117.30, 122.03, 123.52, 127.07, 128.51, 133.25	213.60 215.28
$CH(OH)(CH_3)_2$	74.60	121.12, 124.60, 126.05, 129.53	207.82
$COCH_3$	74.78	113.42, 118.52, 121.38, 126.47	217.03
$CH(CH_3)OCOCH_3$	74.76	113.42, 118.52, 121.38, 126.47, 122.33, 122.37, 124.72	213.67 214.90

2.

H
R
F

R	Isomer	ϕ CF$_2$ p.p.m.	ϕCFR p.p.m.	ϕ CFH p.p.m.
CH$_2$OH	trans	(116.35 – 147.03	195.67	234.17
"	cis		189.30	211.00
CH(OH)CH$_3$	trans	(116.18 – 148.40	197.233	237.73, 240.23
"	cis		199.867	210.217
CH(OH)C$_2$H$_5$	trans	(116.08 – 148.83	193.17	230.25, 233.33
"	cis		197.17	209.83
CH(OH)C$_3$H$_7$	trans	(116.28 – 148.58	193.17	230.66, 233.67
"	cis		197.58	210.17
CH$_3$CO	trans	117.83 – 148.300	193.15	231.33
"	cis	116.05 – 141.00	176.53	212.917

3.

$$\quad \text{(hexagon with F, H, R)}$$

R	Isomer	ϕ CF_2 p.p.m.	ϕ CF= p.p.m.	ϕ CFR p.p.m.	ϕ CFH p.p.m.
CH_2OH	trans	} 98.57 – 124.83	} 154.700	190.83	224.58
"	cis			185.47	206.62
$CH(OH)CH_3$	trans	} 98.82 – 126.62	} 154.98	187.42	223.72, 221.00
"	cis			196.72	206.03
CH_3CO	cis & trans	100 – 125	~ 155(2 peaks)	183.83	222.17
				191.33	228.83
$CH(CH3)OCOCH_3$	three isomers	~ 100 – 125	~ 155	6 peaks	

4. [structure: cyclohexene ring with F] CH$_2$OH :- ϕ CF$_2$, 112.28 - 135.48 p.p.m.

ϕ CF=, 127.28 p.p.m.

5. [structure: benzene-type ring with F] CH$_2$OH :- ϕ CF$_2$, 106.80, 115.23 p.p.m.

ϕ CF=, 132.43, 155.05, 160.10 p.p.m.

6.   (c) CF$_3$ F(b)

$$\begin{array}{c} \text{CF}_3 \\ \diagdown \\ \text{F(a)} \end{array} C = C \begin{array}{c} \text{F(b)} \\ \diagup \\ \text{R} \end{array}$$

Peak positions and coupling constants:-

R	CH(OH)C$_2$H$_5$	CH(OH)C$_2$H$_5$	CH(OH)(CH$_3$)$_2$
Isomer	trans	cis	trans
ϕ a p.p.m.	174.84	143.128	169.503
ϕ b p.p.m.	157.522	153.333	147.250
ϕ c p.p.m.	68.793	66.448	68.295
Jac cycles sec^{-1}	10.3 $\pm$ 0.3	8.6 $\pm$ 0.2	9.5 $\pm$ 0.2
Jbc cycles sec^{-1}	21.8 $\pm$ 0.2	12.1 $\pm$ 0.1	22.5 $\pm$ 0.2
Jab cycles sec^{-1}	134.3 $\pm$ 0.5	27.7 $\pm$ 0.3	134.9 $\pm$ 0.8
JbH cycles sec^{-1}	24.8 $\pm$ 0.3		
JaH cycles sec^{-1}	4.9 $\pm$ 0.3	2.7 $\pm$ 0.1	

1. CF₃CFHCF₂CH₂OH Liquid

2. CF₃CFHCF₂CHOH / CH₃ Liquid

160

3

CF₃CFHCF₂CHOH
     C₂H₅
Liquid

4

CF₃CFHCF₂COH
          CH₃
Liquid   CH₃

191

5

CF_3CFHCF_2CHOH
$CH_2CH_2CH_3$

Liquid

3610 3367 2959 2928 2870

1466 1577 1293 1255 1183 1169 1098 1088 837 892 848 875 962 773 763 696 688 675 625

