A study of addition products of fluorocarbon olefins

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A THESIS

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:-

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


(R = CF_3 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.

CHAPTER 1.

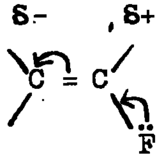
INTRODUCTION

INTRODUCTION

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

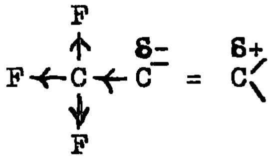
IONIC ADDITIONS With highly fluorinated olefins electrophilic attack occurs much less readily than with hydrocarbon olefins, owing to inductive electron withdrawal from the double bond by fluorine and fluoroalkyl groups, while nucleophilic attack is correspondingly easier. Thus while hexafluoropropene 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,



,

with inductive,



$$\mathrm{F\leftarrow\underset{\downarrow\,F}{\overset{F\,\uparrow}{C}}\leftarrow\overset{\delta-}{C}=\overset{\delta+}{C}}$$

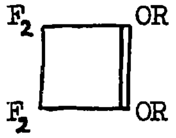
,

and hyperconjugative effects, $\mathrm{CF_3-C=C}\longleftrightarrow\mathrm{F^{-}\quad CF_2=C-\overset{+}{C}}$

e.g. the overall direction of polarisation for a terminal perfluoro-olefin is $\mathrm{R_f\,\overset{\delta-}{CF}=\overset{\delta+}{CF_2}}$.

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 $\mathrm{ROCF_2\overset{}{\underset{/}{C}}{:}C\!\!<}$ [3,] many alcohol additions give both saturated, $\mathrm{RO{-}\overset{\backslash}{\underset{/}{C}}{-}\overset{/}{\underset{\backslash}{C}}{-}}$, and vinyl, $\mathrm{RO-\underset{/}{C}{=}\overset{/}{\underset{\backslash}{C}}}$, 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



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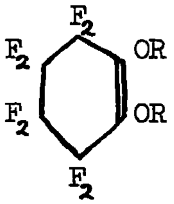
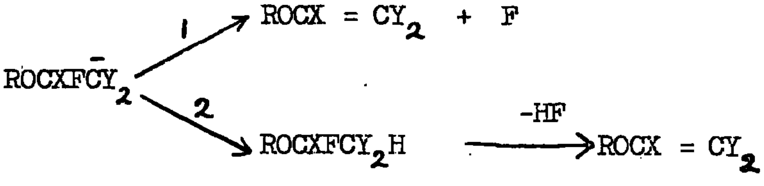


The mechanism has been postulated as direct S_N2 substitution of vinylic fluorine [8] or stabilisation of an intermediate anion by either (1) loss of fluoride ion, or (2) proton addition, with subsequent elimination of hydrogen fluoride [11] .



$$\begin{tikzcd}
 & \mathrm{ROCX=CY_2} + F^- & \\
\mathrm{ROCXF\bar{C}Y_2} \arrow[ur, "1"] \arrow[dr, "2"'] & & \\
 & \mathrm{ROCXFCY_2H} \arrow[r, "-HF"] & \mathrm{ROCX=CY_2}
\end{tikzcd}$$

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]

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

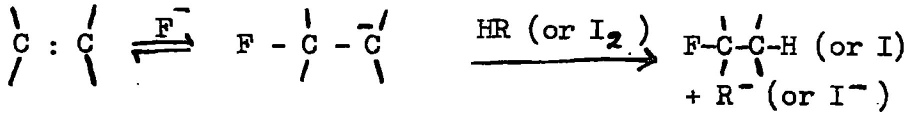
α-hydrofluoronitrites [17],

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

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]



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

$$CF_3\ CF\ :\ CF_2 \overset{F^-}{\rightleftharpoons} (CF_3)_2\ \bar{C}F \xrightarrow{R_fCOF} (CF_3)_2CFCOR_f + F^-$$

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 fermation 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
$CF_2 : CCl_2$	$R\ CH_2OH$ 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.

Reagent / Olefin	Silanes	Thiols	H S	CF SCl	SF Cl	S Cl	Phosphines	NaHSO
$CF_2 : CF_2$	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_5F_{10}-1, C_7F_{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							
$CH_2 :CHC_2F_5$	82, 83							
$CH_2 :CHC_3F_7$	81, 83 82							
$CH_2 :\underset{CH_3}{C}\ C_2F_5$	82							
$CH_2 :\underset{CH_3}{C} - C_3F_7$	82							

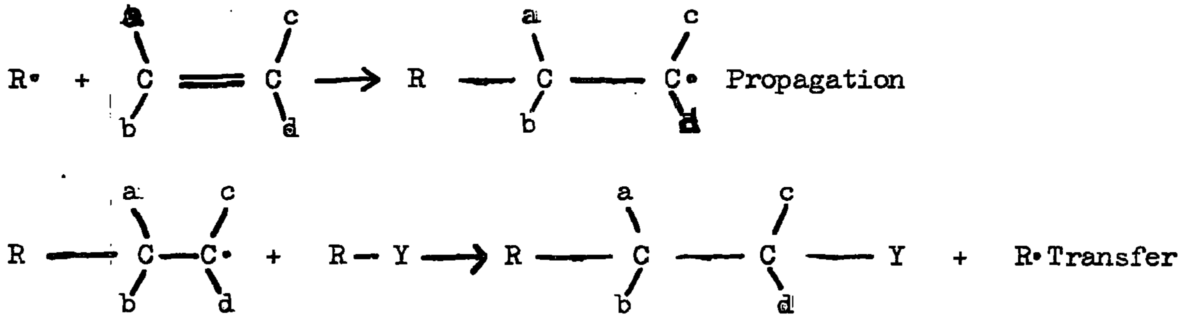
Additions to both fluoro- and hydro-carbon olefins follow a similar course, the only difference being in the ease of reaction, especially with radicals of highly polar character. In considering theoretical aspects of free radical additions to fluoro-olefins reference will therefore be made to many reactions 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 → R· + Y· Initiation (Y = usually H or halogen)

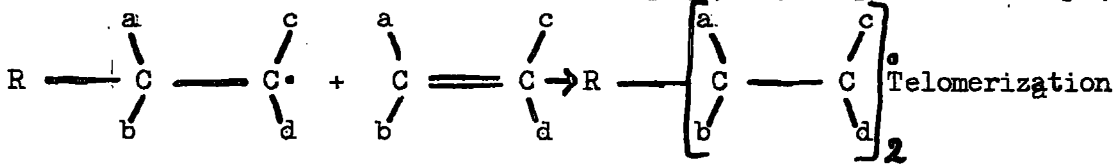
(2)

(3)



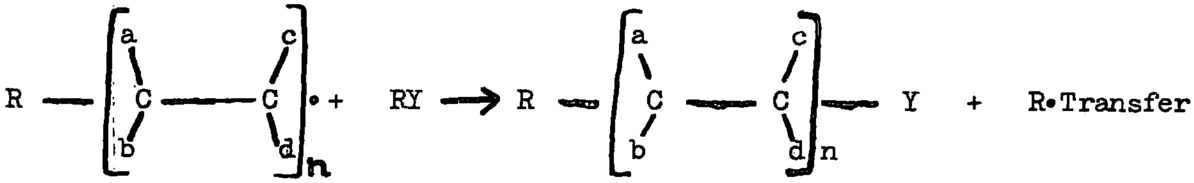
Where the olefin is homopolymerisable step (4) may compete with step (3)

(4)



and successive additions of olefin are followed by step (5) to give a telomer molecule

(5)



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.

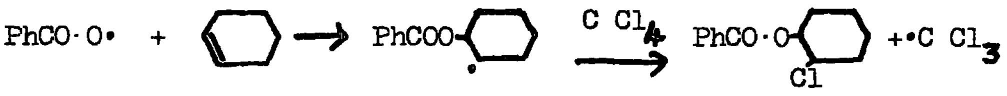
These sources may supply directly the energy necessary for rupture of the R - Y bond, or may bring about cleavage of molecules of chemical initiator i.e. compounds containing bonds of low dissociation energy, such as O - O (peroxides), N - N (azo compounds) and S - S (disulphides) The chain carrying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

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

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]

$$(PhCO\cdot O)_2 \longrightarrow 2\,PhCO\cdot O\cdot \quad (\longrightarrow 2Ph\cdot + 2CO_2\ )$$



Formation of chlorobenzene by direct abstraction of chlorine by phenyl radicals accounts for only 10% of the initiator.

$$Ph\cdot + C\,Cl_4 \longrightarrow PhCl + \cdot C\,Cl_3$$

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,

$$\mathrm{RR'CHOH} \longrightarrow \mathrm{RR'\underset{\bullet}{C}OH} + \mathrm{H\cdot}$$

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.

$$\mathrm{RCHO} \longrightarrow \mathrm{R\underset{\bullet}{C}O} + \mathrm{H\cdot}$$

Similarly acids, esters, ethers and amines [98, 99, P.288] add to olefins to give the corresponding α-alkyl substituted compounds.

$$\mathrm{RR'CH{-}COOR''} \longrightarrow \mathrm{RR'\underset{\bullet}{C}{-}COOR''} + \mathrm{H\cdot}$$

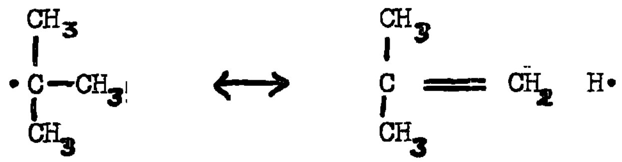
$$\mathrm{RR'CH{-}OR''} \longrightarrow \mathrm{RR'\underset{\bullet}{C}{-}OR} + \mathrm{H\cdot}$$

$$\mathrm{RR'CH\ NR''R'''} \longrightarrow \mathrm{RR'\underset{\bullet}{C}NR''R'''} + \mathrm{H\cdot}$$

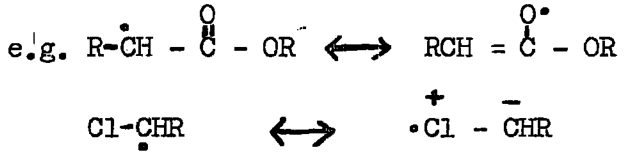
In the case of thiols, however, the S - H bond is more easily broken than the C - H bond, so that thioethers are obtained as from nucleophilic additions.

$$\mathrm{RR'CHSH} \longrightarrow \mathrm{RR'CHS\cdot} + \mathrm{H\cdot}$$

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



and Tedder [100] suggests that radical formation should also be favoured by any α-substituent with π electrons (e.g. $-\overset{O}{\overset{\|}{C}}-OR$, $-CH{=}CH_2$, $-\overset{O}{\overset{\|}{C}}R$) or non-bonded p-electrons (e.g. halogen, alkoxy) because of the possibilities of resonance stabilisation.



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

$$Cl{-}\underset{\bullet}{C}HR \longleftrightarrow \cdot\overset{+}{Cl} - \overset{-}{CHR}$$

A number of workers have drawn up orders of the relative stabilising powers of different substituents

e.g. $-Ph > -CN \approx -CO- > -CO{\cdot}OEt \approx -CO{\cdot}OH > Me$ [101]

$I > Br > Cl > F > H$ [102]

$C_2F_5 > CF_3 > F$ [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)

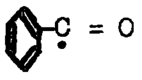
$$(2)\quad R\cdot + \text{olefin} \rightarrow R\,(\text{olefin})\cdot$$

$$(3)\quad R\,(\text{olefin})\cdot + RY \rightarrow R(\text{olefin})\,Y + R\cdot$$

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]

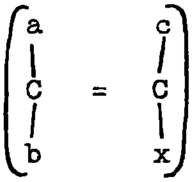
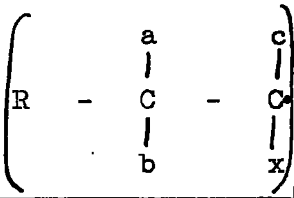
e.g.  , is the decrease in reactivity sufficient to prevent chain propagation.

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 $\cdot CH_3$ to $\cdot CF_3$, 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.

Reactivity of olefin 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  $\left(\begin{matrix} a & & c \\ \vert & & \vert \\ C & = & C \\ \vert & & \vert \\ b & & x \end{matrix}\right)$	Radical  $\left(\begin{matrix} R & - & \overset{a}{\underset{b}{C}} & - & \overset{c}{\underset{x}{C\cdot}} \end{matrix}\right)$
-OAc, - Me	2.5	4
$-CH{:}CH_2$, $-C_6H_5$	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
$PhMeC{:}CH_2$	1890
$Ph_2C{:}CH_2$	2240
trans-$PhCH{:}CHPh$	205
$Ph_2C{:}CHPh$	85
$Ph_2C{:}CPh_2$	<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 attracting 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 $R_2\overset{+}{C}\cdot OH \leftrightarrow R_2C{:}\overset{+}{O}H$, 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], $\cdot SiCl_3$ [78], have received more attention, and the expected reverse order of olefin reactivity has been observed e.g. $CH_2{:}\ CH_2 > CF_2{:}\ CH_2 > CF_2CF_2 > CF_3CF{:}CF_2 > CF_3CF{:}CFCF_3$ [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.

<u>Reactions competing with chain propagation</u>

a) <u>Reaction of R· with initiator</u> 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:

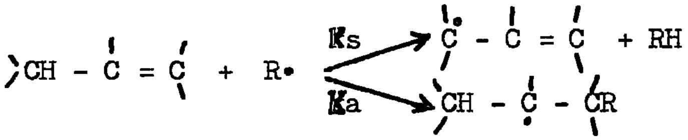
(i) $(Ph\cdot CO\cdot O)_2 \longrightarrow 2\ Ph\cdot CO\cdot O\bullet$

(ii) $Ph\cdot CO\cdot O\bullet \quad + \quad R_2CHOH \rightarrow Ph\cdot COOH \quad + R_2\dot{C}OH$

(iii) $R_2\dot{C}OH \quad + \quad (Ph\cdot CO\cdot O)_2 \rightarrow R_2C(OH)O\cdot COPh \quad + PhCO\cdot O\bullet$

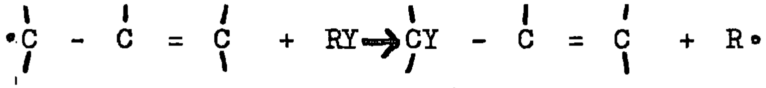
it is not surprising that step (iii) competes successfully with the propagation step, R• + olefin → R(olefin)•. That this is probably due to some extent to polar factors is supported by the fact that alcohol additions to fluoro-olefins can be initiated by benzoyl peroxide, indicating that affinities 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.



$$>CH-\overset{|}{C}=C< + R\bullet \begin{cases} \xrightarrow{K_s} \bullet\overset{|}{C}-\overset{|}{C}=C< + RH \\ \xrightarrow{K_a} >CH-\overset{|}{\dot{C}}-CR< \end{cases}$$

Unless the allyl radical is too stable to continue the chain, reaction with RY results in allylic substitution products.



$$\bullet C< - \overset{|}{C} = C< + RY \rightarrow >CY - \overset{|}{C} = C< + R\bullet$$

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)•, 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 $\overset{\delta+}{RCH}{:}\,\overset{\delta-}{CH_2}$ (R = Me, Cl or F) or $\overset{\delta-}{RCH}\,:\,\overset{\delta+}{CH_2}$ (R = CF_3, CN or CO_2Me).

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,

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

$$(R \div Y = CF_3 - I,\ C\,Cl_3 - Br \text{ or } Br - H)$$

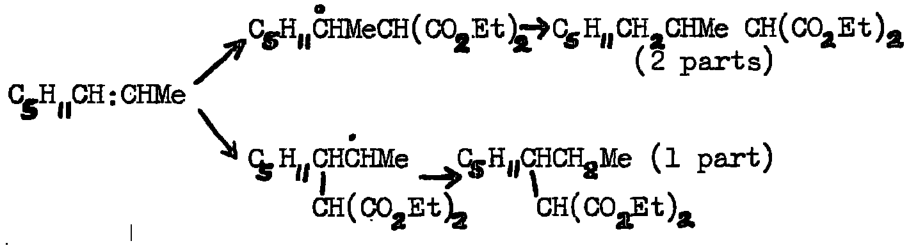
indicating that while steric effects may play a significant part in determining the direction of addition there are other factors of even greater importance.

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]



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
$\overset{*}{C}F_2:CFCF_3$	$\cdot C_3F_7$	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
$CF_2 : \overset{*}{C}FH$	$\cdot CFCl_2$	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
$CF_2 : \overset{*}{C}H_2$	$(\cdot SCF_3)$	(100)	(85)
	$\cdot C_3F_7$	95	120
$\overset{*}{C}F_2 : CFCl$	$\cdot CF\,Cl\,CF_2Cl$	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).

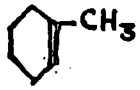
The observed variations are obviously dependent upon the nature of the radicals, and can be correlated with their relative electrophilicities, which increase in the series $\cdot SCH_3 < \cdot SCH_2CF_3 < \cdot SCF_3$, $\cdot SF_5$ and $\cdot SiMe_3 < \cdot SiMe_2H < \cdot SiMeH_2 < \cdot SiH_3$. Preferential 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 $\underset{\delta+}{\overset{*}{C}F_2} : \underset{\delta-}{CF}\ CF_3$, 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 $\overset{*}{C}F_2$. 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 $\underset{\delta+}{CF_2} : \underset{\delta-}{\overset{*}{C}FH}$ and $\underset{\delta+}{CF_2} : \underset{\delta-}{\overset{*}{C}H_2}$, 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.

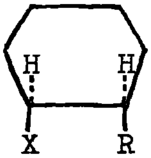
Stereochemistry of Radical Additions. The study of the stereochemical aspects of radical additions is a relatively recent addition to the field of free radical chemistry. The results of this work have been reviewed by Bohm and Abell[127], and attention will here be confined to additions to cyclohexene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

Table IV

Olefin.	Reagent.	% Trans Addition.	Reference.
	NO_2Cl	62	122
	N_2O_4	58	122
	n-C_3F_7I	cis and Trans) no) figures	128
	i-C_3F_7I	cis and Trans) 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.

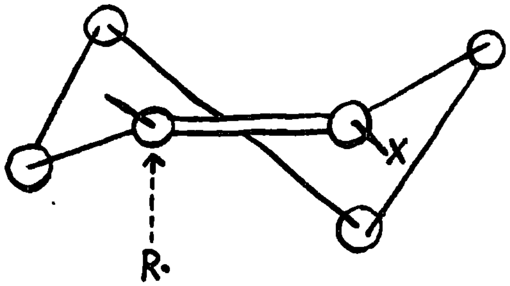
It is seen that trans-addition predominates even though with RH this type of addition to 1-substituted cyclohexenes gives the thermo dynamically less stable cis isomer [129],

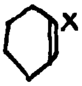


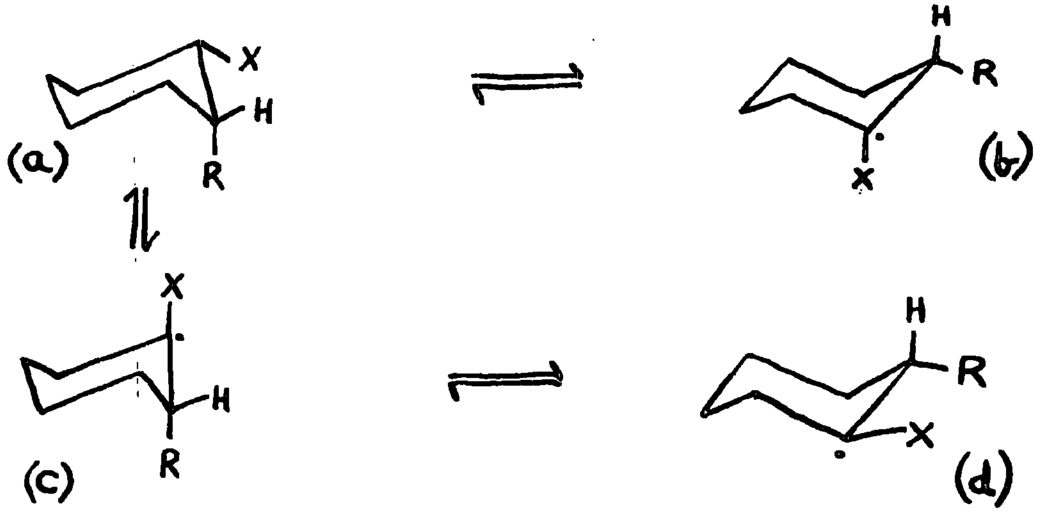
.

