Durham University

Durham E-Theses

Some free radical additions to polyfluorobut-2-enes

Palmer, Anthony James

How to cite:

Palmer, Anthony James (1967) *Some free radical additions to polyfluorobut-2-enes*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/8565/

Use policy

The full-text may be used and/or reproduced, and given to third parties in any format or medium, without prior permission or charge, for personal research or study, educational, or not-for-profit purposes provided that:

- a full bibliographic reference is made to the original source
- a link is made to the metadata record in Durham E-Theses
- the full-text is not changed in any way

The full-text must not be sold in any format or medium without the formal permission of the copyright holders.

Please consult the full Durham E-Theses policy for further details.

Academic Support Office, The Palatine Centre, Durham University, Stockton Road, Durham, DH1 3LE
e-mail: e-theses.admin@durham.ac.uk Tel: +44 0191 334 6107
http://etheses.dur.ac.uk

UNIVERSITY OF DURHAM

A THESIS

entitled

SOME FREE RADICAL ADDITIONS TO POLYFLUOROBUT-2-ENES

Submitted by

ANTHONY JAMES PALMER, B.Sc.

(Van Mildert College)

A candidate for the degree of

Doctor of Philosophy.

1967

21 SEP 1967
SCIENCE LIBRARY

ACKNOWLEDGEMENTS

I wish to record my thanks to Professor W.K.R. Musgrave and Dr. R.D. Chambers for their continual help and encouragement during their supervision of this work.

I should also like to thank the Science Research Council for the award of a Research Studentship, Drs. D.T. Clark and J.W. Emsley for helpful discussions and the many technical and laboratory staff of the Chemistry Department for their considerable help and co-operation.

MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1964 and July 1967. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

SUMMARY

Pure geometrical isomers of octafluorobut-2-ene have been prepared by the dehydrobromination of pure diastereomers of the hydrogen bromide adduct 2H-3-bromooctafluorobutane, using aqueous potassium hydroxide.

$$CF_3CF{=}CFCF_3 \xrightarrow[\text{u.v.}]{HBr} \underset{\substack{\text{Separable}\\ \text{diastereomers(V.P.C.)}}}{CF_3CHFCFBrCF_3} \xrightarrow{KOH} CF_3CF{=}CFCF_3$$

A reinvestigation of the reaction between hexachlorobutadiene and potassium fluoride in N-methyl-2-pyrrolidone solvent has shown that the product is almost pure ($>$ 95%) trans-2H-heptafluorobut-2-ene.

$$CCl_2{=}CCl{-}CCl{=}CCl_2 \xrightarrow[200^{o}]{KF} CF_3CH{=}CFCF_3 \quad \text{(Trans)}$$

The free radical additions of both chlorine and bromine to trans-2H-heptafluorobut-2-ene have been found to be stereoselective one diastereomer of each of the products, 2H-2,3-dichloroheptafluorobutane and 2H-2,3-dibromoheptafluorobutane, being formed preferentially.

$$\underset{\text{Trans}}{CF_3CH{=}CFCF_3} + X_2 \xrightarrow{\text{u.v.}} \underset{\text{Separable diastereomers(V.P.C.)}}{CF_3CHXCFXCF_3} \quad (X = Cl,Br)$$

Dehydrohalogenation of pure diastereomers of these adducts with aqueous potassium hydroxide has given pure geometrical isomers of 2-chloroheptafluorobut-2-ene and 2-bromoheptafluorobut-2-ene.

$$CF_3CHXCFXCF_3 \xrightarrow{KOH} CF_3CX{=}CFCF_3 \quad (X = Cl, Br)$$

Dechlorination of pure diastereomeric forms of 2H-2,3-dichloroheptafluorobutane using zinc dust in methylated spirits gave both cis - and trans-2H-heptafluorobut-2-ene, the latter being formed in excess in each case.

$$CF_3CHClCFClCF_3 \xrightarrow[Zn/EtOH]{} CF_3CH{=}CFCF_3$$

Cis and Trans

The free radical additions of some organic molecules to octafluorobut-2-ene, and 2H-, 2-chloro-, and 2-bromo-heptafluorobut-2-ene have been studied using γ-radiation or benzoyl peroxide for initiation. The addition of alcohols yielded the expected fluorine-containing alcohols.