2.5 3 3.5 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19

6

$CF_3CFHCF_2CHOCOCH_3$
CH_3

3847 3003 2950

1754 1392 1371 1265 1294 1042 1030 1000 833 862 943 885 1471 1353 1287 1189 1175 1101 1066 741 714 697 681 656 633 604 526 515

2.5 3 3.5 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19

7

CF₃ CFH CF₂ C CH₃
              ‖
              O

Liquid

3484   2985   1748   1715 1538   1379 1364 1418   1282 1255 1258 1168 1105 1043 1003 870 844 826 709 694 645 592 543
       2913

2.5   3   3.5   5   6   7   8   9   10   11   12   13   14   15   16   17   18

8

⬡—CH₂OH
  |
  H

Liquid

3856   2945   1877   1463   1321 1290 1226 1171 1185 1084 1071 1041 1000 975 926 885 820 767 755 713 662 621 601 583

2.5   3   3.5   5   6   7   8   9   10   11   12   13   14   15   16   17   18

163

10

C₃H₆ / CHOH / H (structure on phenyl ring, "P")

Liquid

3425 3610 2971 2941 2885 1464 1374 1316 1279 1180 1058 1022 971 957 935 889 852 818 802 776 751 721 675 699 661 621 599 594 577

11

C₃H₇ / CHOH / H (structure on phenyl ring, "P")

Liquid

3401 3610 2969 2929 2874 1446 1372 1316 1282 1251 1044 1020 952 914 880 853 818 802 784 756 719 710 697 680 660 621 600 594 675

165

12

F ⬡ H COCH₃

Liquid

3484 2982 2935

1788 1706 1489 418 1344 1311 1280 1185 1045 1042 1019 943 840 808 787 662 645 618 597 656 514

2·5   3   3·5   5   6   7   8   9   10   11   12   13   14   15   16   17   18   19   20

166

13

F ⬡ H COCH₃

Liquid

3484 2972 2924

1745 1414 1364 1335 1300 1244 1208 1190 1156 1168 1111 1091 1049 1045 1013 980 935 877 840 830 808 790 775 712 714 684 643 635 620 593 549

2·5   3   2·5   5   6   7   8   9   10   11   12   13   14   15   16   17   18   19   20

14a

14b

167

15

CH₂
CHOH
F
H

Liquid

3401
2985 2941
1754
1440
1626
1587 1563
1507
1484 1460
1148
1060 990
887
715
760
840
812
718
488

2·5 3 3·5 5 6 7 8 9 10 11 12 13 14 15

16

CH₃
CHOCOCH₃
F
H

3489
2976
1748
1451
1429
1370 1342
1307
1170
1148
1040
992
943
885 871
855
813
730 719
698
680
633
600
571
534

2·5 3 3·5 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19

17

⬡—CH₂OH

Liquid

3576
3636
3706
2957 2907
1712
1502
1387
1359
1235
1207
1177
1140
1120
1072
1085
1025
952
934
467 445

18

⬡—CH₂—CHOH (with CH₃)

Solid. melt

3367
1692
1427
1350
1318
1297
1252
1226
1175
1130
1105
1073
1085
1031
957
931
866
820
662

19

Ph—CH₂OH

Liquid

3371

2950 2871

1774 1721

1637

1593

1346

1261

1287

1219

1191

995

957

918

2·5 3 3·5 5 6 7 8 9 10 11 12 13 14 15

20

$CF_3CF=CFCH_2OH$

Liquid

3355

2913 2874

1733

1636

1453

1355

1277

1193

1143

1093

1000

943

769

714

650

2·5 3 3·5 5 6 7 8 9 10 11 12 13 14 15

171

22

$CF_3 \atop F$ C=C $F \atop C(CH_3)_2OH$ Liquid

3616
2885
2941
2985
1713
3390
1468
1366 1352 1252 1171 1142 1104
952
901 917
826
719
736 761 769
636
680
606 685
517
877
1005
1044

21

$CF_3CF=CFCHOH$ (cis and trans) C_2H_5 Liquid

3610
3676
3855
2971 2941
2883
1724
1631
1460 1470
1374
1353
1114
1193
1285
941
1015 1045 1076
885
842 873
800
746 719
694
999