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-stereospecificity 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  will be expected to give initially an intermediate of conformation (a) with X occupying an equatorial position.

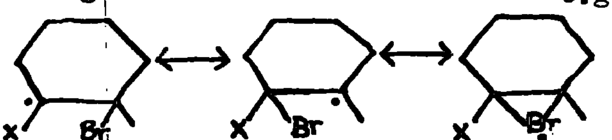


Inversion at the trigonal carbon may then occur to give (c), and both (a) and (c) may undergo ring inversion to (b) and (d) respectively. Brand and Stevens [122] ignore the latter two conformations on the assumption that ring inversion occurs much more slowly than chain transfer, and this step is considered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

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

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 $CH_3OH < C_3H_7OH < (CH_3)_2CHOH < C_2H_5OH$ 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 $R_2\dot{C}OH$ with the peroxide,

$$R_2\dot{C}OH + (PhCOO)_2 \rightarrow R_2C\text{-}(OH)\text{-}OCOPh + PhCOO\cdot$$

competes with the propagation step,

$$R_2\dot{C}OH + RfCF:CF_2 \rightarrow Rf\dot{C}F\ CF_2C(OH)R_2$$

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]

Properties of alcohol adducts. 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]

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

and p-toluene sulphonic acid [135]

$$Rf\ CH_2OH + HOSO_2C_6H_4CH_3 \longrightarrow RfCH_2OSO_2C_6H_4CH_3$$

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. $CF_3CH_2ONa + CF_2ClCH_3 \longrightarrow CF_3CH_2OCF_2CH_3 + NaCl$

$$CF_3CH_2OH + CH_2N_2 \longrightarrow CF_3CH_2OCH_3 + N_2$$

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].

$$Rf\ CFH\ CF_2CH_2OH \longrightarrow Rf\ CFH\ CF_2COOH$$

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

$$Rf\ CFH\ CF_2CHROH \longrightarrow Rf\ CFH\ CF_2COR$$

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]

$$\mathrm{Rf\ CH_2OH} \xrightarrow[h\nu]{Cl_2} \mathrm{Rf\ CHO} \quad + \quad \text{other products.}$$

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].

$$\mathrm{Rf\ CH\ (OH)\ CH_2\ R} \xrightarrow{P_2O_5} \mathrm{Rf\ CH = CHR}$$

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 $\mathrm{H\ (CF_2CF_2)_n}$--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% $\mathrm{Na_2CO_3}$ 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.

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

hydrocarbon aldehydes to fluoro-olefins.

$$\mathrm{Rf\ CF : CF_2 + RCHO \longrightarrow Rf\ CFH\ CF_2COR}$$

$$\mathrm{(R = CH_3,\ C_2H_5,\ n\text{-}C_3H_7,\ i\text{-}\ C_3H_7)}$$

With i-butyraldehyde some halohydrocarbon formation was also observed, probably resulting from the side reaction:

$$\mathrm{(CH_3)_2\ CH\dot{C}O \longrightarrow (CH_3)_2\dot{C}H + CO}$$

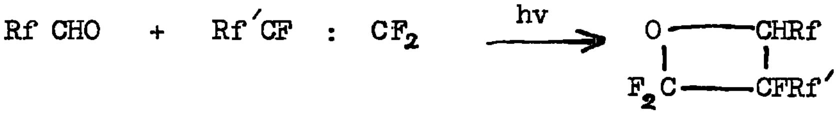
$$\mathrm{(CH_3)_2\dot{C}H + CF_2 : CFCl \longrightarrow (CH_3)_2CHCF_2\dot{C}\ Cl_2}$$

$$\downarrow \mathrm{(CH_3)_2\ CHCHO}$$

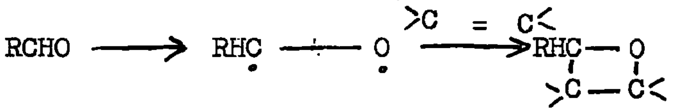
$$\mathrm{(CH_3)_2\ CHCF_2CCl_2H + (CH_3)_2CH\dot{C}O}$$

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].

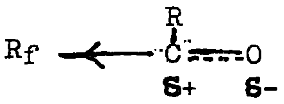
When Harris and Coffman [70] attempted the ultra-violet initiated addition of perfluoroaldehydes to fluoro-olefins, they obtained fluorotrimethylene oxide derivatives instead of ketones.



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-$\dot{C}$O, 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.



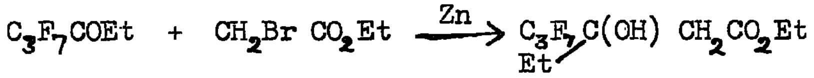
Properties of aldehyde adducts The inductive effect of fluorine results in decreased electron density at the carbonyl group of fluorinated ketones.



$$\overset{\delta+}{\underset{}{R_f \leftarrow \overset{R}{C}}} = \overset{\delta-}{O}$$

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 $\alpha - \beta$ unsaturated esters and acids obtained with hydrocarbon ketones), owing to the resistance to dehydration derived from the increased C - O bond strength e.g.



$$C_3F_7COEt \quad + \quad CH_2Br\ CO_2Et \xrightarrow{Zn} C_3F_7C(OH)(Et)\ CH_2CO_2Et \qquad 144$$

$$CF_3COCH_3 \quad + \quad CH_2(CO_2H)_2 \longrightarrow CF_3(CH_3)C\ (OH)\ CH_2CO_2H \qquad 145$$

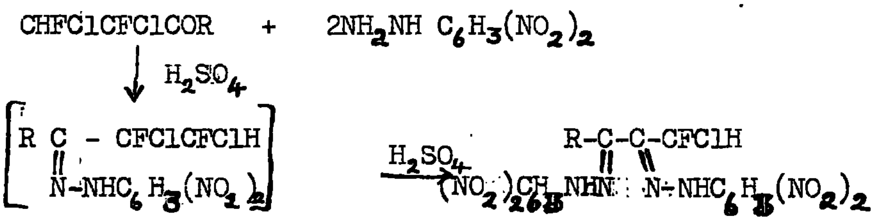
Aldol formation has been accomplished using sodamide or sodium ethoxide in organic solvents at low termperatures [146].

$$2CF_3COCH_3 \longrightarrow CF_3(CH_3)C(OH)CH_2COCF_3$$

but with dilute aqueous alkali haloform cleavage predominates [146,147]

$$Rf\ COR \xrightarrow{NaOH} RfH \quad + \quad RCOONa$$

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].



Reduction of fluoroketones to alcohols has been successfully carried out by catalytic hydrogenation [74] and with lithium aluminium hydride [147],

$$\text{Rf COR} \longrightarrow \text{Rf CH(OH)R}$$

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

$$\text{RfCFHCF}_2\text{COR} \xrightarrow{\text{KMnO}_4\text{ /acetone}} \text{RfCFHCF}_2\text{COOH}$$

3. Carboxylic acid derivative additions 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,

$$\text{RCH}_2\text{CO}_2\text{X} \longrightarrow \text{R}\dot{\text{C}}\text{HCO}_2\text{X} + \text{H}\cdot \quad (\text{X} = \text{H,R}')$$

$$\text{RCH}_2\text{CN} \longrightarrow \text{R}\dot{\text{C}}\text{HCN} + \text{H}\cdot$$

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

e.g. $$\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3 \begin{cases} \longrightarrow \cdot\text{CH}_2\text{CO}_2\text{Et} + \text{H}\cdot & \text{(A)} \\ \longrightarrow \text{CH}_3\text{CO}_2\dot{\text{C}}\text{HCH}_3 + \text{H}\cdot & \text{(B)} \end{cases}$$

$$\text{RCH:CH}_2 + \text{(A)} \longrightarrow \text{RCH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}$$

$$\text{RCH:CH}_2 + \text{(B)} \longrightarrow \text{RCH}_2\text{CH}_2\text{CH(CH}_3\text{) OCOCH}_3$$

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

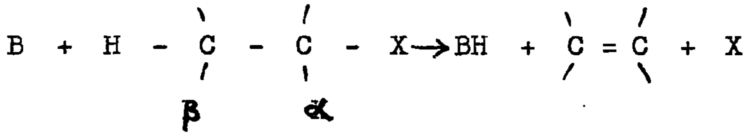
Reagents Concentrated aqueous potassium hydroxide has been successfully used for dehydrofluorinating perfluorocyclohexanes [159 ÷ 163, 165 ÷ 172], cyclopentanes [173], and cyclobutanes [174 - 5], while 3,3,3-trifluoropropionic acid has been dehydrofluorinated by the addition of dilute sodium hydroxide 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

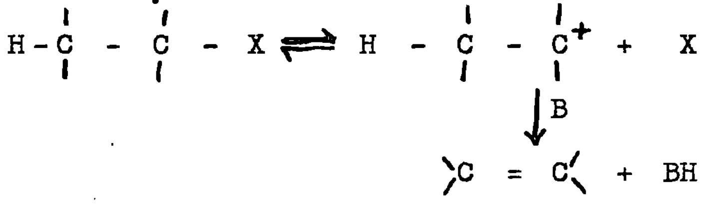
The mechanisms of olefin-forming elimination reactions have recently been reviewed by Bunnett [182] and Ingold [183]. Three possible mechanisms have been distinguished for the reaction



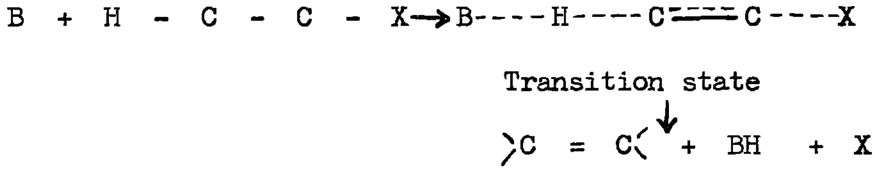
$$B + H - \underset{\beta}{\overset{\backslash}{\underset{/}{C}}} - \underset{\alpha}{\overset{/}{\underset{\backslash}{C}}} - X \rightarrow BH + \overset{\backslash}{\underset{/}{C}} = \overset{/}{\underset{\backslash}{C}} + X$$

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:-

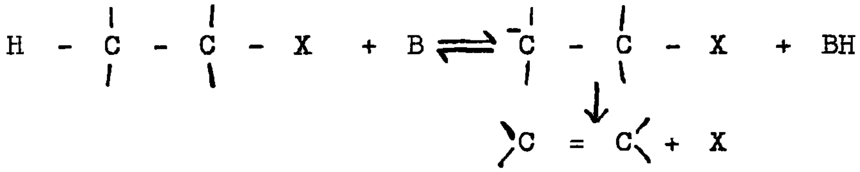
1. The E 1 mechanism in which the bonds C-H and C-X are broken in separate steps, C-X rupture occurring first to give a carbonium ion intermediate which then loses the β-proton.



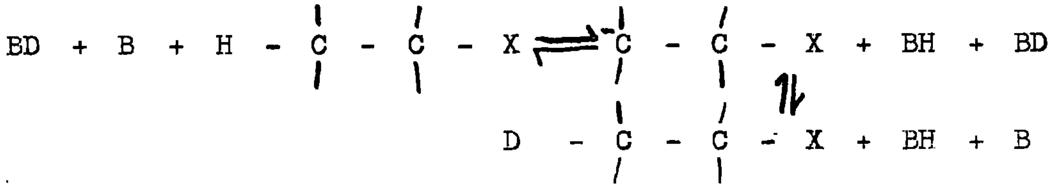
2. The E2 mechanism in which the C-H and C-X bonds are broken in a single step.



3. The E 1 cb or carbanion mechanism in which the C - H bond is broken first.

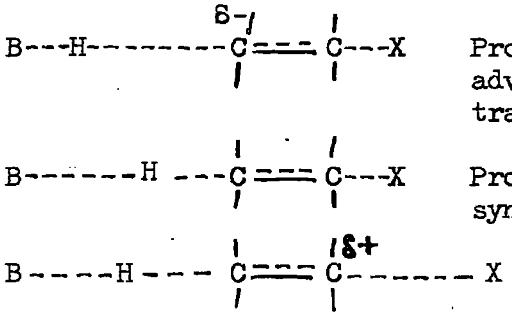


The latter two mechanisms both show second order kinetics, and while they are therefore easily distinguished from the E 1 mechanism, it is more difficult to determine by which of the two a given second order elimination occurs. Positive proofof a E1 cb mechanism can be given by some incorporation of deuterium in starting material recovered from a reaction carried out in a deuterated solvent,



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.



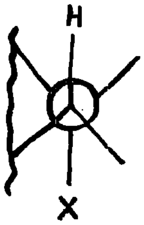
Proton transfer more advanced than electron transfer

Proton and electron transfer synchronous

Electron transfer more advanced than proton transfer

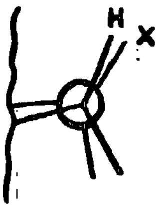
For synchronous E 2 eliminations the transition state of lowest energy requires the four centres concerned to be in one plane [191].

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

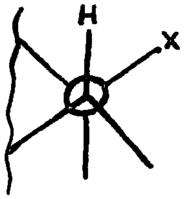


(Dihedral ∠ between H and X = 180°)

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 coplanar cis-elimination would necessitate considerable ring deformation and is therefore far less likely to occur.



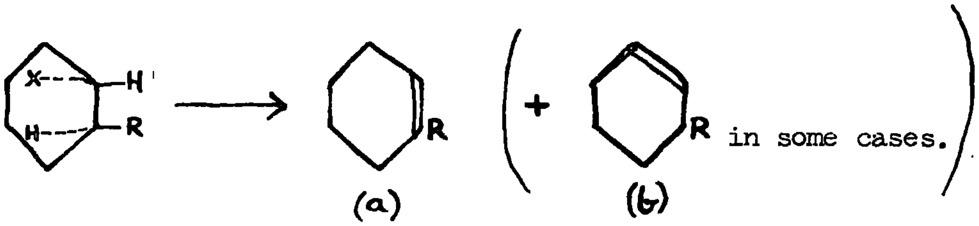
Cyclopentyl cis elimination.
(Dihedral $\angle$ between Hand
$X \simeq 0^\circ$)

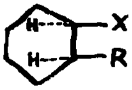


Cyclohexyl cis-elimination
(Dihedral $\angle$ between Hand
$X = 45^\circ$)

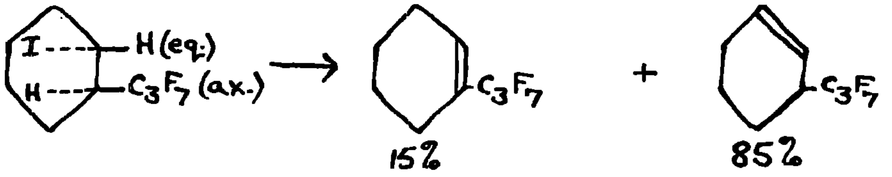
Studies of the dehydrochlorination of benzene hexachloride isomers[184 - 7] have shown that while trans-elimination occurs readily, the reaction rate shows a marked decrease in those cases in which only cis-elimination is possible. While Hughes et al[187] think that an E 2 mechanism still operates here, 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.



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.



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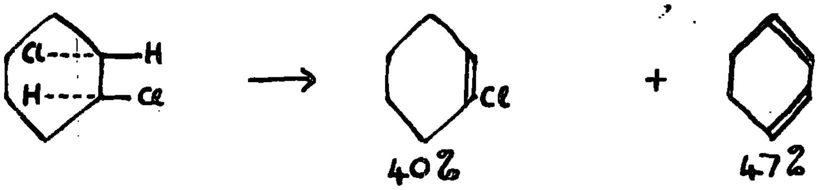

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Phenyl, which can conjugate with the cyclohexene double bond in (a) but not in (b) also favours cis-elimination [194 - 5, 197].

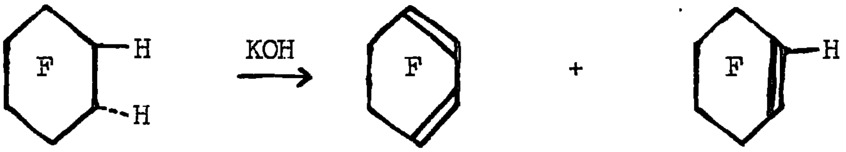
It is not certain however whether these eliminations proceed by an Elcb or E2 mechanism. If the reaction does occur by the latter path, the electron attracting β-substituent is likely to cause proton release from the β-carbon to be considerably more advanced than electron transfer from the α-carbon in 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 dehydrofluorination 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.

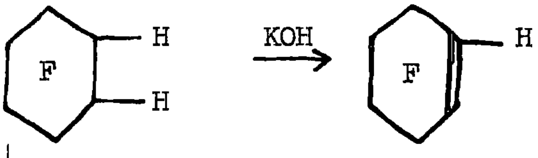
Since fluoride ion is more easily removed from a CFH group than from a CF_2 or CF_3 group, the reaction is further favoured by attachment of hydrogen, or another activating substituent, to the carbon from which the fluorine is to be eliminated, while hydrogen elimination is encouraged by neighbouring fluorines which increase its acidity [163].

In the system (a), - $CF_2CHF\ CF_2$-, the hydrogen is more acidic than in (b), -$CF_2CHF\ CHF\ CF_2$-, 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].

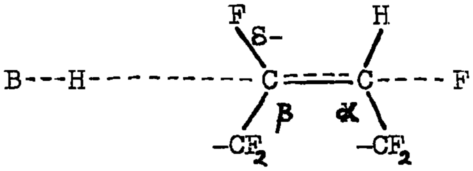
Where the steric and electronic effects are in opposition trans-elimination does not however occur exclusively. Thus with trans-1H,2H-decafluorocyclohexane some of the electronically favoured 1H-nonafluorocyclohex-1-ene is formed in addition to the octafluorocyclohexa-1,3- diene which is favoured sterically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



Rapid, exclusive formation of 1H-nonfluorocyclohex-1-ene occurs with the cis isomer, since this product is favoured by both steric and electronic factors.



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.