e.g. $$CF_3CF{=}CFCF_3 + RCH_2OH \longrightarrow CF_3CHFCF(CF_3)CHOHR$$

$$(R = H,\ CH_3,\ C_2H_5)$$

Addition of methanol to 2-chloroheptafluorobut-2-ene gave only 3-chloro-2,4,4,4-tetrafluoro-(2-trifluoromethyl)-butan-1-ol, $CF_3CHClCF(CF_3)CH_2OH$. Similarly addition to 2-bromoheptafluorobut-2-ene appeared to take

place in one direction only, yielding the equivalent product.

$$CF_3CX{=}CFCF_3 + CH_3OH \longrightarrow CF_3CHXCF(CF_3)CH_2OH$$

$$(X = Cl, Br)$$

Addition of methanol to 2H-heptafluorobut-2-ene gave both 3,4,4,4-tetrafluoro-(2-trifluoromethyl)-butan-1-ol and 2,4,4,4-tetrafluoro-(2-trifluoromethyl)-butan-1-ol.

$$CF_3CH{=}CFCF_3 + CH_3OH \longrightarrow CF_3CHFCH(CF_3)CH_2OH$$
$$+ CF_3CH_2CF(CF_3)CH_2OH$$

The free radical addition of aldehydes to the polyfluorobut-2-enes yielded the expected fluoroketones, and in the addition of acetaldehyde to the unsymmetrical olefins the orientation of addition was similar to that of methanol.

e.g. $$CF_3CF{=}CFCF_3 + RCHO \longrightarrow CF_3CHFCF(CF_3)COR$$

$$(R = CH_3,\ C_2H_5)$$

The addition of methanethiol to octafluorobut-2-ene and 2H-heptafluorobut-2-ene gave fluorine containing thio-ethers. Only the product resulting from radical attack at the 2-position was definitely characterised in the case of the latter olefin.

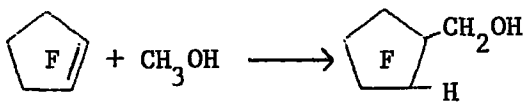
$$CF_3CF{=}CFCF_3 + CH_3SH \longrightarrow CF_3CHFCF(CF_3)SCH_3$$

$$CF_3CH{=}CFCF_3 + CH_3SH \longrightarrow CF_3CHFCH(CF_3)SCH_3$$

The major product from the addition of ethyl acetate to octafluorobut-2-ene was 2,3,4,4,4-pentafluoro-(1-methyl)-(2-trifluoromethyl)-butyl acetate, resulting from the cleavage of a secondary hydrogen atom in the ethyl group of the ester.

$$CF_3CF{=}CFCF_3 + CH_3COOC_2H_5 \longrightarrow CF_3CHFCF(CF_3)CH(CH_3)OCOCH_3$$

Methanol has been added to octafluorocyclopentene giving the cis and trans forms of 2H-octafluorocyclopentylmethanol.



The free radical addition of methanol, aldehydes and methanethiol to pure geometrical isomers of some of the polyfluorobut-2-enes using γ-ray initiation has been investigated. In all cases the two diastereomeric forms of the adducts were produced in the same proportions from either isomer of the olefin, indicating that inversion of the intermediate radicals preceeds the displacement step. The aldehydes showed the greatest stereoselectivity of addition. The temperature of the reaction appears to have only a minor effect on the proportions of the diastereomers of the adducts produced in the addition of methanol and acetaldehyde to 2-chloroheptafluorobut-2-ene. The adducts resulting from the addition of ethanol, n-propanol and

ethyl acetate have three asymmetric centres and all four diastereomeric forms were produced when these addenda were added to trans-octafluorobut-2-ene.

An initial attempt to assign the structures of the diastereomers of the adduct resulting from the addition of acetaldehyde to octafluorobut-2-ene $CF_3CHFCF(CF_3)COCH_3$, by the scheme below was unsuccessful.

$$CF_3CHFCF(CF_3)COCH_3 \xrightarrow[\text{Anhyd.HF}]{SF_4} CF_3CHFCF(CF_3)CF_2CH_3 \xrightarrow{-HF} CF_3CF{=}C(CF_3)CF_2CH_3$$

CONTENTS

Page

CHAPTER 1.