23

Liquid

1733

24

Liquid

1761

25

Liquid

REFERENCES

1. Miller, Fried and Goldwhite, J.A.C.S., 1960, 82, 3091.

2. Miller, Freedman, Fried and Koch, J.A.C.S., 1961, 83, 4105.

3. Henne, Smook and Pelley, J.A.C.S., 1950, 73, 4756.

4. Henne and Arnold, J.A.C.S., 1948, 70, 758.

5. Hanford & Rigby, U.S.Patent, 2,409,274 (1946).

6. Miller, Fager and Griswold, J.A.C.S., 1948, 70, 431.

7. Park, Vail, Lea and Lacher, J.A.C.S., 1948, 70, 1550.

8. Park, Sharrah and Lacher, J.A.C.S., 1949, 71, 2337.

9. Coffman, Raasch, Rigby, Barrick and Hanford, J.Org.Chem.1949, 14, 747.

10. Henne and Smook, J.A.C.S., 1950, 72, 4378.

11. Barr, Rapp, Pruett, Bahner, Gibson and Lafferty, J.A.C.S., 1950, 72, 4480.

12. Park, Sharrah, Breen and Lacher, J.A.C.S., 1951, 73, 1329.

13. Tarrant and Brown, J.A.C.S., 1951, 73, 1781.

14. Tarrant and Brown, J.A.C.S., 1951, 73, 5831.

15. Park, Snow and Lacher, J.A.C.S., 1951, 73, 2342.

16. Knunyants, Shchekotikhin and Fokin, Izvest.Akad.Nauk.S.S.S.R., Otdel.Khim.Nauk. 1953, 282. (Chem.Abs.1954, 48, 5787h)