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-1H,2H- decafluorocyclohexanes 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 yieldsin 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 $(CH_3)_2C{\cdot}OH$ 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	(-	4.9
	(- (42°)	3.6

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

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

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

(2) $R. + CF_3CF : CF_2 \longrightarrow CF_3.CF\ CF_2R$

Polar effects

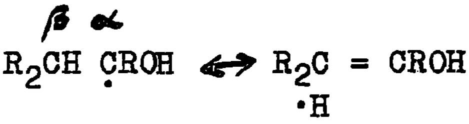
Since fluorine substituents reduce the electron density at the double bond of the olefin, radicals of the electron-donor type react most readily with fluoro-olefins, and the high reactivity of alcohols as a class has been explained on these grounds (p.17). Electron donating substituents in the α-hydroxyalkyl 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 facters 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



$$\overset{\beta}{R_2CH}\ \overset{\alpha}{\underset{\bullet}{C}}ROH \longleftrightarrow \underset{\bullet H}{R_2C} = CROH$$

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.

$$CH_2 : CH\ \underset{\bullet}{C}HOH \leftrightarrow \underset{\bullet}{C}H_2CH : CHOH$$

$$\begin{tikzcd} CH_3CH : CH\ \underset{\bullet}{C}HOH \arrow[r, leftrightarrow] & CH_3\underset{\bullet}{C}HCH : CHOH \arrow[d, leftrightarrow] \\ & H.\ CH_2 : CHCH : CHOH \end{tikzcd}$$

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

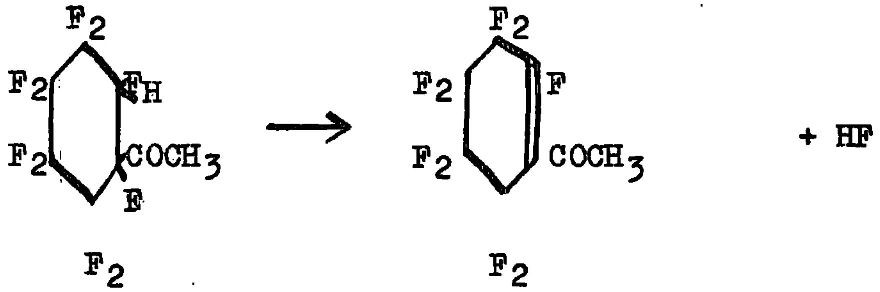
The case of ethylene glycol deserves special mention. Irradiation of a 5 : 1 mixture of the alcohol and C_3F_6 for 7 days at room temperature and then for 8 days at 76° resulted in conversion of 74% of the olefin to a complex mixture of compounds. The infrared spectrum of the mixture shows strong absorption 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 $-(CH_2)-$; 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 Inukai[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 perfluorocyclohexene, 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-C_6F_8	26.3
1,4-C_6F_8	18.6
C_6F_{10}	7.3

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

$$\cdot CF_3 + \text{olefin} \longrightarrow CF_3\,(\text{olefin})\cdot$$

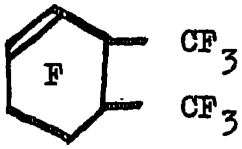
lies in the order:

*

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

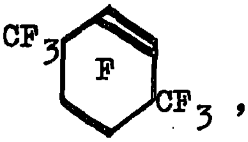
Examination of the reaction products showed that only 22% of the total product from the addition to the 1 , 3-diene was likely to be 1 : 1 adduct. (Although insufficient pure material was isolated for analytical purposes, comparison of its infrared spectrum with that of the 1 : 1 adduct from the 1,4-diene supports the supposition that it is the product of addition of trifluoromethyl 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 perfluorodimethylcyclohexene. An infrared absorption band at 1733 cm^{-1} proved the presence of a double bond; and n.m.r. spectroscopy favoured the structure

*  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 perfluorocyclohexene[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-trifluoromethyldecafluorocyclohexane 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.

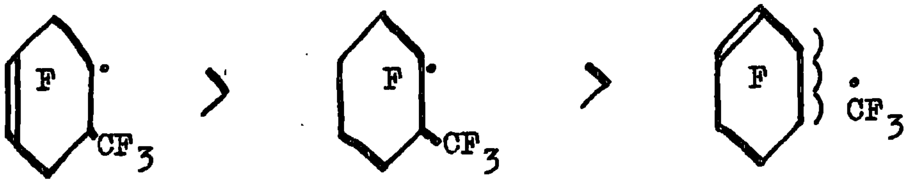
Considering these products it is seen that the initially formed CF_3 (olefin)· radical may react in one of three ways.

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

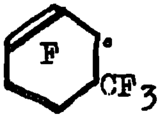
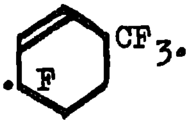
(ii) CF_3 (olefin)· + $CF_3I \rightarrow CF_3$(olefin)CF_3 + I· (chain transfer)

(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 .

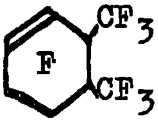
An attempt to add heptafluoroisopropyl iodide to octafluorocyclohexa-1,3-diene, using the thermal initiation conditions which proved suitable for the trifluoromethyl iodide additions, gave only trace amounts of three products. This reduced yield, with an iodide which should be a better chain transfer agent than trifluoromethyl iodide, is probably due to steric hindrance of attack by the perfluoroisopropyl 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:-

$$1,3\text{-}C_6F_8 > 1,4\text{-}C_6F_8 > C_6F_{10}$$

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

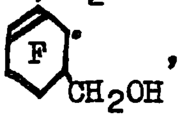
This order does however resemble the one found for conversion of the olefins to CF_3 (olefin)I adducts. This order has been attributed to the relative ease with which the radicals derived from the olefins undergo chain transfer, and a similar explanation seems likely in this case.

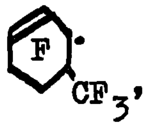
In the trifluoromethyl iodide additions the overall yield of products depended on the rate of the propagation step, since those radicals which failed to undergo chain transfer (step i) could combine with trifluoromethyl radicals (step iii). In the case of methanol there is no evidence of the formation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

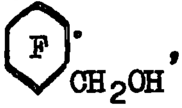
$$\cdot CH_2OH \quad + \quad \text{olefin} \longrightarrow \cdot(\text{olefin})CH_2OH$$

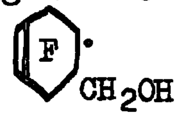
is high, the total yield of adduct will depend on the rate of the transfer step,

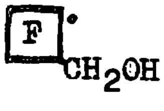
$$\cdot(\text{olefin})CH_2OH \quad + \quad CH_3OH \longrightarrow H(\text{olefin})CH_2OH \quad + \quad \cdot CH_2OH.$$

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) <u>Adducts of cyclic perfluoro-olefins</u>

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.

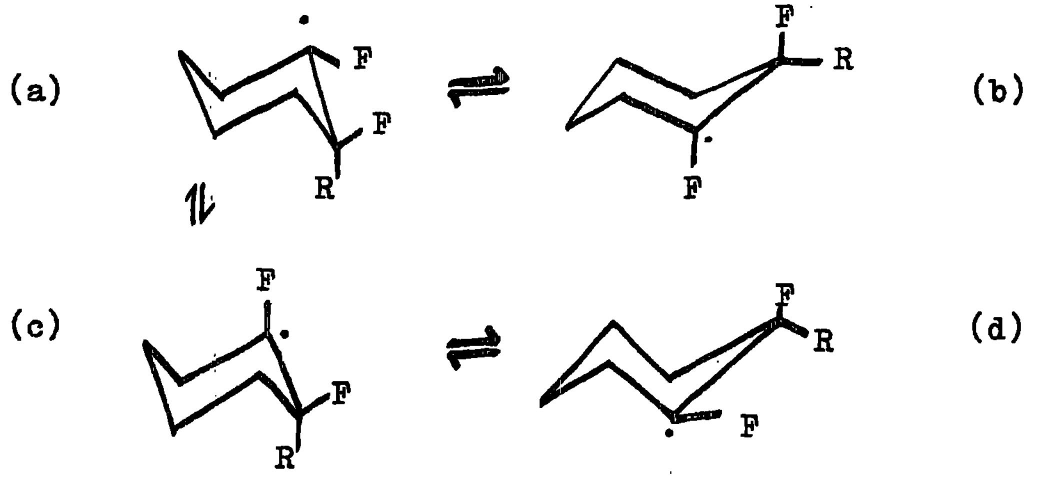
Since the alcohol adducts show similar chemically shifted groups, they too are believed to be mixtures of trans, e,e and cis e(H), a(R) isomers. The reasons for these assignments are discussed in the section on n.m.r. spectra, P.100-105

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).



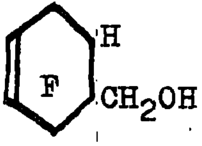
If inversion to (c) occurs before the chain transfer step, $RC_6F_{10}\cdot + HR \rightarrow RC_6F_{10}H + R\cdot$, the product will be the observed cis e(H), a (R) adduct. It is of interest to note that a slight decrease in the proportion of cis isomer formed can be traced on passing from the addition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

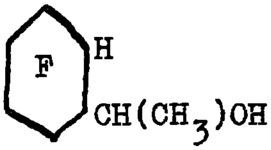
The trans adduct which is obtained is the sterically more favoured e,e. conformer; and while it may be derived from radical (b) following ring inversion of radical (a), there is also the possibility that it arises after chain transfer by inversion of the less stable a, a conformer.

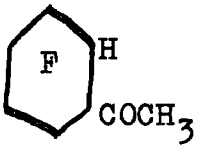
It is difficult to suggest why almost exclusive trans addition of acetaldehyde to perfluorocyclohexene should occur, since factors such as chain transfer efficiency and intramolecular electrostatic attractions which might favour trans addition, would be expected to have a similar effect upon addition 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. 

, 

, 

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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.

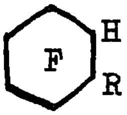
e.g.

Compound	B.p.°c. (X = H)	B.p.°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 ($\phi = 155$ 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_2R group. The direction of addition is therefore CF_3CFHCF_2R, 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. Esterification. 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.

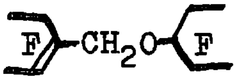
$$CF_3CFHCF_2COCH_3 + (NO_2)_2C_6H_3NHNH_2 \rightarrow CF_3CFHCF_2C(CH_3)NNHC_6H_3(NO_2)_2$$

3. <u>Oxidation</u>. The cis isomer of methyl (2H - decafluorocyclohexyl) 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.

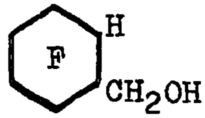
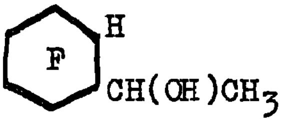
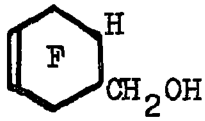
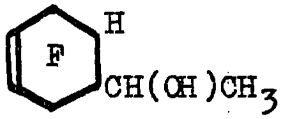
4. <u>Dehydrofluorination</u>. <u>Reaction conditions</u>. In attempts to find the optimum dehydrofluorination conditions for cyclic fluoro-olefin alcohol adducts, 2H-octafluorocyclohex-4-enyl methanol was treated with potassium hydroxide in mineral oil at temperatures of up to 130°; anion exchange resin at 20 - 55°; and aqueous potassium hydroxide. The first two methods yielded mixtures of liquid products (Fig. 2a, Page 141) 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  . Haszeldine[153] has reported a similar type of polymer from the reaction of $C_6F_5CH_2Br$ with aqueous potassium hydroxide.

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

$$n+2(C_6F_5CH_2O^-) \rightarrow C_6F_5CH_2O - (C_6F_4CH_2O -)_n \; C_6F_4CH_2O^- + n+1 \; F^-$$

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 2½ 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:-

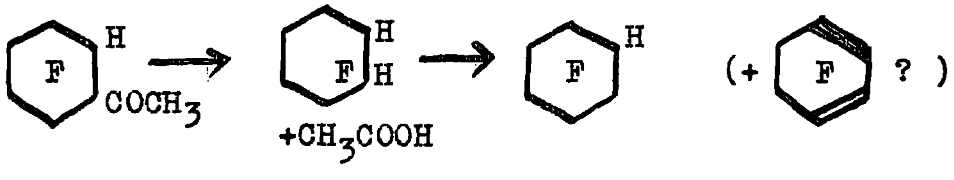
Alcohol	Ratio olefin to unchanged starting material	Ratio trans : cis isomers in starting material
	3 : 1	∼1.5 : 1
	1.7 : 1*	
	2 : 1*	2 : 1
	3 : 1⊕	2.5 : 1

* 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:-

Alcohol	Reaction time	No. of Products	% unchanged starting material
$CF_3CFHCF_2CH(OH)C_2H_5$	2½ 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 ½ 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 9½ 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	ν (cm^{-1})	Reference
$CF = CF_2$	c-C_4F_8-$CF=CF_2$	1785	155
	$C_2F_5CF=CF_2$	(1792	154
		(1799	41
	$CF_3CF=CF_2$	(1798	52
		(1799	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

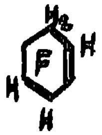
It is clear that in all the alcohols the double bond is internal rather than terminal i.e. the correct structure is (c) rather than (d). This is to be expected since bond strength differences suggest that a 'secondary' fluorine atom on the β carbon will be more easily removed than a 'primary' fluorine on the δ carbon in $\overset{\delta}{CF_3}\ \overset{\gamma}{CFH}\ \overset{\beta}{CF_2}\ \overset{\alpha}{CH(OH)R}$. (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.)

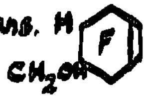
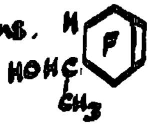
N.M.R. studies confirm this position of the double bond, and show that $CF_3CF = CF\ CH(OH)C_2H_5$ is a mixture of cis and trans- geometric isomers, while $CF_3CF = CFC(OH)(CH_3)_2$, which will suffer greater steric interaction in the cis form, exists predominantly as the trans isomer. (P. 106). By analogy 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,-hexafluoropropyl 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
	CF=CH	(1714 (1710 (1707	157 160 165
	CF=CH	1710	204
	CF=CH	1717	157,163
	CF=CH	1713	157,163
	CF=CH	1715	161
Trans Cis 	CF=CH CF=CH	1722 1720	}157
	CF=CH	1711	162
	CF=CH	1710	162
	CF=CH	1710	162
	CF=CF	(1745(liq.) (1754(gas) (1739(C Cl4)	* 158 159
	CF=CF	1752	157

Compound Cyclohexenes	C = C bond	ν (cm^{-1})	Reference
	CF=CF	1747	157
Trans Cis 	CF=CF CF=CF	1750 1745	}157,163
Trans Cis 	CF=CF CF=CF	1755 1746	}157,163
Cis+trans. Cis 	CF=CF CF=CF	1748 1742	* *
Cis+trans. Cis 	CF=CF CF=CF	1754 1751	* *
	CF=CF	1754	159
	CF=CF	1761	*
	CF=CF	1733	*
Cyclohexa-1,4-dienes			
	CF=CF	(1745(liq.) (1739(gas) (1739(C CCl$_4$)	* 157 159
	(CF=CF) (CH=CH)	1770,1688	163
	CF=CH	1744,1711	161

Cyclohexa-1,4-dienes

	CF=CH	1737(weaker) 1707	161
	(CF=CH) (CH=CH)	1729,1676	162
	(CF=CF) (CF=C Cl)	1789,1718	164

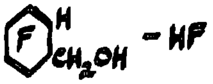
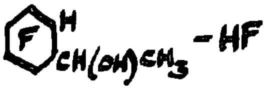
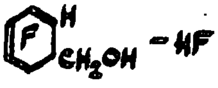
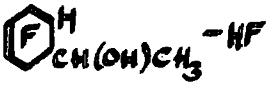
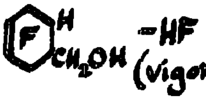
Cyclohexa-1,3-dienes

	CF=CF	(1751,1709(liq) (1754,1721(gas) ((1753,1713(C Cl_4)	* Durham-workers 159
	(CF=CF) (CH=CH)	1734,1635	161,163

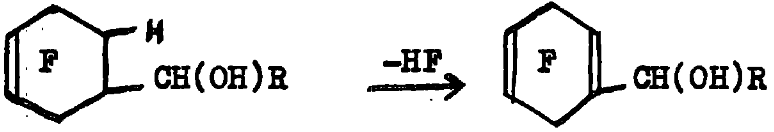
* = present work

These examples show that for cyclohexenes CF=CF absorption generally occurs at 1739-1755 cm^{-1}, regardless of substituentsat 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:-

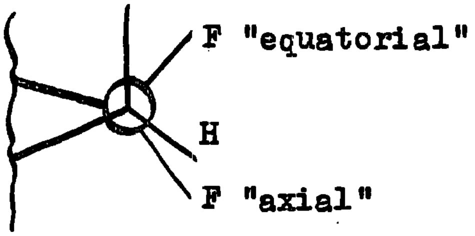
Compound	ν (cm^{-1})
	1712
	1692
	1776,1721
	1773, 1715
 (vigorous reaction conditions)	1786,1757,1724,(1639)

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,  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 cyclohexenyl alcohols are therefore consistent with structure (a),  CH(OH)R, rather than with (b),  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.



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,



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.

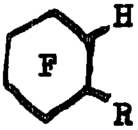
The ^{19}F spectra of the adducts in which R=CH_2OH, $CH(OH)CH_3$, $CH(OH)C_2H_5$, $CH(OH)C_3H_7$, $CH(CH_3)_2OH$, $COCH_3$ and $CH(CH_3)OCOCH_3$, all show peaks in the CFH range ϕ=207-217 p.p.m., with J_{FH} coupling constants from 43-48 c/s, while CF_2R fluorine nuclei resonate in the region ϕ=113-135 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.