INTRODUCTION PART 1.

General History of Free Radical Addition Reactions with Reference to Fluoroölefins.

1. Early History of Free Radical Addition Reactions 1

2. Types of Molecules which Undergo Addition

A. Formation of Carbon-Carbon Bonds 3

B. Formation of Carbon-Hetero Atom Bonds 5

3. Mechanism of Radical Addition Processes 6

4. Effect of the Structure of the Olefin and Addend 8

5. Processes Competing with Radical Addition 16

A. Telomer Formation 16

B. Allylic Attack 18

C. Rearrangements 19

6. Orientation of Addition 20

7. Methods of Initiation 25

8. Aldehyde Additions 26

9. Alcohol Additions 31

10. Ester and Acid Additions 35

11. Thiol Additions 37

12. Other Additions 39

Page

CHAPTER 2.

INTRODUCTION PART 2.

The Stereochemistry of Free Radical Addition Reactions.

1. Introduction 40

2. Addition of Hydrogen Bromide 40

3. Addition of Reagents Containing Sulphur 62

4. Addition of Polyhalomethanes 70

5. Addition of Bromine and Iodine 72

6. Other Additions and Conclusion 74

CHAPTER 3.

DISCUSSION OF EXPERIMENTAL WORK PART 1.

Preparation of Pure Geometrical Isomers of Octafluorobut-2-ene and 2H-, 2-Chloro-, and 2-Bromoheptafluorobut-2-ene.

1. Introduction 77

2. Separation of Cis and Trans Isomers of Octafluorobut-2-ene 78

3. Preparation of Trans-2H-Heptafluorobut-2-ene 85

4. Preparation of 2-Chloroheptafluorobut-2-ene 91

5. Preparation of 2-Bromoheptafluorobut-2-ene 97

6. Dechlorination of 2H-2,3-Dichloroheptafluorobutane 100

Page

CHAPTER 4.

DISCUSSION OF EXPERIMENTAL WORK PART 2.

Stereochemical Aspects of the Free Radical Addition of Some Organic Molecules to Polyfluorobut-2-enes

1. Introduction 106

2. Reaction Conditions and Yields 108

a. Alcohol Additions 108

b. Aldehyde Additions 114

c. Thiol Additions 118

d. Addition of Ethyl Acetate to Octafluorobut-2-ene 119

3. Orientation of Addition 121

4. Addition of Methanol to Octafluorocyclopentene 126

5. Stereochemistry of Addition 127

a. Alcohol Additions 128

b. Aldehyde Additions 132

c. Addition of Methanethiol 135

d. Addition of Ethyl Acetate to Trans-Octafluorobut-2-ene 137

6. Attempted Determination of the Structures of the Diastereomers of the Adduct of Acetaldehyde and Octafluorobut-2-ene 137

Page

CHAPTER 5.

EXPERIMENTAL WORK

Part 1. Preparation of Polyfluorobut-2-enes

Addition of Hydrogen Bromide to Octafluorobut-2-ene (Cis-Trans Mixture) 141

Preparation of Trans-2H-Heptafluorobut-2-ene 142

Addition of Halogens to 2H-Heptafluorobut-2-ene

Chlorine 143

Bromine 144

Dehydrohalogenation Reactions 145

2H-3-Bromoöctafluorobutane 146

2H-2,3-Dichloroheptafluorobutane 146

2H-2,3-Dibromoheptafluorobutane 148

Dechlorination of 2H-2,3-Dichloroheptafluorobutane 149

Part 2. Free Radical Additions of Organic Molecules to Fluoroölefins

Alcohol Additions.

Additions to Octafluorobut-2-ene (Cis-Trans Mixture)

Methanol 150

Ethanol 151

n-Propanol 152

Addition of Methanol to Trans-2H-Heptafluorobut-2-ene 154

Page

Addition of Methanol to 2-Chloroheptafluorobut-2-ene (Cis-Trans Mixture) 155

Addition of Methanol to 2-Bromoheptafluorobut-2-ene (Cis-Trans Mixture) 156

Addition of Methanol to Octafluorocyclopentene 156

Aldehyde Additions.