17. Knunyants, German and Dyatkin, Izvest.Akad.Nauk. S.S.S.R., Otdel. Khim.Nauk., 1956, 1353 (Chem.Abs.1957, 51, 8037f).

18. Park, Sweeney, Hopwood and Lacher, J.A.C.S., 1956, 78, 1685.

19. Koshar, Simmons and Hoffman, J.A.C.S., 1957, 79, 1741.

20. Meier and Böhler, Chem.Ber.1957, 90, 2342.

21. Park, Cummings & Lacher, J.Org.Chem. 1958, 23, 1785.

22. Shepard, Lessoff, Domijan, Hilton and Finnegan, J.Org.Chem., 1958, 23, 2011.

23. Demiel, J.Org.Chem. 1960, 25, 993.

24. England, Melby, Dietrich and Lindsey, J.A.C.S. 1960, 82, 5116.

25. Rapp, Pruett, Barr, Bahner, Gibson and Lafferty, J.A.C.S., 1950, 72, 3642.

26. Knunyants and Fokin, Izvest. Akad.Nauk. S.S.S.R.Otdel.Khim.Nauk., 1952, 261. (Chem.Abs.1953, 47, 3221b).

27. Rapp, Pruett, Barr, Bahner, Gibson and Lafferty. J.A.C.S. 1950, 72, 3646.

28. Stephens, Intern.Symposium, Fluorine Chem.Birmingham, 1959.

29. Carboni and Lindsey. J.A.C.S. 1958, 80, 5793.

30. Parker, J.A.C.S. 1959, 81, 2183.

31. Krespan, J.Org.Chem. 1962, 27, 1813.

32. Smith, Fawcett and Coffman, J.A.C.S. 1962, 84, 4285.

33. Chambers, Musgrave and Savory, Proc.Chem.Soc.1961, 113.

34. Chambers, Musgrave and Sacory. J.C.S. 1961, 3779.

35. Henne and Kaye, J.A.C.S. 1950, 72, 3369.

36. Harmon, U.S.Patent 2,404,374 (1946).

37. Haszeldine, J.C.S. 1953, 3565.

38. Haszeldine and Osborne. J.C.S. 1956, 61.

39. Hauptschein, Braid and Fainberg, J.A.C.S. 1961, 83, 2495.

40. Haszeldine and Steele, J.C.S. 1954. 923.

41. Haszeldine, J.C.S. 1952, 4423.

42. Henne and Nager, J.A.C.S. 1951, 73, 5527.

43. Brice and Simons, J.A.C.S. 1951, 73, 4017.

44. McBee, Pierce and Chen, J.A.C.S. 1953, 75, 2324.

45. Haszeldine, J.C.S. 1949, 2856.

46. Haszeldine, J.C.S. 1951, 2495.

47. Haszeldine, J.C.S. 1953, 922.

48. Haszeldine & Leedham, J.C.S. 1953, 1548.

49. Haszeldine J.C.S. 1953, 3761.

50. Haszeldine, J.C.S. 1952, 2504.

51. Haszeldine & Steele, J.C.S. 1953, 1199.

52. Haszeldine & Steele, J.C.S. 1953, 1592.

53. Haszeldine, J.C.S. 1953, 3559.

54. Haszeldine & Steele, J.C.S. 1954, 3747.

55. Haszeldine & Steele, J.C.S. 1955, 3005.

56. Haszeldine & Steele, J.C.S. 1957, 2193.

57. Haszeldine & Steele, J.C.S. 1957, 2800.

58. Tarrant, Lovelace & Lilyquist, J.A.C.S. 1955, 77, 768, 2783 and
     3640.

59. Hauptschein, Braid & Lawlor, J.A.C.S. 1957, 79, 2549.

60.   idem,   J.A.C.S. 1958, 80, 846.

61. Hauptschein, Braid & Fainberg, J.A.C.S. 1958, 80, 851.

62. Coscia, J.Org.Chem. 1961, 26, 2995.

63. Stacey and Harris, J.Org.Chem. 1962, 27, 4089.

64. Joyce, U.S.Patent, 2,559,628 (1951)

65. Hanford & Joyce, U.S.Patent, 2,562,547 (1951)

66. Hanford, U.S.Patent 2,411,158. (1946).

67. Hanford, U.S.Patent, 2,411,159 (1946)

68. Hanford, U.S.Patent, 2,433,844 (1948)

69. du Pont, Brit.Patent, 583,874 (1947)