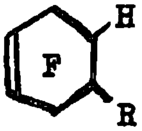
Where R contains an asymmetric carbon atom i.e. when R=$CH(OH)CH_3$, $CH(OH)C_2H_5$, $CH(OH)C_3H_7$ and $CH(CH_3)OCOCH_3$, the ^{19}F spectrum of the adduct shows two groups of peaks of equal intensity in the CFH region, each with geminal FH coupling, while the CF_2R region shows two overlapping AB quartets, 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. <u>Cyclic perfluoro-olefin adducts</u>

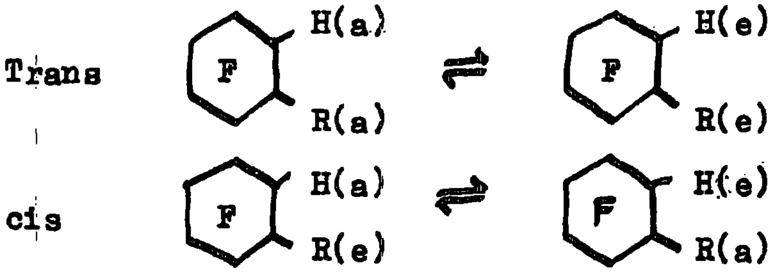
The ^{19}F spectra of the adducts  (where $R=CH_2OH$, $CH(OH)CH_3$, $CH(OH)C_2H_5$, $CH(OH)C_3H_7$ and $COCH_3$) all show a number of peaks with chemical shifts in the range ϕ=116-149 p.p.m. which are assigned to the ring CF_2 fluorine nuclei. In compounds of the type  ($R=CH_2OH$, $CH(OH)CH_3$, $COCH_3$ and $CH(CH_3)OCOCH_3$), peaks arising from the resonances of the CF_2 fluorines occur in the range ϕ=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 perfluorocyclohexene 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 

and 

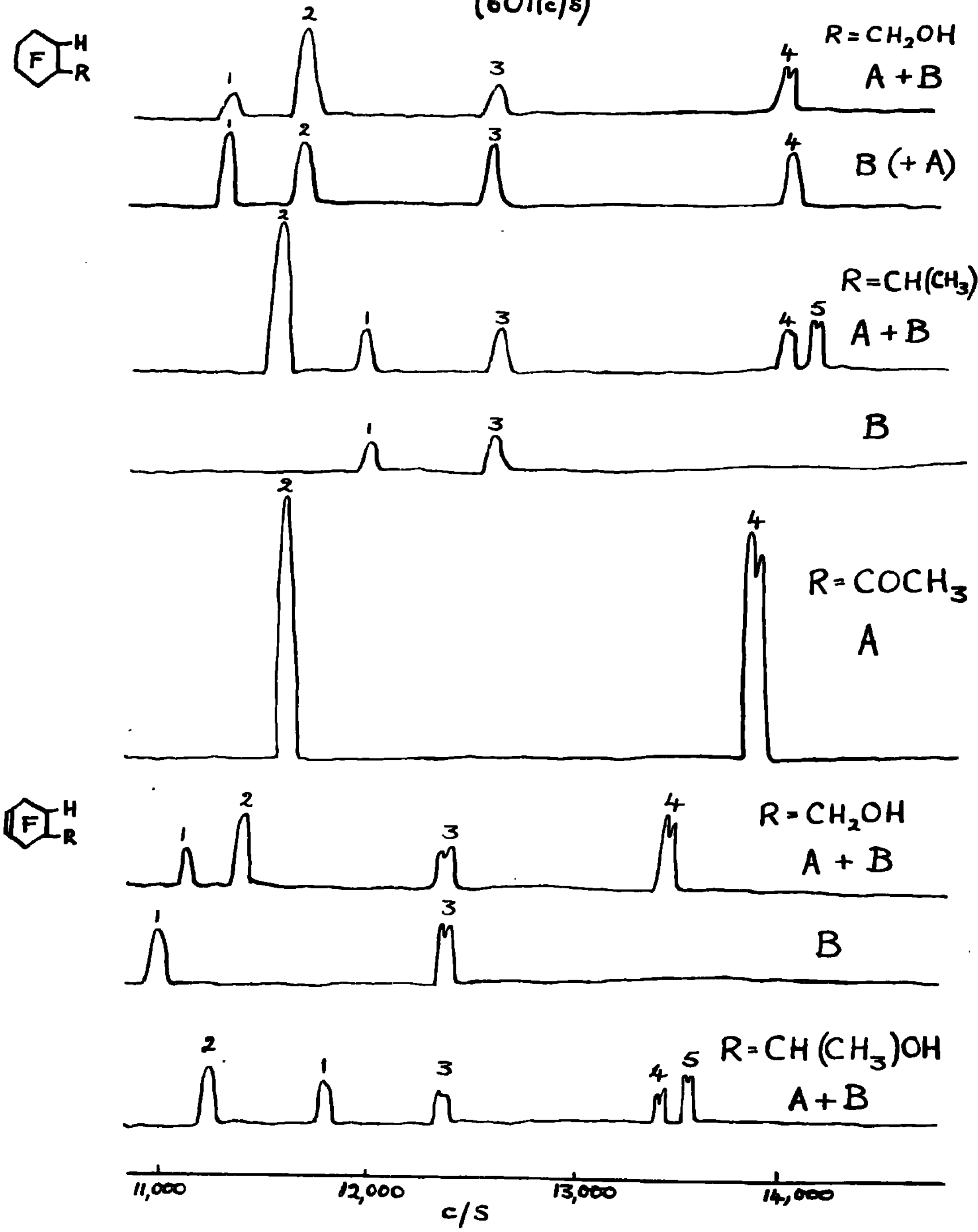
can exist in both cis and trans forms, and for each geometric isomer there are two possible conformations, i.e. in the transform both substituents may be either axially or equatorially situated, while the cis form may have H axial and R equatorial or vice versa.



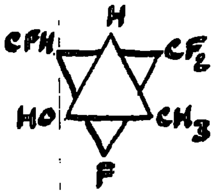
A sample containing cis and trans isomers, both of which were only slowly interconverting between the two conformations, would therefore show eight chemically shifted peaks in the high field region (4 $C\underline{F}R$ and 4 $C\underline{F}H$). If the rate of interconversion of the conformers was rapid 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 comtains an asymmetric carbon two

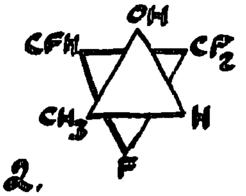
High Field Region of ^{19}F Spectra (60Mc/s) Fig. (i)



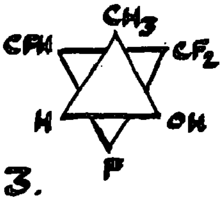
optical isomers are possible for each conformer (or mixture of interconverting conformers), and this is the explanation suggested for the appearance of a third CFH peak in the spectra of the higher alcohol adducts. The number of CFR peaks remains unchanged, indicating that while the CFH fluorine nuclei 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:



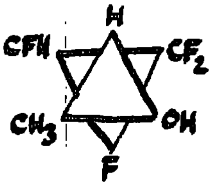
1.



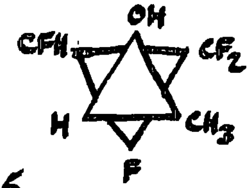
2.



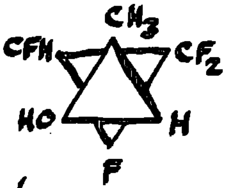
3.



4.



5.

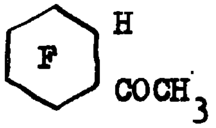


6.

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.

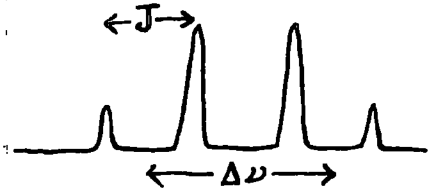
The chemical shifts of the two high field peaks of the major adduct of perfluorcyclohexene and aceteldehyde are so close to those of peaks 2 and 4 of the alcohol adducts that it is reasonable to conclude that this compound has the same conformation as the alcohols of type A. The sharpness of the ketone spectrum makes it a particularly suitable example for closer study.

Configuration A

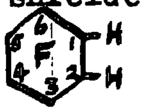
In order to interpret the spectrum of 

(A) a number of assumptions are made, based on observations of the spectra of perfluorocyclohexane[198] and dihydrodecafluorocyclohexanes[199,200].

While the ^{19}F spectrum of perfluorocyclohexane consists of a single broad line at room temperature, at -66°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°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 , 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.

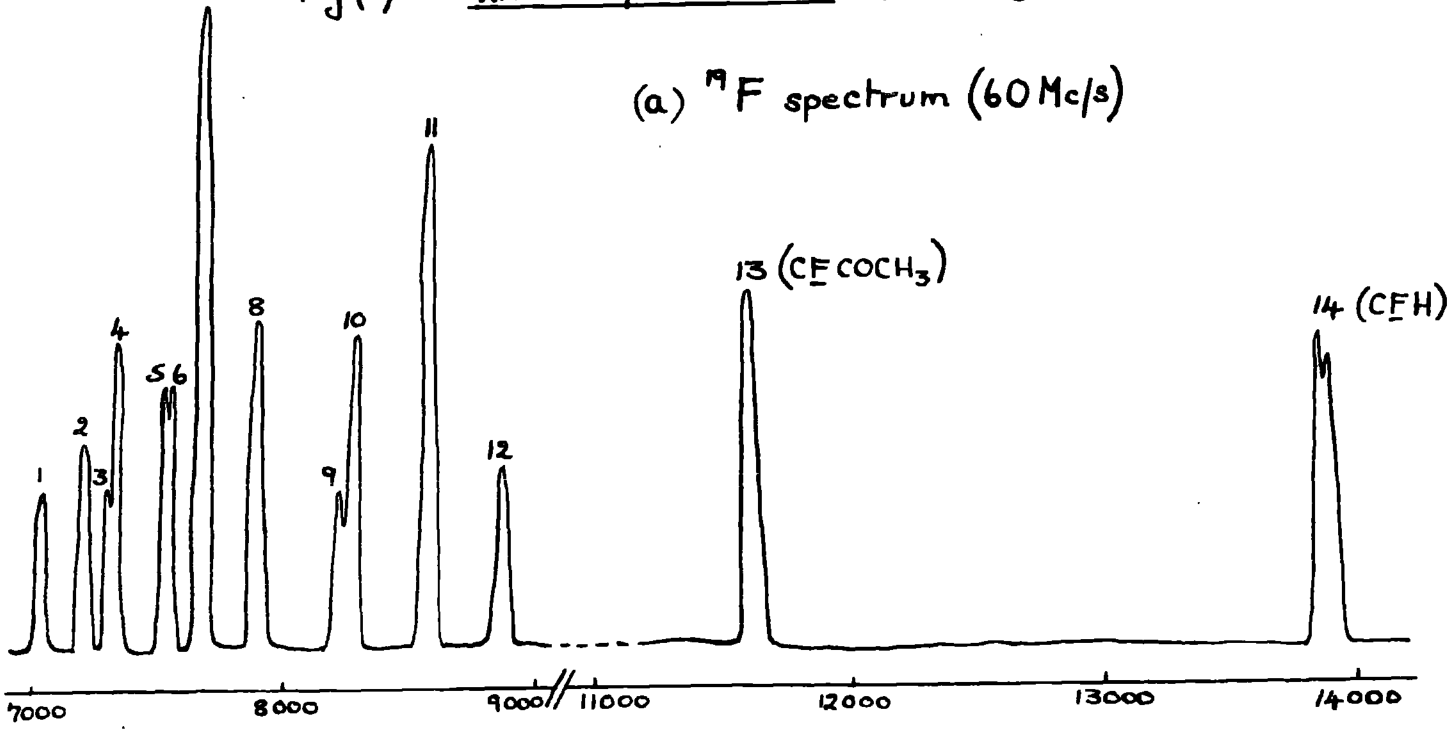
The ^{19}F spectrum at 60 Mc/s of  (isomer A) shows twelve peaks in the range 7000-9000 c/s arising from the resonances of the CF_2 groups (Fig.(ii)a). Peak 7 can be attributed to two equivalent geminal fluorine nuclei, and the other eleven peaks comprise three AB quartets with two peaks overlapping 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

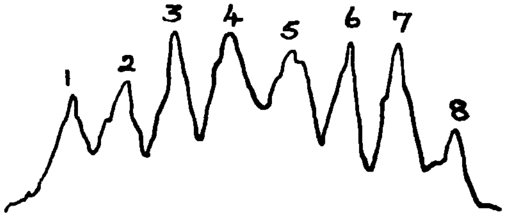
Comparison of these values with the chemical shift of 1095 c/s (18.2 p.p.m.) between axial and equatorial fluorine nuclei in perfluorocyclohexane suggests that these quartets arise from three pairs of different geminal fluorine atoms. If the principles derived from study of the dihydro compounds are 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  (A)



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



(b) ^{19}F spectrum CF̲H fluorine nucleus. (c) ^{1}H spectrum CFH̲ 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.

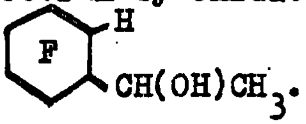
If the CFH fluorine were in an equatorial position, in addition to coupling with the geminal H it would couple equally with each of the three vicinal fluorine nuclei, giving a pair of quartets. If however both R and H occupy equatorial positions, the axial CFH fluorine will have two axial and one equatorial 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

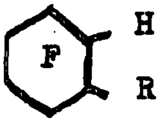
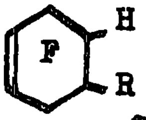
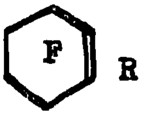
Only a trace of adduct thought to have the same conformation as the alcohols of type B was obtained by addition of acetaldehyde to perfluorocyclohexene. However it was possible to obtain sufficient of this ketone for study of its n.m.r. spectrum by oxidation of a sample of the pure B isomer of



The ^{19}F spectrum of the ketone contains nine peaks in the CF_2 region (Ø=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  and  (where R=CH$_2$OH,etc) could give either (a)  and  or (b)  and  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 ϕ=200 p.p.m. The intensities and positions of the five peaks in the ^{19}F spectrum of  are consistent with a structure containing three CF=groups (ϕ=132-160 p.p m.) and two CF$_2$ groups (ϕ=106-115 p.p.m.), while  has the four expected CF$_2$ peaks (ϕ=112-136 p.p.m.).

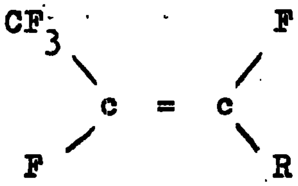
and one CF= peak (ϕ=127 p.p.m.).

(ii) Straight chain olefins. 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 ϕ=143-175 p.p.m. and one group in the region ϕ=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,



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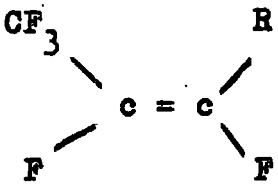
The spectrum of the other isomer of $CF_3CF{=}CF\ CH(OH)C_2H_5$ contains coupling constants assigned to cis F-F coupling (27.7 c/s), trans CF_3-F coupling (12.1 c/s) and geminal CF_3-F coupling (8.6 c/s), which is adequate proof that this is the cis isomer,



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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

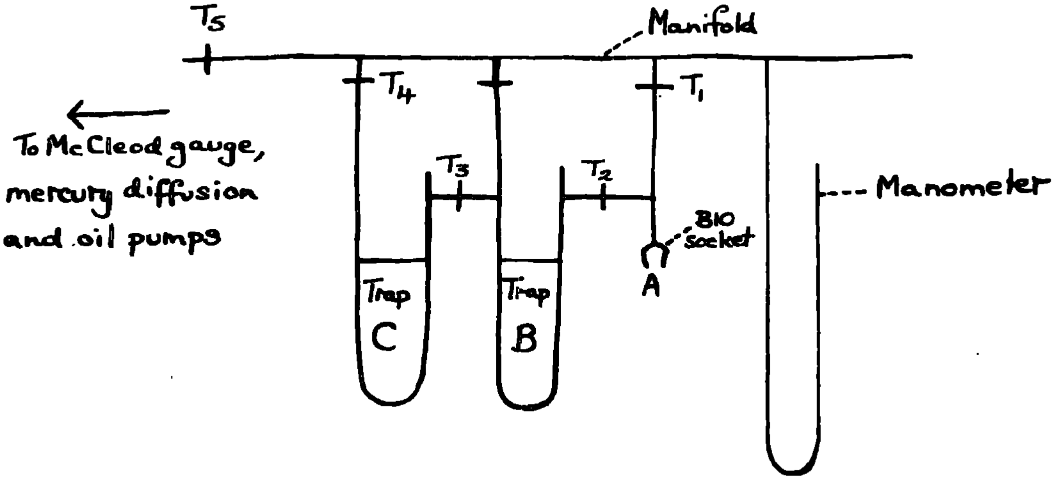


FIG. 1 VACUUM FRACTIONATING SYSTEM.

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. 160).

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. 155).

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 $\frac{1}{4}$ 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 $\frac{1}{4}$ 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 $\frac{1}{8}$ 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°/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°/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°/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-hexafluorohexan-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 chromatogram 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-hexafluoropentan-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-hexafluoropentanone-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 8½ min) plus small amounts of two compounds of retention times 5½ and 14 min. Therefore the total weight of the major product, identified from its ^{19}F and ^{1}H 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) γ-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.

Allyl alcohol. 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).

Crotonyl alcohol. 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°.

Ethylene glycol. 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 infrared 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 2899cm^{-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 4½ 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°(7.0g). Analytical V.P.C. (tricresyl phosphate at 68°; N_2 flow rate 0.9 l/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°, 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 malenate 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.

<u>Ethanol.</u> 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°/745mm; n_D^{21} 1.3479. Found: F,61.9%. $C_8H_6F_{10}O$ requires F,61.7%. Infrared spectrum No.9a.

<u>n-Propanol.</u> 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°/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 spctrum No.10.

Isopropanol. 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.

n-Butanol. 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 perfluorocyclohexene (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 l/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).

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

Diethyl ether. 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 0.9l/hr) to consist of C_6F_{10} and roughly equal quantities of four components with retention times of 2, 3½, 7 and 8 min. respectively.

Anisole. 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°.

Formamide. 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.

Methyl acetate. 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^{P}. Unchanged starting materials were removed by distillation at 20°/0.01mm. 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 9½ and 10½ min.

Ethyl acetate. Only a trace of product (retention time 7½ 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 perfluorocyclohexene 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 l/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 add 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 langer 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.

Benzaldehyde. 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°.

Acetone. Octafluorocyclohexa-1,4-diene (4.2g, 0.019 moles) and acetone (9.5g, 0.164 moles) were heated with benzoyl peroxide (0.2g) for 21½ hrs. at 125°. The residue (0.4g) from the distillation of unchanged starting materials was distilled at 100°/0.01mm, 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}.

Methanethiol

1; **Peroxide initiation.** 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°. 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; **γ-Ray Initiation.** A Carius tube charged with octafluorocyclohexa-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 $20-90^{\circ}/0.01$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°/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. Recrystallisation 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-hexafluoropentanone-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 (½ 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°/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-trifluoromethyloctafluorocyclohexene (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-trifluoromethyldecafluorocyclohexane (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°. (Haszeldine 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 trifluoromethyliodide (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 ½ 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 trifluoromethyliodide (10.4g, 0.053 moles) was irradiated for 8 days (1 k.w. lamp).

<u>Attempted Addition of Heptafluoroisopropyl iodide to Octafluorocyclohexa-1,3-diene.</u>

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°, 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

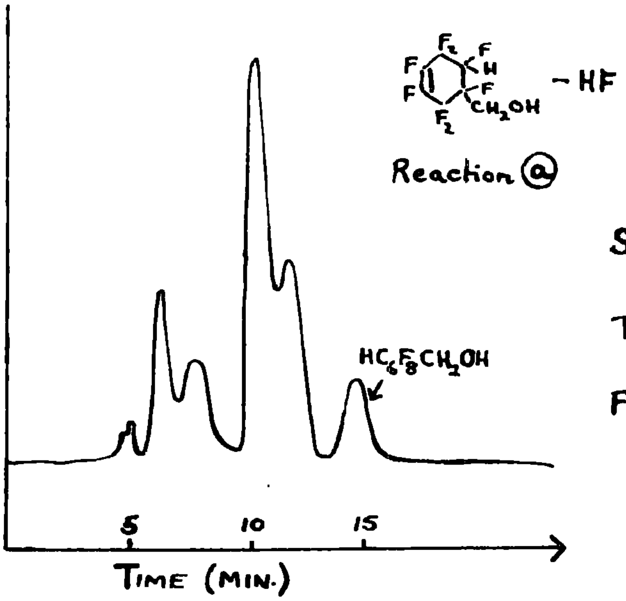
The starting materials were the mixtures of isomers obtained by free radical addition of alcohols to the appropriate perfluoro-olefins.

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 4½ 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

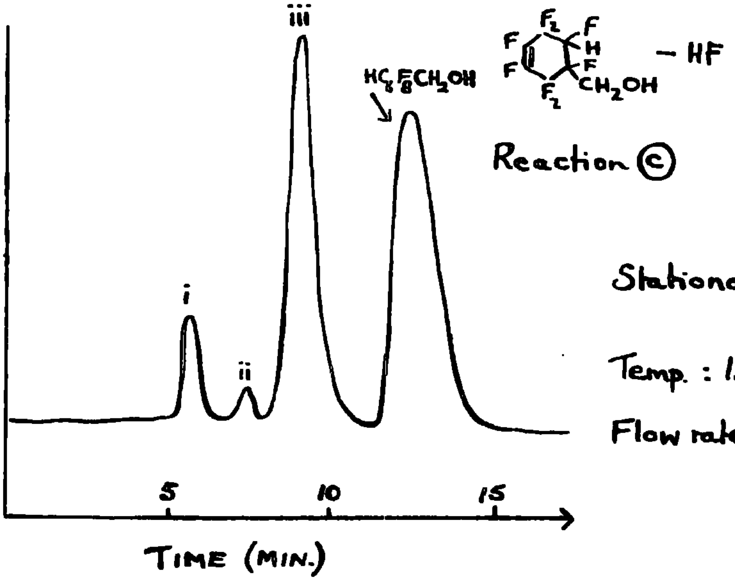


Stationary phase: Silicone elastomer

Temp. : 142°

Flow rate : 1 l N_2 /hr.