Additions to Octafluorobut-2-ene (Cis-Trans Mixture)

Acetaldehyde 157

Propionaldehyde 158

Addition of Acetaldehyde to Trans-2H-Heptafluorobut-2-ene 159

Addition of Acetaldehyde to 2-Chloroheptafluorobut-2-ene (Cis-Trans Mixture) 160

Addition of Acetaldehyde to 2-Bromoheptafluorobut-2-ene (Cis-Trans Mixture) 161

Thiol Additions.

Addition of Methanethiol to Octafluorobut-2-ene (Cis-Trans Mixture) 162

Addition of Methanethiol to Trans-2H-Heptafluorobut-2-ene 163

Ester Addition.

Addition of Ethyl Acetate to Octafluorobut-2-ene (Cis-Trans Mixture) 164

Page

Part 3. γ-Ray Initiated Additions of Organic Molecules to Pure Geometrical Isomers of the Polyfluorobut-2-enes 165

Addition of Hydrogen Bromide to Octafluorobut-2-ene (U.V. Initiation) 168

Part 4. Reactions on the Adducts

Reaction of $CF_3CHFCF(CF_3)COCH_3$ with Sulphur Tetrafluoride 169

Attempted Dehydrofluorination of $CF_3CHFCF(CF_3)CF_2CH_3$ 170

Reaction of $CF_3CHFCF(CF_3)COCH_3$ with Potassium Hydroxide in Di-n-butyl Ether 171

Part 5. Source Dosimetry 172

Appendix 1. N.M.R. Data 176

Appendix 2. Infrared Spectra 188

Future Work 206

References 207

CHAPTER 1.

INTRODUCTION PART 1.

GENERAL HISTORY OF FREE RADICAL ADDITION REACTIONS WITH REFERENCE TO FLUOROOLEFINS.

1. Early History of Free Radical Addition Reactions.

Early work in the field of free radical additions to olefins was concerned with the addition of hydrogen bromide, thiols, thio acids, and bisulphites. In 1928 Ashworth and Burkhardt, repeating the early work of Posner who first reported the anti-Markownikoff addition of thiophenol to styrene[1], noted that exposure to sunlight increased the rate of addition and that piperidine retarded it[2].

$$C_6H_5SH + C_6H_5CH{=}CH_2 \longrightarrow C_6H_5SCH_2CH_2C_6H_5$$

This was followed by Kharasch and Mayo's report in 1933 that oxygen and peroxides affected the direction of addition of hydrogen bromide to allyl bromide[3-5]

$$CH_2{=}CHCH_2Br + HBr \longrightarrow CH_3CHBrCH_2Br$$ Ionic addition product.

$$CH_2{=}CHCH_2Br + HBr \longrightarrow CH_2BrCH_2CH_2Br$$ 'Abnormal product'

Oxygen or peroxides present.

Previous to this discovery many hypotheses were current regarding the factors which controlled the direction of addition of hydrogen bromide to olefins.

Subsequent work by Kharasch and co-workers, and others, demonstrated that oxidising agents also determine the direction of addition of various addenda to a large number of ethylene derivatives, and this early work was comprehensively reviewed by Mayo and Walling

21 SEP 1967
SECTION LIBRARY

in 1940[6] and from a different viewpoint by Smith[7-9]. The 'abnormal' addition of hydrogen bromide was formulated in terms of the presently accepted chain mechanism involving bromine atoms simultaneously and independently by Kharasch et al.[10] and Hey and Waters[11], though the latter did not give details.

$$HBr + O_2 \longrightarrow H\text{-}O\text{-}O\bullet + Br\bullet$$

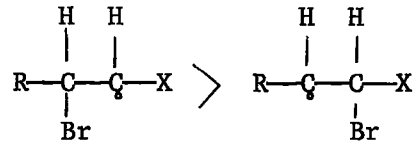
$$RCH{=}CH_2 + Br\bullet \longrightarrow R\dot{C}HCH_2Br$$