70. Harris & Coffman, J.A.C.S. 1962, 84, 1553.

71. Muramatsu, J.Org.Chem. 1962, 27, 2325.

72. Muramatsu, and Inukai, J.Org.Chem. 1962, 27, 1572.

73. Hauptschein and Lesser, J.A.C.S. 1956, 78, 676.

74. LaZerte and Koshar, J.A.C.S. 1955, 77, 910.

75. Plimmer, Ph.D.Thesis, Durham 1962.

76. Haszeldine and Marklow, J.C.S. 1956, 962.

77. Geyer and Haszeldine, J.C.S. 1957, 1038.

78. McBee, Roberts and Puerckhauer, J.A.C.S. 1957, 79, 2329.

79. Haszeldine & Young. J.C.S. 1960. 4503.

80. Burch, Goldwhite and Haszeldine, J.C.S. 1963, 1083.

81. Geyer, Haszeldine, Leedham & Marlow, J.C.S. 1957, 4472.

82. El-Abbady and Anderson, J.A.C.S. 1958. 80, 1737.

83. Tarrant, Dyckes, Dunmire and Butler, J.A.C.S. 1957, 79, 6536.

84. Hanford, U.S.Patent, 2,443,003 (1948)

85. Harris and Stacey, J.A.C.S. 1961, 83, 840.

86. Ellingboe, U.S.Patent, 2,439,203 (1948)

87. Fokin, Skladnev and Knunyants, Doklady Akad.Nauk.S.S.S.R. 1961, 138, 1132 (Chem.Abs.1961, 55, 24549e).

88. Arthur and Bell, J.C.S. 1962, 4866.

89. Yarovenko and Vasil'eva, Zh.Obshch.Khim. 1961, 31, 3021 (Chem. Abs.1962, 56, 15347f).

90. Harris, J.A.C.S. 1962, 84, 3148.

91. Case, Ray and Roberts, J.C.S. 1961, 2070.

92. Parshall, England and Lindsey, J.A.C.S. 1959, 81, 4801.

93. Park, Seffl and Lacher, J.A.C.S. 1956, 78, 59.

94. Park, Abramo, Hein, Gray and Lacher. J.Org.Chem. 1958, 23, 1661.

95. Barrick, U.S.Patent, 2,403,207 (1946)

96. Koshar, Trott and LaZerte, J.A.C.S. 1953, 75, 4595.

97. Kooyman and Farenhorst, Rec.Trav.Chim. 1951, 70, 867.

98. Urry, Juveland and Stacey, J.A.C.S. 1952, 74, 6155.

99. Walling, "Free Radicals in Solution", John Wiley and Sons,Inc.
     New York, N.Y. 1957.

100. Tedder, Quart.Rev.1960, 14, 336.

101. Huang, J.C.S. 1957, 1342.

102. Haszeldine, J.C.S. 1953, 1764.

103. Patrick, J.Org.Chem. 1952, 17, 1009.

104. Stefani, Herk and Szwarc, J.A.C.S. 1961, 83, 4732.

105. Mayo and Walling, Chem.Revs.1950, 46, 191.

106. Leavitt, Levy, Szwarc and Stannett, J.A.C.S. 1955, 77, 5493.

107. Buckley and Szwarc, J.A.C.S. 1956, 78, 5696.

108. Szwarc, J.A.C.S. 1957, 79, 6343.

109. Friedlander and Kharasch, J.Org.Chem.1949, 14, 239.

110. Kharasch and Sage, J.Org.Chem.1949, 14, 537.

111. Walling and Helmreich, J.A.C.S. 1959, 81, 1144.

112. Huyser, J.Org.Chem. 1961, 26, 3261.

113. Lewis and Mayo, J.A.C.S. 1948, 70, 1533.

114. Urry, Stacey, Huyser and Juveland, J.A.C.S. 1954, 76, 450.

115. Walling, Seymour and Wolfstirn, J.A.C.S. 1948, 70, 2559.

116. Bartlett and Nozaki, J.A.C.S. 1947, 69, 2299.

117. Patrick, J.Org.Chem. 1952, 17, 1269.

118. Allen, Cadogan, Harris & Hey. J.C.S. 1962. 4468.

119. Miller and Fried, J.A.C.S. 1959, 81, 2078.

120. Hauptschein & Oesterling, J.A.C.S. 1960. 82, 2868.

121. Harris and Stacey. J.A.C.S. 1963, 85, 749.

122. Brand and Stevens, J.C.S. 1958, 629.

123. Goering, Abell and Aycock, J.A.C.S. 1952, 74, 3588.

124. Goering and Sims, J.A.C.S. 1955, 77, 3465.

125. Goering, Relyea and Larsen, J.A.C.S. 1956, 78, 348.

126. Bordwell and Hewett, J.A.C.S. 1957, 79, 3493.

127. Bohm and Abell, Chem.Revs. 1962, 62, 599.

128. Brace, J.A.C.S. 1962, 84, 3020.

129. Beckett, Pitzer and Spitzer, J.A.C.S. 1947, 69, 2488.

130. Henne and Francis, J.A.C.S. 1953, 75, 991.

131. Haszeldine, J.C.S. 1953, 1757.

132. Hauptschein, O'Brien, Stokes and Filler, J.A.C.S. 1953, 75, 87.

133. Faurote, Henderson, Murphy, O'Rear and Ravner, Ind.& Eng.Chem.
     1956, 48, 445.

134. Berry and Bittles, U.S.Patent, 2,559,751 (1951)

135. Tiers, Brown and Reid, J.A.C.S. 1953, 75, 5978.

136. Ahlbrecht and Codding, J.A.C.S. 1953, 75, 984.

137. Benning, U.S.Patent, 2,559,749 (1951).

138. Berry, U.S.Patent, 2,559,629 (1951)

139. McBee, Pierce and Marzluff, J.A.C.S. 1953, 75, 1609.