FIG. 2b



Stationary phase: Silicone elastomer

Temp. : 125°

Flow rate : 1·5 l N_2 /hr.

(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°/0.01mm. yielded a yellow distaillate (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}.

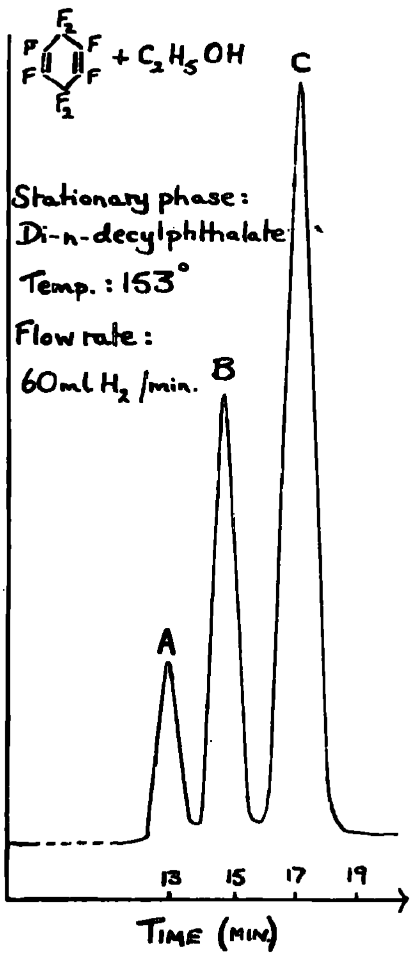
(d) Dilute aqueous potassium hydroxide

1N potassium hydroxide (2.8g., 0.05 moles, in 50 mls. water) was added dropwise over 2½ hrs. to (2H-octafluorocyclohex-4-enyl) methanol (13.7g., 0.054 moles) with stirring at room temperature. Stirring was continued for a further 21½ 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.

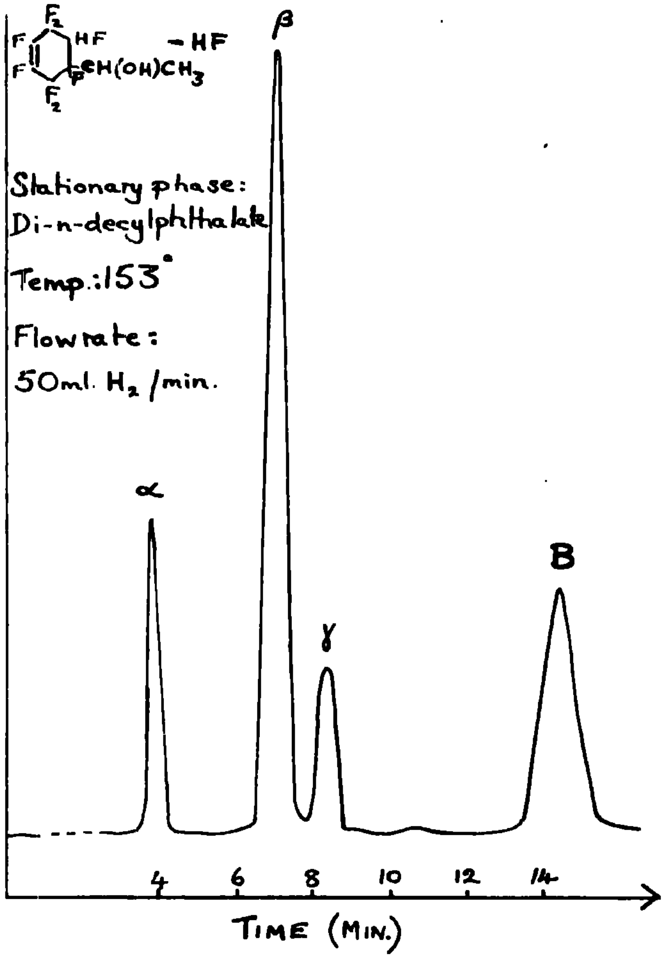
II. Methyl (2H-octafluorocyclohex-4-enyl) methanol

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°/0.01mm. 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.



F₂
F F
F F
F₂
+ C_2H_5OH
C
Stationary phase:
Di-n-decylphthalate
Temp.: 153°
Flow rate:
60ml H_2 /min.
B
A
13
15
17
19
TIME (MIN.)

Fig. 3



F₂
F HF
F F CH(OH)CH_3
F₂
−HF
β
Stationary phase:
Di-n-decylphthalate
Temp.: 153°
Flow rate:
50ml. H_2 /min.
α
γ
B
4
6
8
10
12
14
TIME (MIN.)

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 2½ 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. <u>4.5N KOH at 65°</u>

(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 3½ hrs., during which time the reaction mixture became dark brown. Ether extraction of the acidified mixture, followed by distillation at 80°/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 6½ min.).

5. <u>Addition of 0.9N KOH at 21°</u>

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°/0.01mm. 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°). 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 stereoisomer. m.p. 57° (colourless needles recrystallised from pet. ether 60-80°). 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 2½ hrs. The ether extract of the reaction mixture was distilled at 20°/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°/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. <u>2,2,3,4,4,4-hexafluorobutan-1-ol</u>.

(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 43½ 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 ½ 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 7½ 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 perfluoropropene

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.)

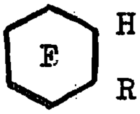
was used to separate the products (0.9g) from the starting material. The infrared spectrum of the product mixture included the following bands:- 3093(w), 3058(w), 1831(w), 1748(w), 1709(s), 1370-940 Cm^{-1}.

N.M.R. Data

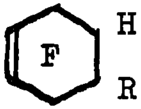
Peak positions of ^{19}F resonances relative to $CFCl_3$ as an internal reference are given in the following tables:-

1. CF_3CFHCF_2R

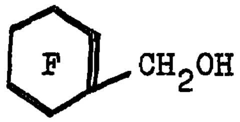
R	ϕ CF_3 p.p.m.	ϕ CF_2 p.p.m.	ϕ CFH ppm.
CH_2OH	75.0	115.43, 119.78, 121.57, 126.08	214.28
$CH(OH)CH_3$	74.91	118.65, 122.54, 123.19, 124.43, 127.00, 128.97, 130.10, 134.68	213.72 215.45
$CH(OH)C_2H_5$	74.71	117.37, 121.97, 123.25, 126.90, 128.38, 132.97	213.57 215.35
$CH(OH)C_3H_7$	74.78	117.30, 122.03, 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. 

R	Isomer	Φ CF$_2$ p.p.m.	ΦCFR p.p.m.	Φ CFH p.p.m.
CH_2OH	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
$CH(OH)C_2H_5$	trans	116.08 - 148.83	193.17	230.25,233.33
"	cis		197.17	209.83
$CH(OH)C_3H_7$	trans	116.28 - 148.58	193.17	230.66, 233.67
"	cis		197.58	210.17
CH_3CO	trans	117.83 - 148.300	193.15	231.33
"	cis	116.05 - 141.00	176.53	212.917

3. 

R	Isomer	ϕ CF_2 p.p.m.	ϕ CF= p.p.m.	ϕCFR 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. 

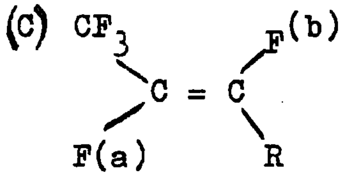
:- ϕCF_2, 112.28 - 135.48 p.p.m.

$\phi CF=$, 127.28 p.p.m.

5. 

:- ϕCF_2, 106.80, 115.23 p.p.m.

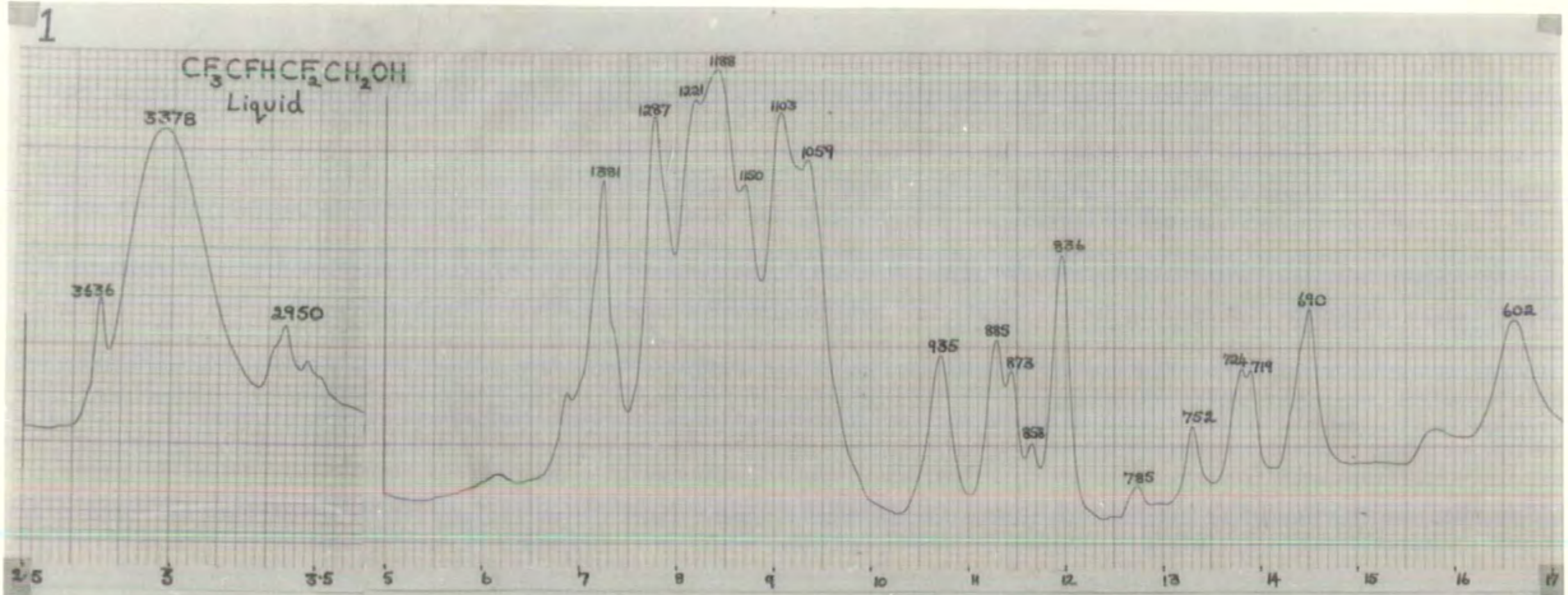
$\phi CF=$, 132.43, 155.05, 160.10 p.p.m.

6. 

Peak positions and coupling constants:-

R	$CH(OH)C_2H_5$	$CH(OH)C_2H_5$	$CH(OH)(CH_3)_2$
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 ± 0.3	8.6 ± 0.2	9.5 ± 0.2
Jbc cycles sec^{-1}	21.8 ± 0.2	12.1 ± 0.1	22.5 ± 0.2
Jab cycles sec^{-1}	134.3 ± 0.5	27.7 ± 0.3	134.9 ± 0.8
JbH cycles sec^{-1}	24.8 ± 0.3		
JaH cycles sec^{-1}	4.9 ± 0.3	2.7 ± 0.1	

1



$CF_3CFHCF_2CH_2OH$
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2950
1381
1287
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1188
1150
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885
873
858
836
785
752
724
719
690
602
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3·5
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17

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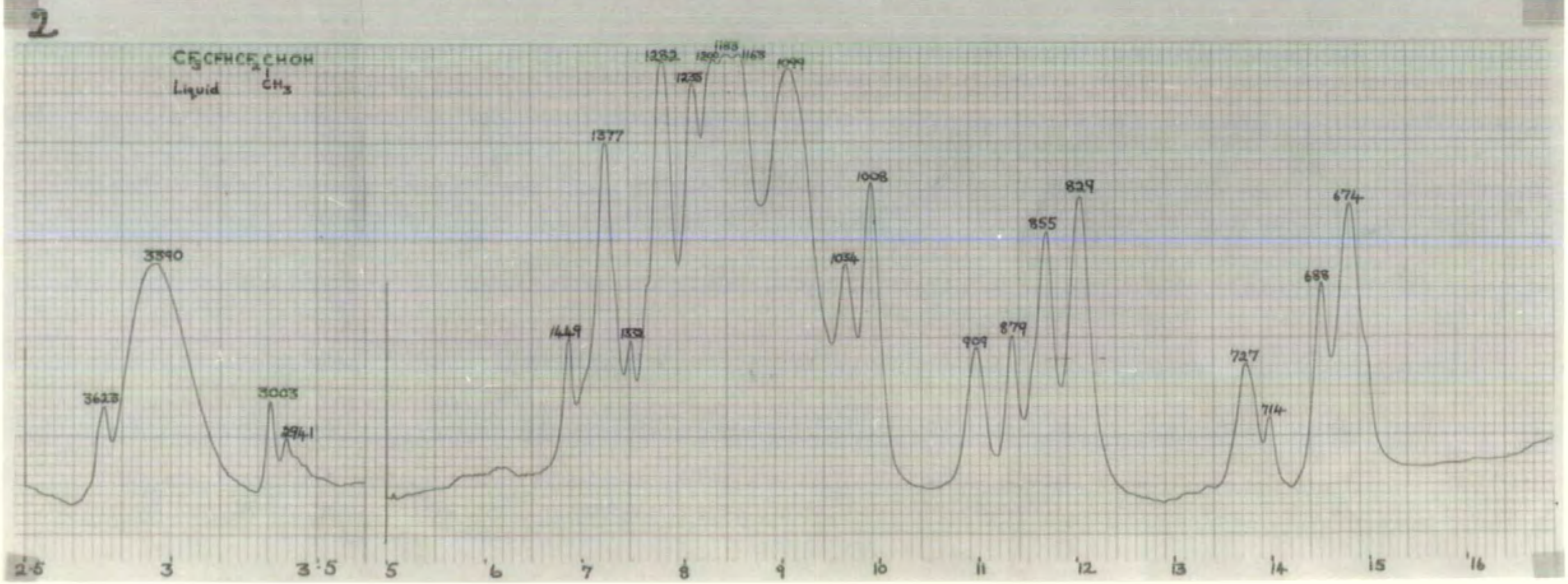

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1034
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879
855
829
727
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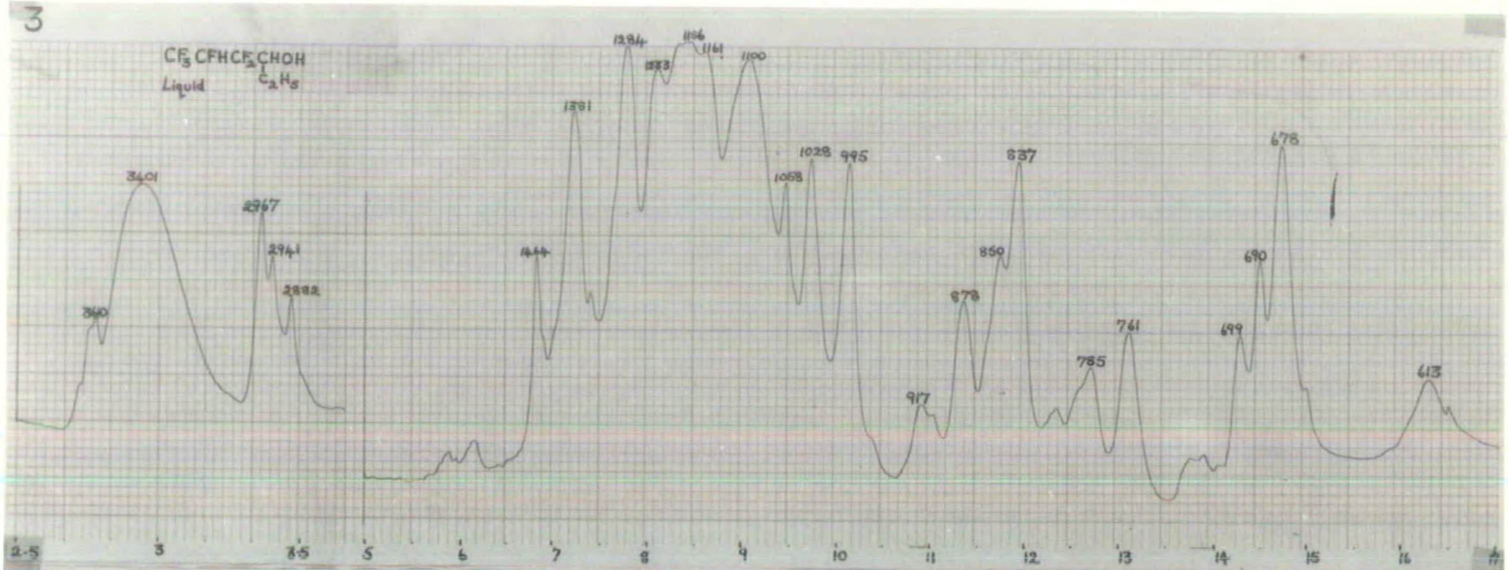

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917
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837
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699
690
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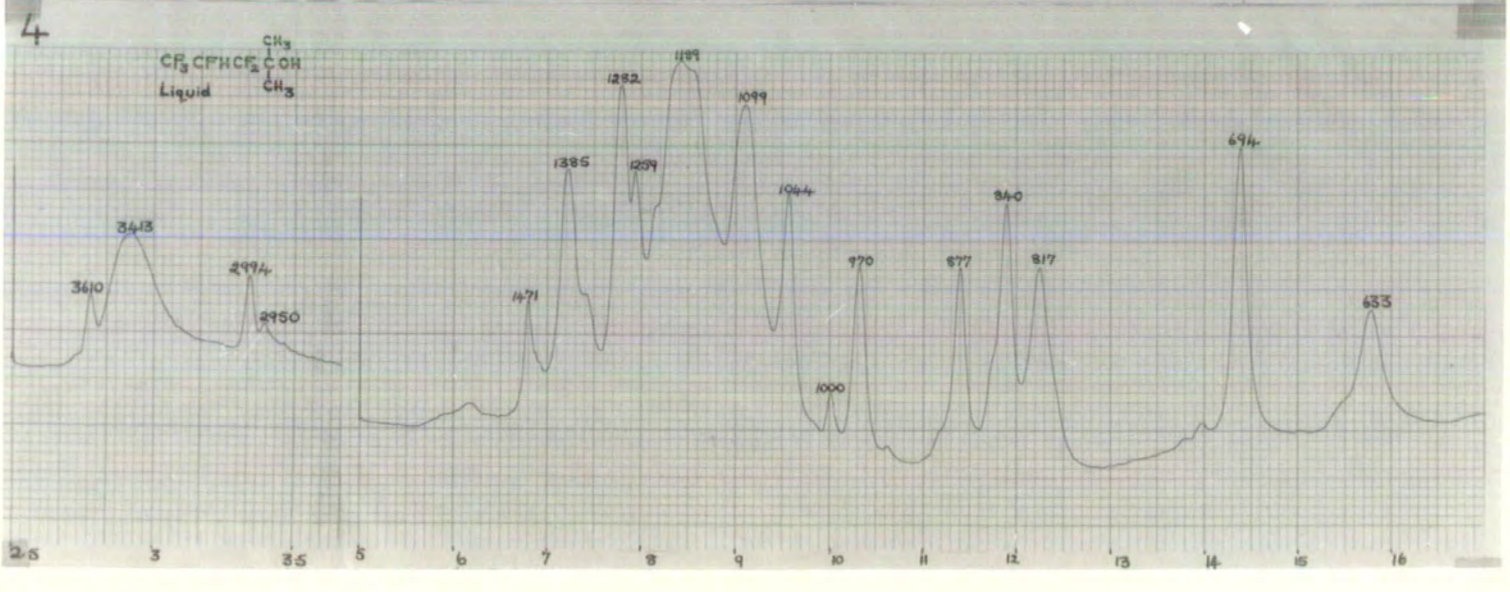

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970
877
840
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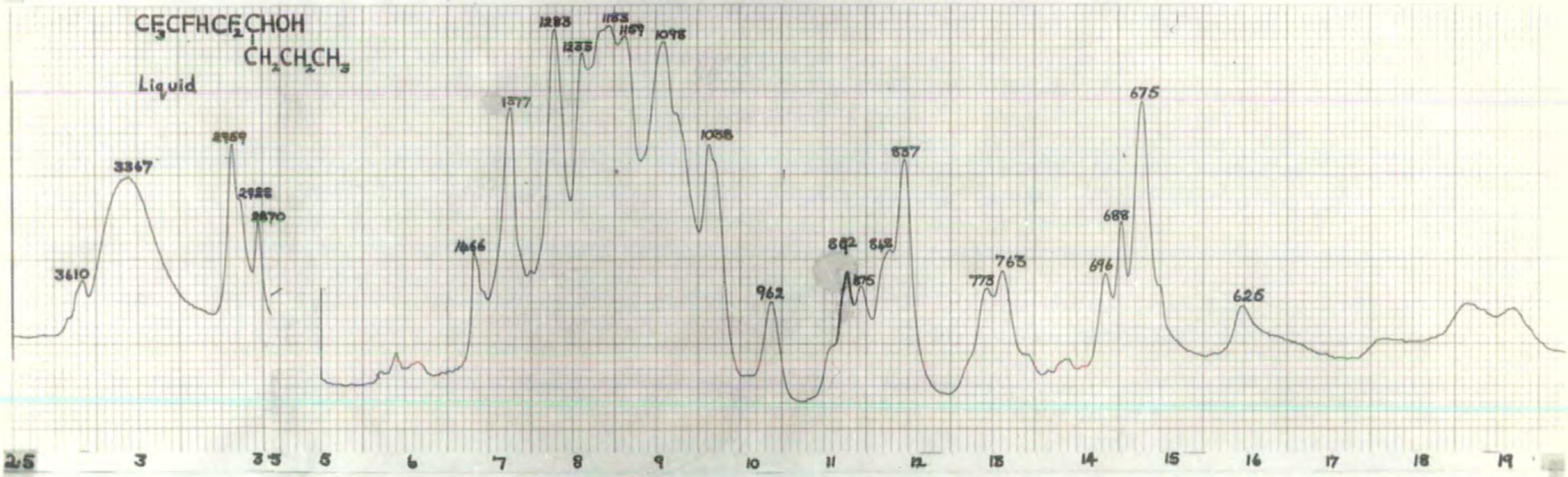
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1157
1098
1038
962
882
875
848
837
773
763
696
688
675
626
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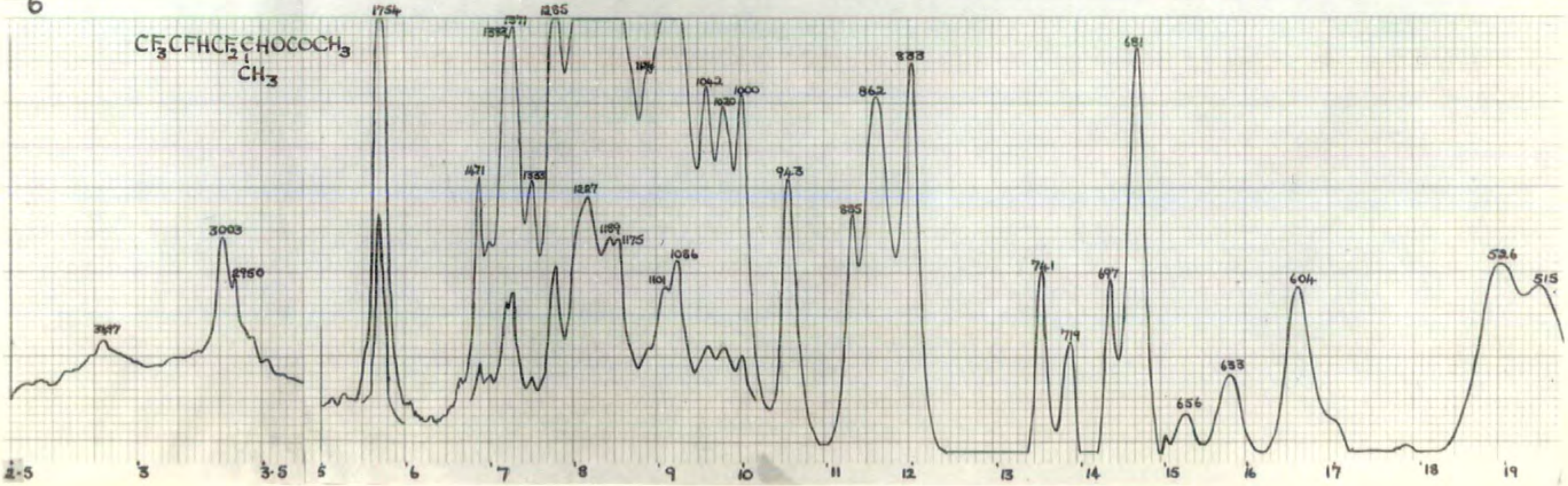
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1101
1086
1042
1020
1000
943
885
862
833
741
719
697
681
656
633
604
526
515
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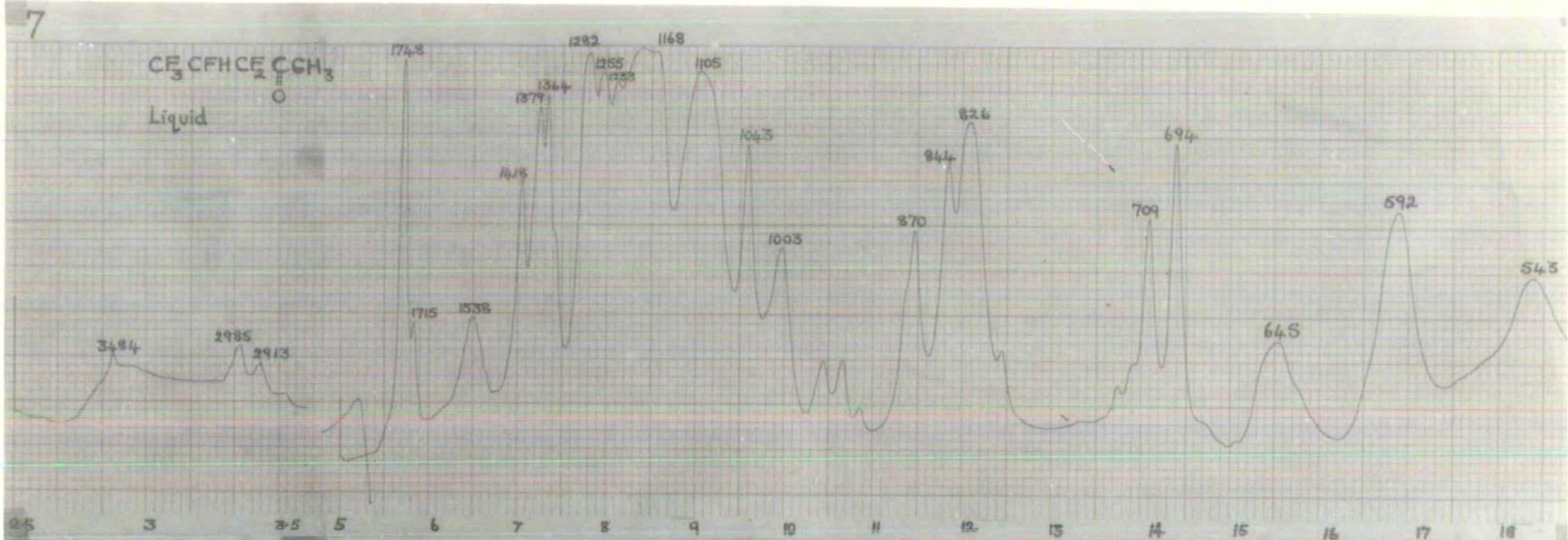
7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1233
1168
1105
1043
1003
870
844
826
709
694
645
592
543
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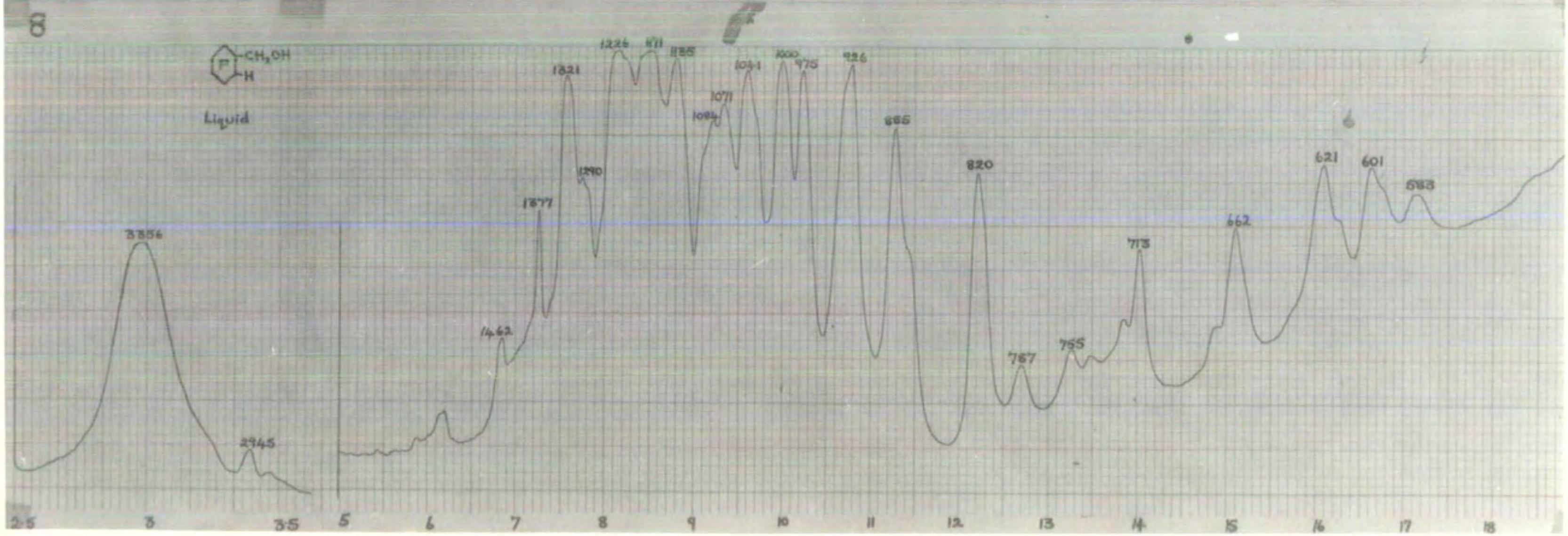
18

8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H
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1000
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926
885
820
787
755
713
662
621
601
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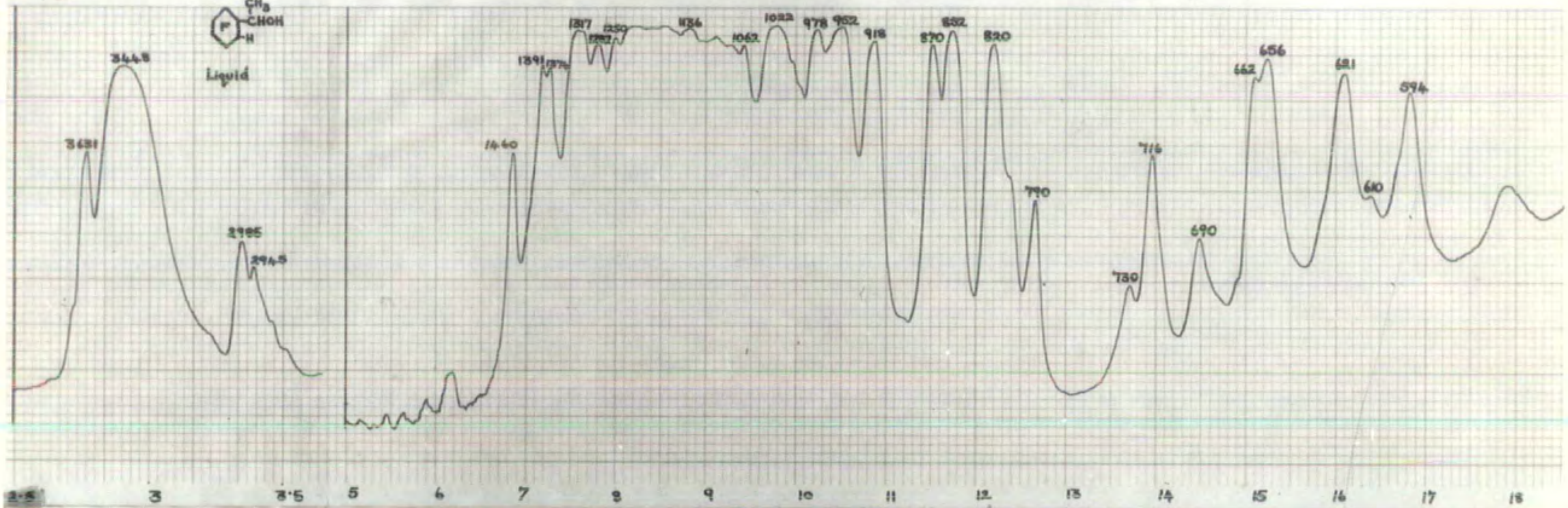
9a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1022
978
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918
870
852
820
770
730
716
690
662
656
621
610
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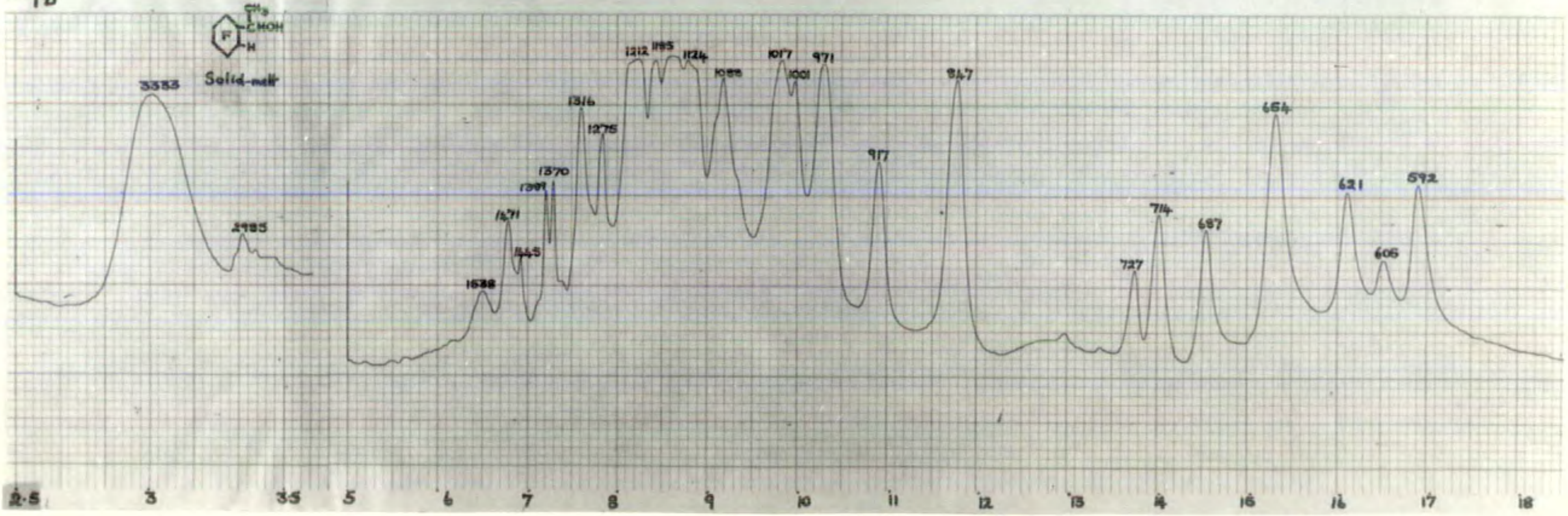
9b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1088
1017
1001
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727
714
687
664
621
606
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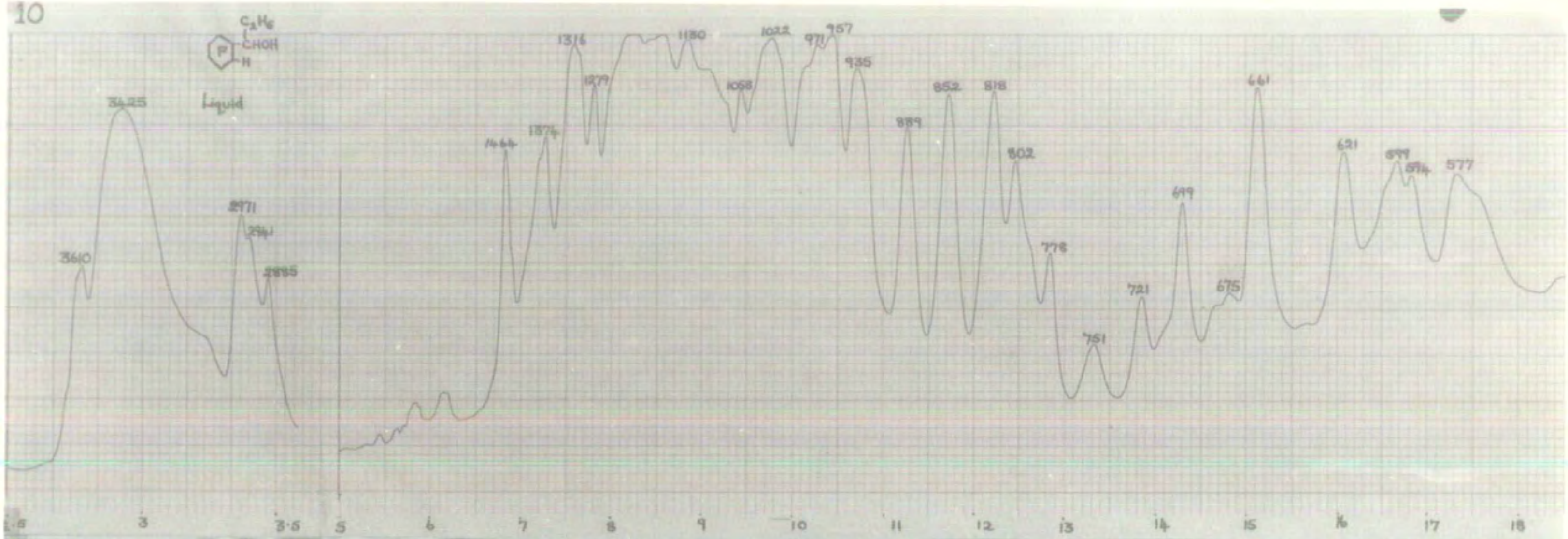
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P
H
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1058
1022
971
957
935
889
852
818
802
778
751
721
699
675
661
621
599
594
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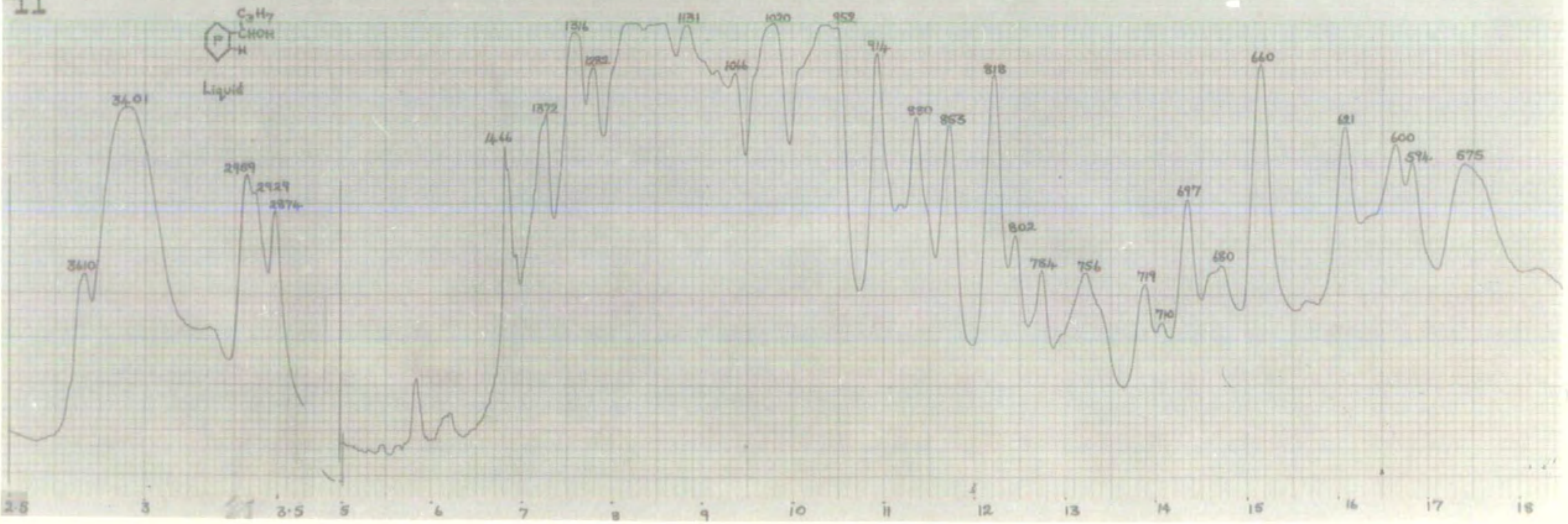
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P
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Liquid
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1066
1020
959
914
880
863
818
802
784
756
719
710
697
680
660
621
600
594
675
2·5
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3·5
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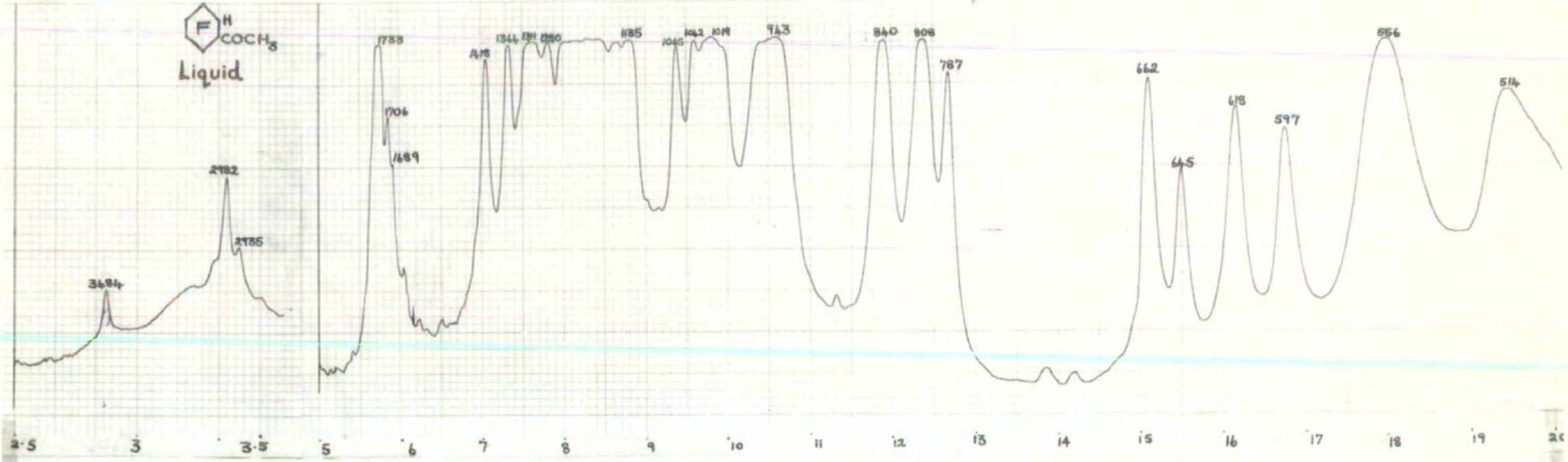
12