140. Brace, J.Org.Chem. 1961, 26, 4005.

141. McBee, Pierce and Chen, J.A.C.S. 1953, 75, 2324.

142. McBee, Higgins and Pierce, J.A.C.S. 1952, 74. 1387.

143. Büchi, Inman and Lipinsky, J.A.C.S. 1954, 76, 4327.

144. McBee, Pierce and Christman, J.A.C.S. 1955, 77, 158.

145. Walborsky, Baum and Loncrini, J.A.C.S. 1955, 77, 3637.

146. McBee, Campbell, Kennedy and Roberts, J.A.C.S. 1956, 78, 4597.

147. Haszeldine, J.C.S. 1953, 1748.

148. Allen, Cadogan and Hey, Chem.& Ind.1962, 1621.

149. Kharasch, Skell and Fisher, J.A.C.S. 1948, 70, 1055.

150. Nikishin, Ogibin and Petrov, Trudy po Khimii i Khim.Tekhn. 1961,
     1, 123. (Chem.Abs.1961, 55, 270521).

151. Bell, J.C.S. 1961, 4973.

152. Haszeldine, J.C.S. 1952, 3423.

153. Birchall and Haszeldine, J.C.S. 1961, 3719.

154. Brice, LaZerte and Hals and Pearlson, J.A.C.S. 1953, 75, 2698.

155. Putnam, Anderson and Sharkey. J.A.C.S. 1961, 83, 386.

156. Hauptschein, J.A.C.S. 1959, 81, 2686.

157. Burdon and Whiffen, Spectrochim.Acta.1958, 12, 139.

158. Birchall and Haszeldine, J.C.S. 1959, 13,

159. Evans and Tatlow, J.C.S. 1954, 3779.

160. Smith and Tatlow, J.C.S. 1957, 2505.

161. Nield, Stephens and Tatlow, J.C.S. 1959, 159.

162. Nield, Stephens and Tatlow, J.C.S. 1960, 3800.

163. Stephens, Tatlow and Wiseman, J.C.S. 1959, 148.

164. Maynard, J.Org.Chem. 1963, 28, 112.

165. Roylance, Tatlow and Worthington, J.C.S. 1954, 4426.

166. Tatlow and Worthington, J.C.S. 1952, 1251.

167. Barbour, Mackenzie, Stacey and Tatlow, J.Appl.Chem.1954, 4, 347.

168. Evans and Tatlow, J.C.S. 1955, 1184.

169. Barlow, Stacey and Tatlow, J.C.S. 1955, 1749.

170. Godsell, Stacey and Tatlow, Nature, 1956, 178, 199.

171. Stephens and Tatlow, Chem.and Ind.1957, 821.

172. Nield, Stephens and Tatlow, J.C.S. 1959, 166.

173. Heitzman, Patrick, Stephens and Tatlow, J.C.S. 1963, 281.

174. Buxton and Tatlow, J.C.S. 1954, 1177.

175. Fuller and Tatlow, J.C.S. 1961, 3198.

176. Henne and Fox, J.A.C.S. 1954, 76, 479.

177. Putnam and Castle, J.A.C.S. 1961, 83, 389.

178. Banks, Bevan and Musgrave, Chem. and Ind. 1959, 296.

179. Chapman and Levy, J.C.S. 1952, 1673.

180. McBee and Bolt, Ind.Eng.Chem. 1947, 39, 412.

181. Bose, Das and Jacob, Chem. and Ind. 1963, 452.

182. Bunnett, Angew, Chem.Internat.Ed. 1962, 1, 225.

183. Ingold, Proc.Chem.Soc. 1962, 265.

184. Cristol, J.A.C.S. 1947, 69, 338.

185. Cristol, Hause and Meek, J.A.C.S. 1951, 73, 674.

186. Cristol and Fix, J.A.C.S. 1953, 75, 2647.

187. Hughes, Ingold and Pasternak, J.C.S. 1953, 3832.

188. Hine, Wiesbeck and Ghirardelli, J.A.C.S. 1961, $\underline{83}$, 1219.

189. Hine, Wiesbeck and Ramsay, J.A.C.S. 1961, $\underline{83}$, 1222.

190. Morris, DePuy and Thurn, J.A.C.S. 1962, $\underline{84}$, 1314.

191. Barton and Cookson, Quart. Rev. 1956, $\underline{10}$, 44.

192. Goering, Relyea and Howe, J.A.C.S. 1957, $\underline{79}$, 2502.

193. Bordwell and Kern, J.A.C.S. 1955, $\underline{77}$, 1141.

194. Cristol and Davies, J.Org.Chem. 1962, $\underline{27}$, 293.

195. Weinstock and Bordwell, J.A.C.S. 1955, $\underline{77}$, 6706.

196. Stevens and Grummitt, J.A.C.S. 1952, $\underline{74}$, 4876.

197. Cristol and Stermitz, J.A.C.S. 1960, $\underline{82}$, 4692.

198. Tiers, Proc.Chem.Soc. 1960, 389.

199. Feeney and Sutcliffe, Trans.Faraday Soc. 1960. $\underline{56}$, 1559.

200. Feeney and Sutcliffe, J.Phys.Chem. 1961, $\underline{65}$, 1894.

201. Brame, Analyt.Chem. 1962, $\underline{34}$, 591.

202. Lee and Sutcliffe, Trans.Farad.Soc. 1959, $\underline{55}$, 880.

203. McConnell, Reilly and McLean, J.Chem.Phys., 1956, $\underline{24}$, 479.

204. Evans, Feast, Stevens and Tatlow. J.C.S.1963, 4828.

205. Johnson, Bauer, Margrave, Frisch, Dreger and Hubbard, J.A.C.S.,
     1961, $\underline{83}$, 606.