F
H
COCH3
Liquid
3484
2982
2935
1733
1706
1689
1418
1364
1311
1280
1185
1045
1042
1019
943
840
808
787
662
645
618
597
556
514
2·5
3
3·5
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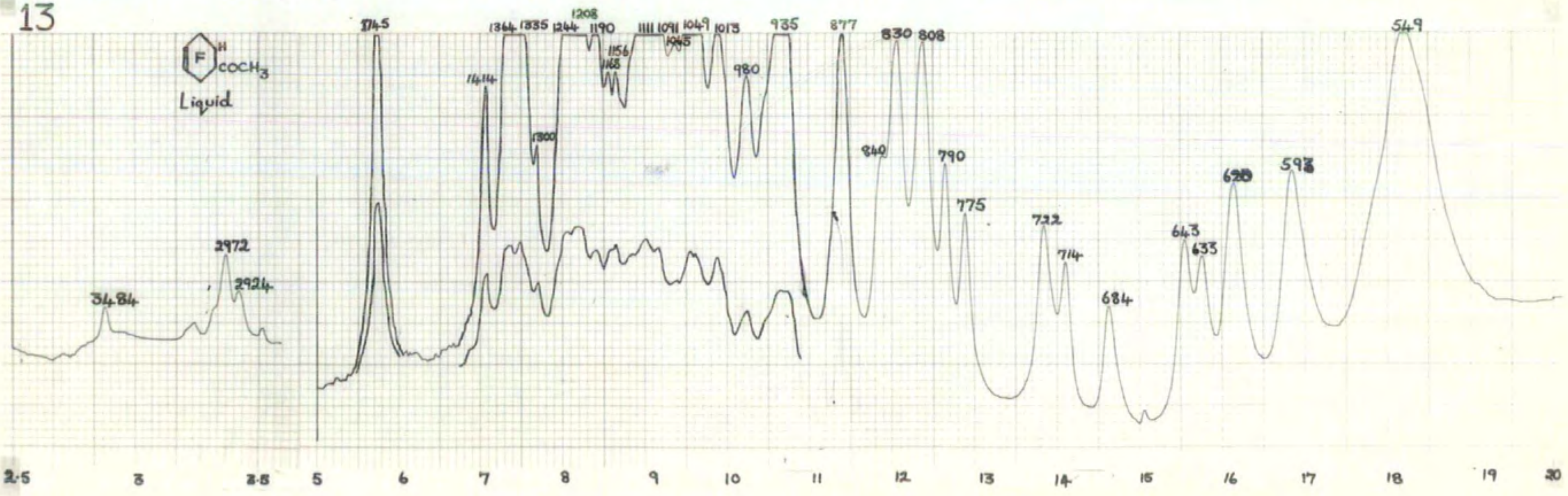
13



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H
COCH3
Liquid
3484
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1745
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1300
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1165
1156
1111
1091
1045
1049
1013
980
935
877
840
830
808
790
775
722
714
684
643
633
620
593
549
2·5
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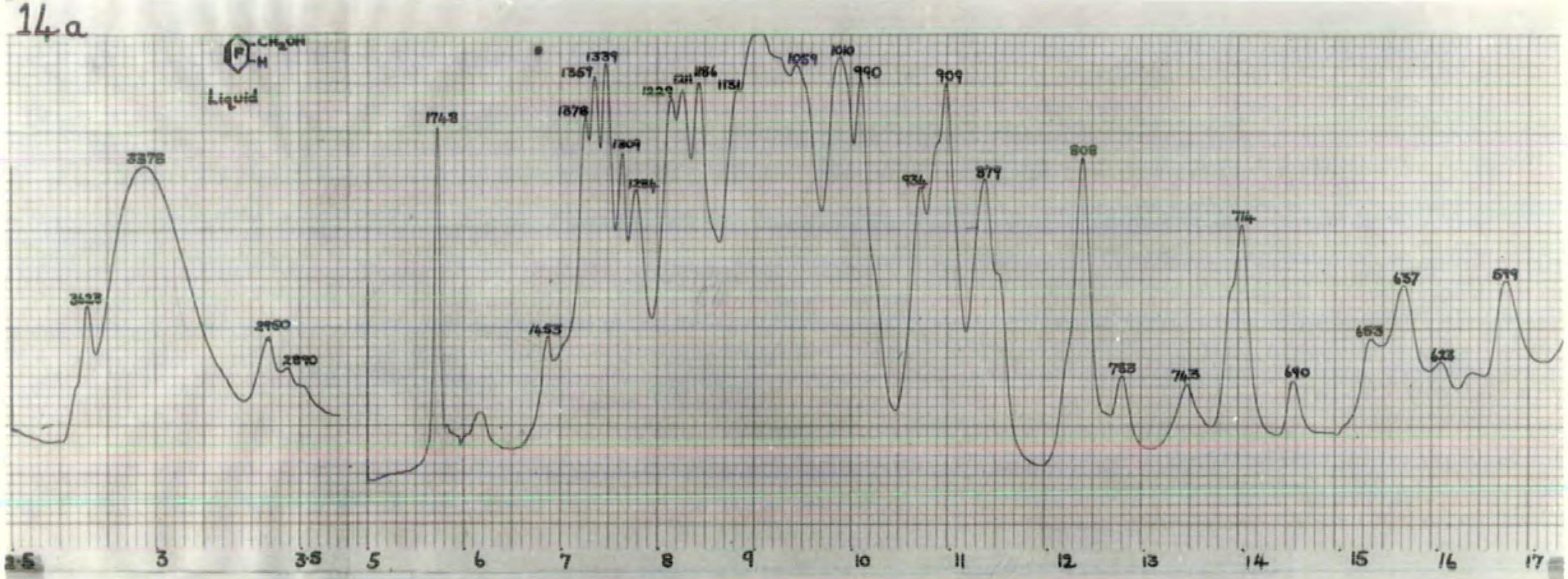
14a



CH₂OH
H
F
Liquid
3378
3425
2950
2890
1748
1453
1378
1367
1339
1309
1286
1229
1211
1186
1151
1059
1010
990
934
909
879
808
783
743
714
690
653
637
623
599
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3·5
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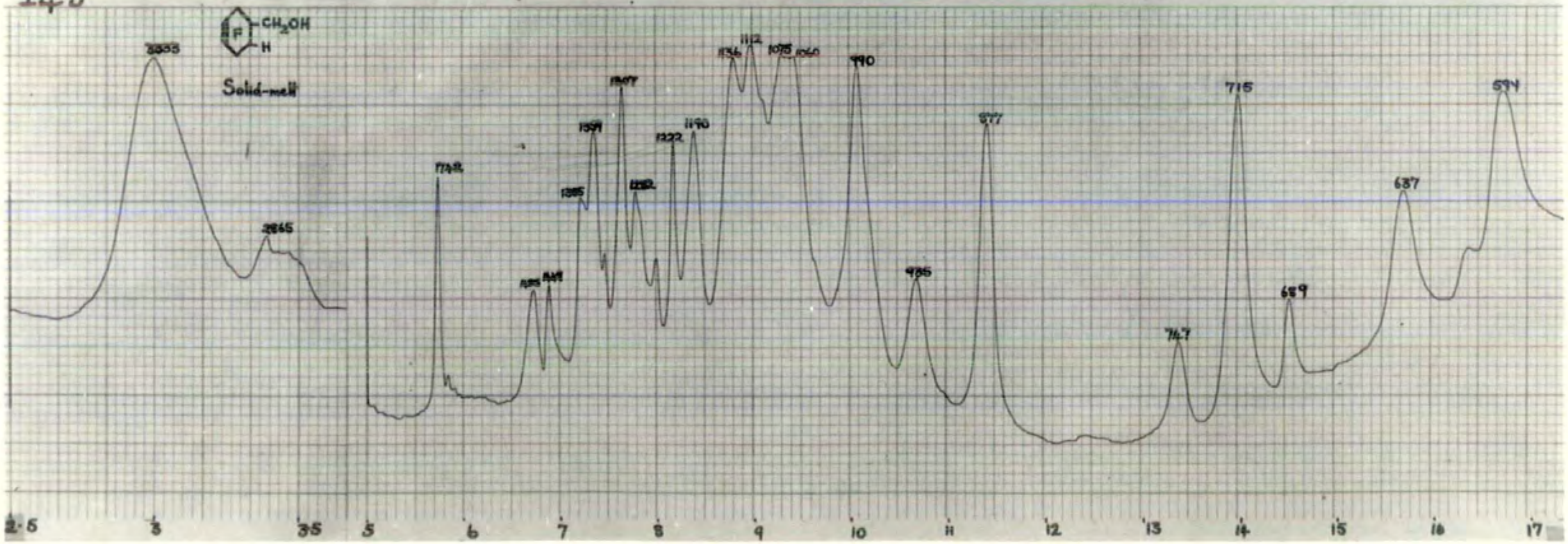
17

14b

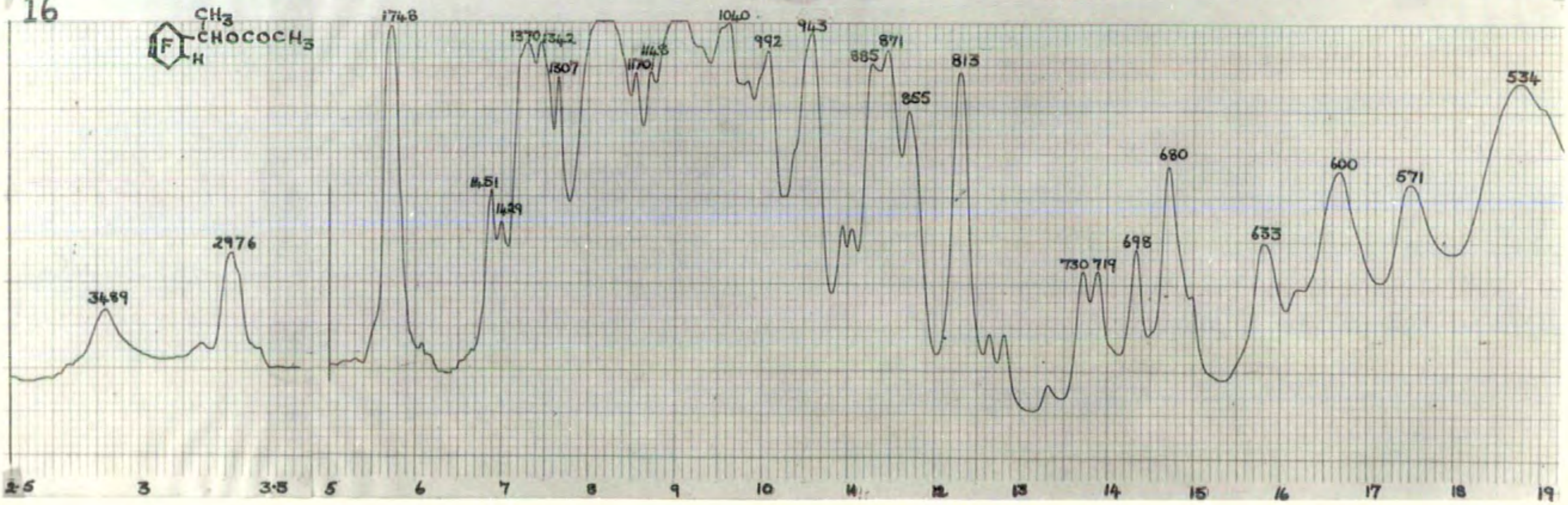


CH₂OH
H
F
Solid-melt
3333
2865
1748
1495
1449
1385
1359
1307
1282
1222
1190
1136
1112
1075
1060
990
935
877
747
715
689
637
594
2·5
3
3·5
5
6
7
8
9
10
11
12
13
14
15
16
17

15


CH3
CHOH
F
H
Liquid
3401
2985
2941
1754
1626
1460
1383
1369
1307
1226
1200
1163
1040
990
915
887
860
812
780
718
688
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
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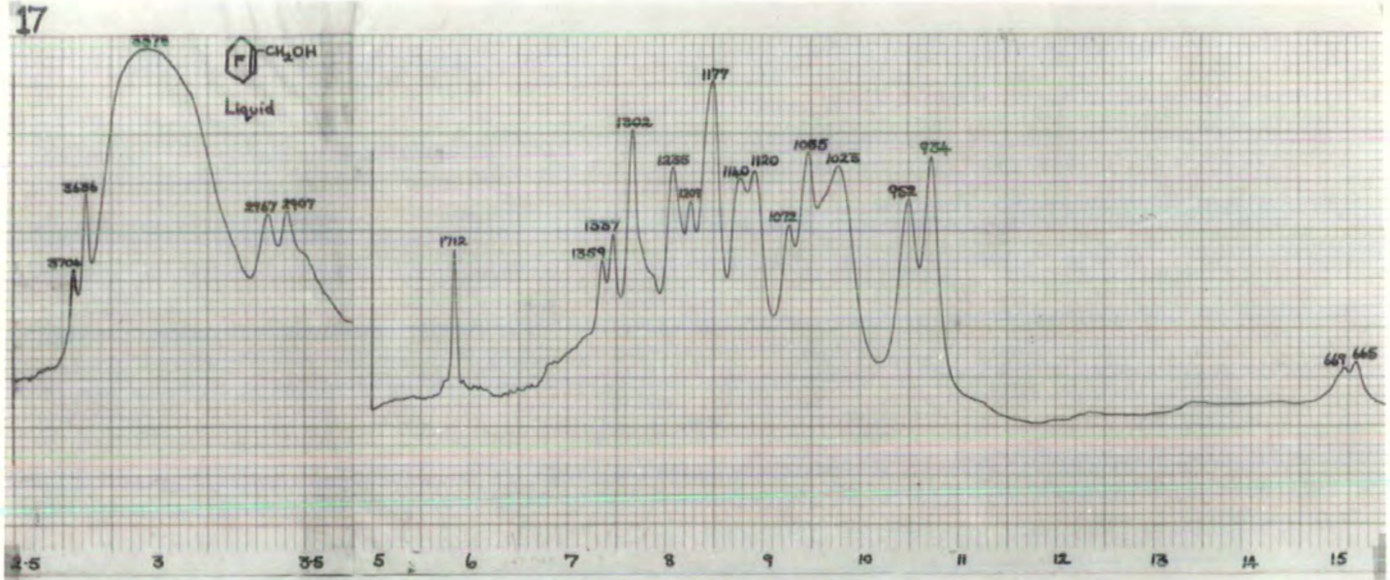
17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-CH2OH
Liquid
3378
3686
3704
2967
2907
1712
1359
1387
1302
1235
1201
1177
1140
1120
1072
1085
1025
952
934
667
665
2·5
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3·5
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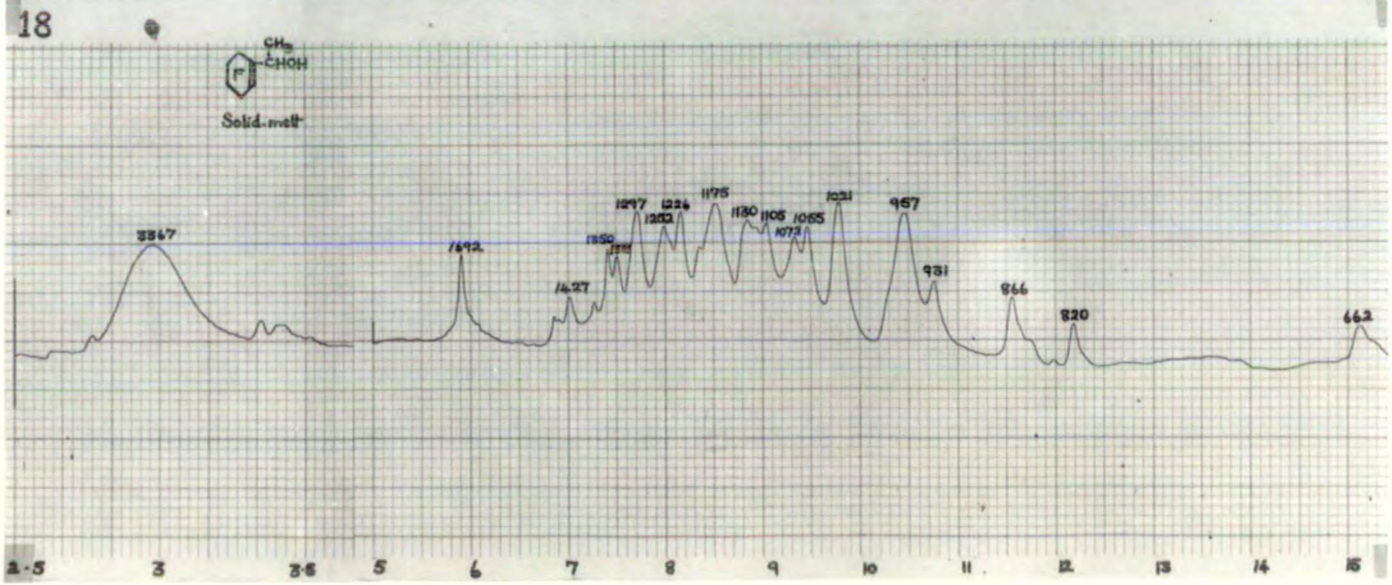
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CHOH
F
Solid-melt
3367
1692
1427
1350
1297
1252
1226
1175
1130
1105
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1065
1031
957
931
866
820
662
2·5
3
3·5
5
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9
10
11
12
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14
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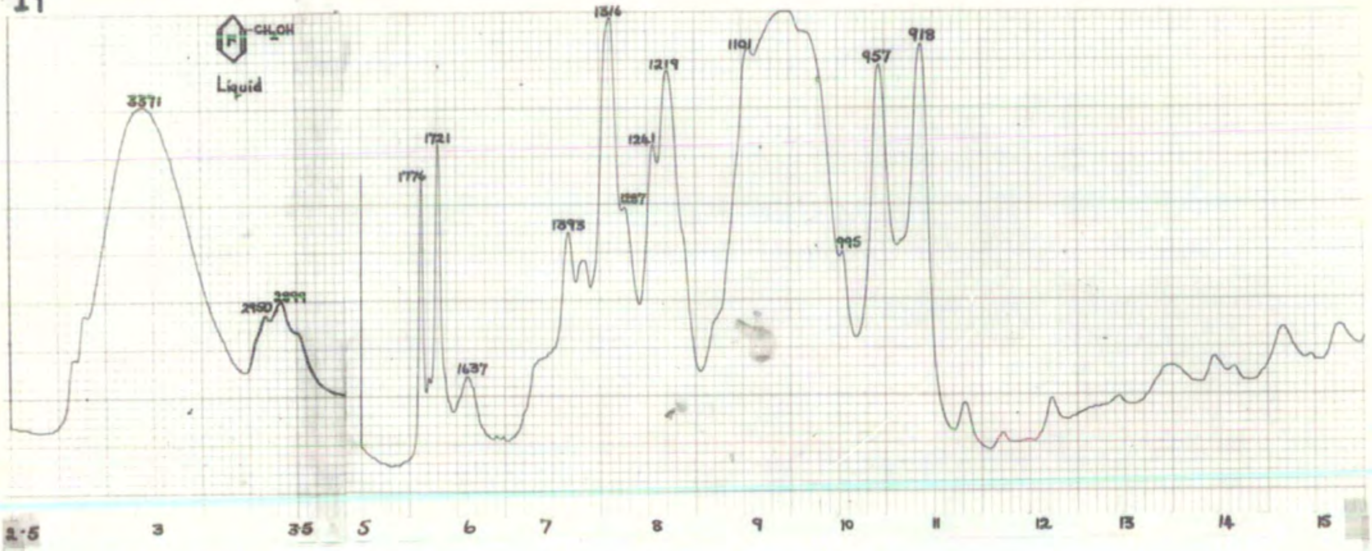
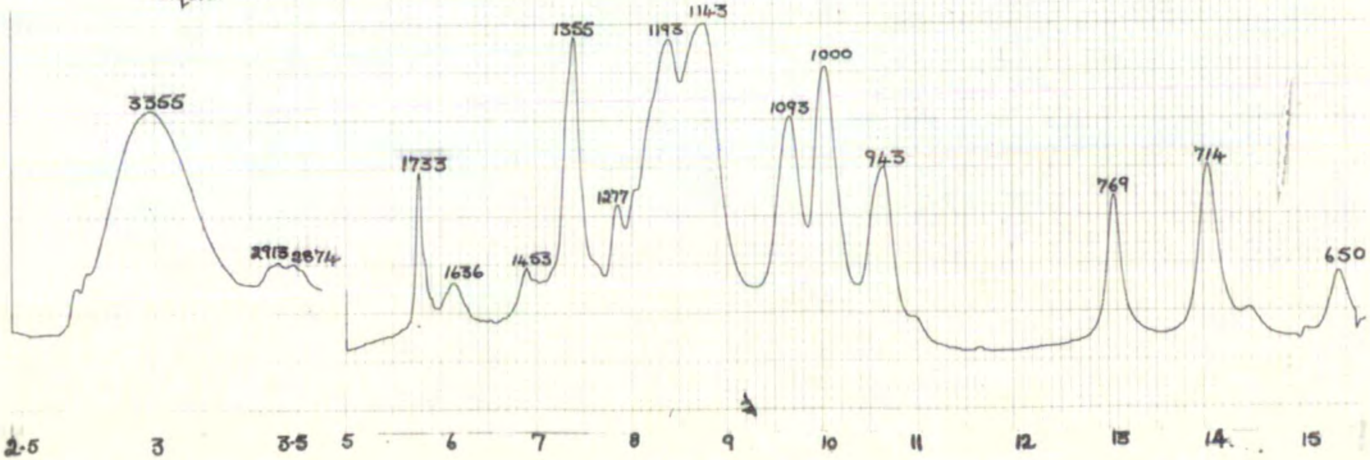
19



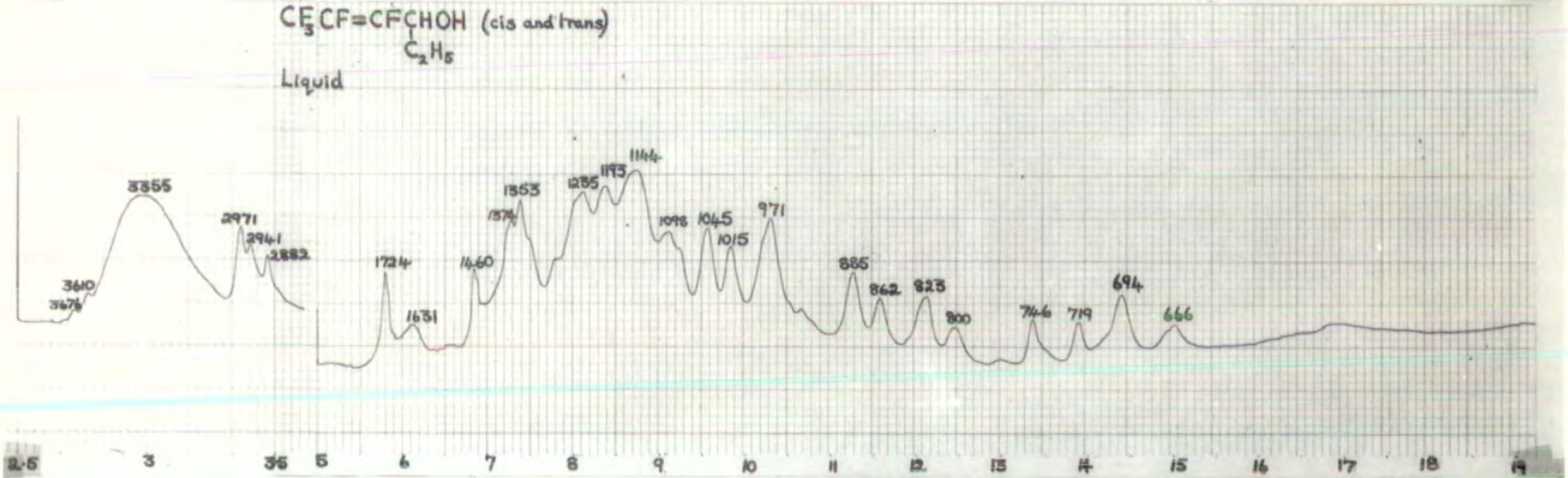
20

CF$_3$CF=CFCH$_2$OH

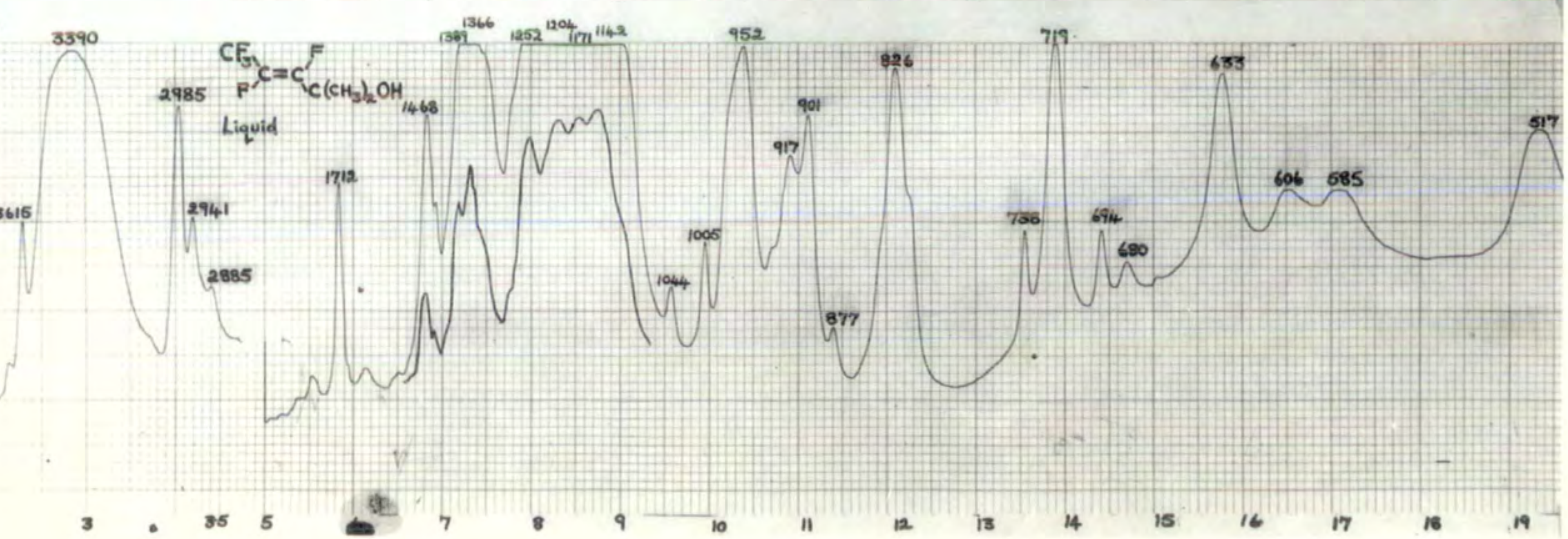
Liquid



21


$CF_3CF=CFCH(C_2H_5)OH$ (cis and trans)
Liquid
3676
3610
3355
2971
2941
2882
1724
1631
1460
1374
1353
1285
1193
1144
1098
1045
1015
971
885
862
823
800
746
719
694
666
2·5
3
3·5
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19

22


$CF_3(F)C=C(F)C(CH_3)_2OH$
Liquid
3615
3390
2985
2941
2885
1712
1468
1389
1366
1252
1204
1171
1142
1044
1005
952
917
901
877
826
738
719
694
680
633
606
585
517
2·5
3
3·5
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7
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9
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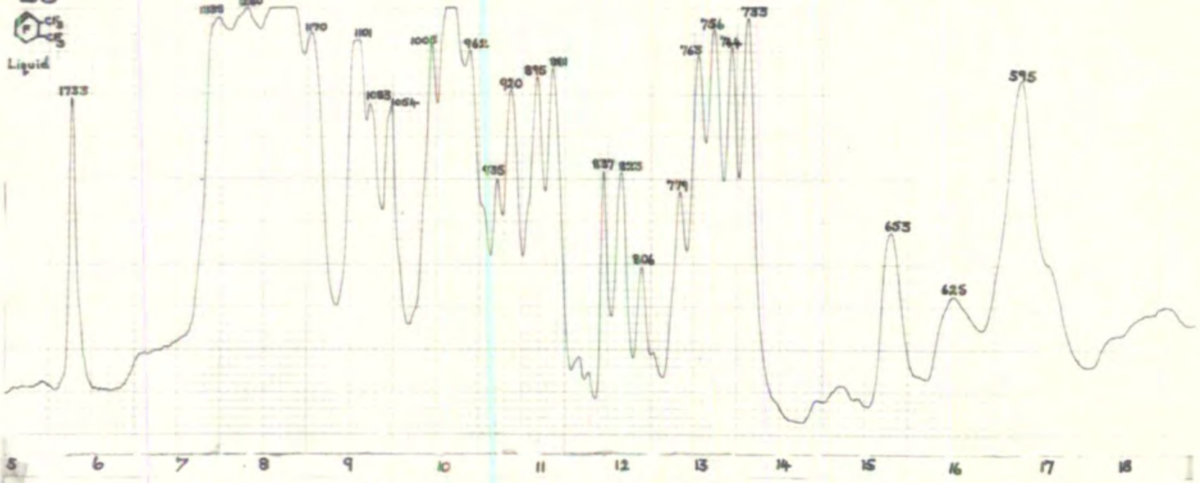
17
18
19

23


F
CF3
CF3
Liquid
1733
1338
1280
1170
1101
1083
1054
1005
962
935
920
895
881
837
823
806
779
763
756
744
733
653
625
595
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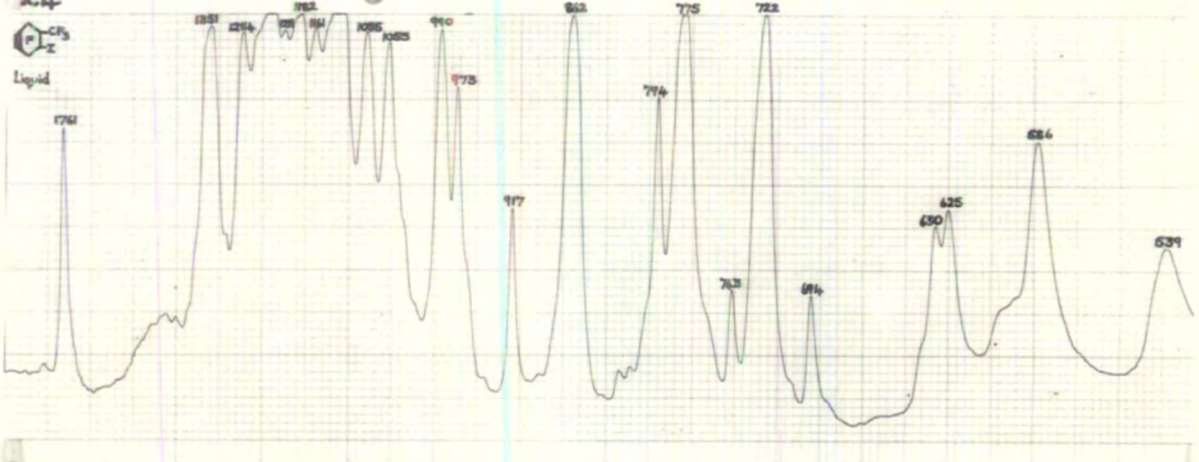
24


F
CF3
I
Liquid
1761
1351
1264
1211
1182
1161
1096
1065
990
973
917
862
774
775
743
722
694
630
625
586
539
5
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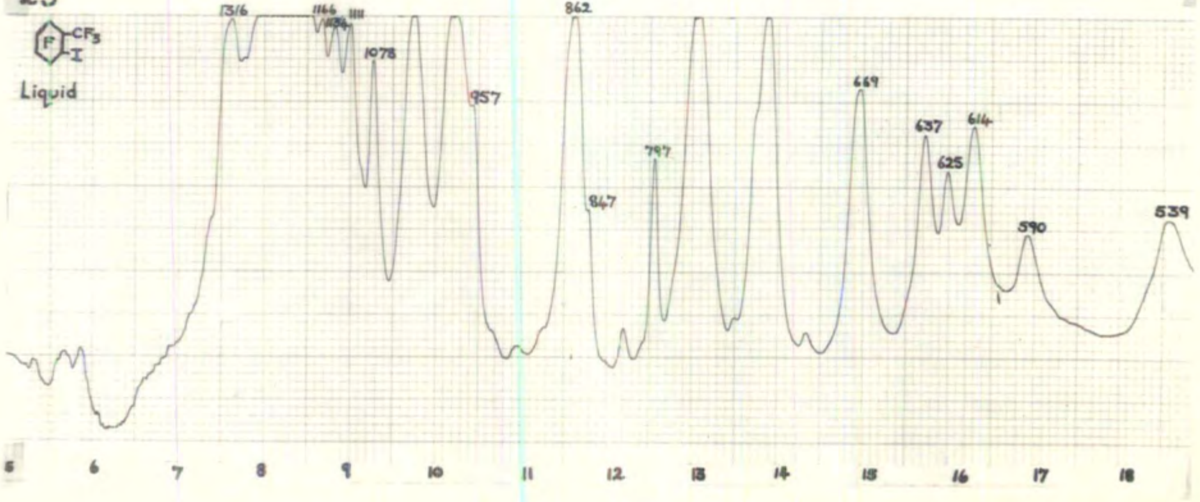
25


F
CF3
I
Liquid
1316
1166
1134
1111
1078
957
862
847
797
669
637
625
614
590
539
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