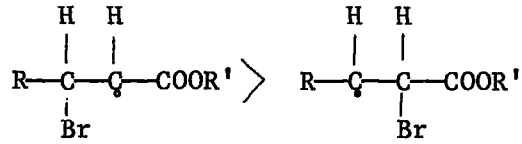
$$R\dot{C}HCH_2Br + HBr \longrightarrow RCH_2CH_2Br + Br\bullet$$

Kharasch and co-workers also proposed similar mechanisms for the additions of thiols[12] and bisulphites[13], though in 1934 Burkhardt had mentioned that the free radical addition of thiophenol to styrene might involve a free radical chain type of reaction[14]. This mechanism was soon accepted over others put forward at the time to account for the effect of oxidising agents on the addition of hydrogen bromide to olefins.

Several theories were put forward to account for the orientation of addition, but the idea that the point of attack by the bromine atom is principally determined by the relative stabilities of the two bromoalkyl radicals which may be formed, which is now accepted was put forward by Mayo and Walling in their review of 1940[6]. The following orders of radical stability were proposed.

Radicals from hydrocarbons: tertiary $>$ secondary $>$ primary.

Radicals from vinyl-type halides: 

Radicals from acids, esters: 

(Radical stability is intended in the sense of a higher heat of formation, with no reference to the mean life of the radical).

2. Types of Molecules which Undergo Addition.

A. Formation of Carbon-Carbon Bonds.

The first examples of free radical addition reactions resulting in the formation of new carbon-carbon bonds was the report by Kharasch and co-workers in 1945 that carbon tetrachloride and chloroform reacted with oct-1-ene to give 1,1,1,3-tetrachlorononane and 1,1,1,-trichlorononane respectively[15]. This was later followed by reports that other classes of compounds also added to olefins by a free radical chain mechanism to form new carbon-carbon bonds and these and the addition products are listed in table 1. In the case of carbon tetrachloride[16] and some of these other compounds it had previously been noted that their presence lowered the degree of polymerization of various olefins. In addition to the work with simple alkenes, addition reactions have been performed with unsaturated compounds containing functional groups e.g. vinyl esters, leading to the formation of di- or

TABLE 1. Products from Free Radical Additions to Olefins involving the Formation of Carbon-Carbon Bonds.[17]

Class	Products
Polyhalomethanes *	Halogenated hydrocarbons
Aldehydes	Ketones
Alcohols	
Primary	Secondary alcohols
Secondary	Tertiary alcohols
Methanol	Primary alcohols
Amines	Amines alkylated on the α-carbon atom
Esters (and other acid derivatives)	α-Alkyl esters (and other acid derivatives)
Formate esters	Monocarboxylic esters
Ethers	Ethers alkylated on the α-carbon atom

* Both C-H and C-X (X = Cl, Br, I) bond rupture may occur.

poly- functional addition products. In many of these cases high yields of the adducts can be attributed to electronic effects.

B. Formation of Carbon-Hetero Atom Bonds.

The formation of carbon-hetero atom bonds by free radical addition to carbon-carbon multiple bonds is an important synthetic route and these reactions have received wide investigation. The reactions of thiols and hydrogen bromide have been extensively studied, the stereochemistry of the addition of these compounds being the subject of much research. Other sulphur compounds producing carbon-sulphur bonds by free radical addition include hydrogen sulphide, bisulphite ion, and sulphonyl and sulphuryl halides, while the addition of sulphenyl chlorides, sulphur chloride pentafluoride and disulphides have also been reported.

Carbon-silicon and carbon-geramnium bonds may be formed by the addition of silanes and germanes, while carbon-phosphorus bonds result from the addition of compounds containing P-H bonds and other phosphorus derivatives. Also the additions of dinitrogen tetroxide, nitryl chloride, and dinitrogen tetroxide- halogen mixtures have resulted in the formation of carbon-nitrogen bonds. Very few additions of hydrogen chloride have been demonstrated while scattered reports of the formation of carbon-selenium, carbon-oxygen, and carbon-tin bonds by this mechanism have appeared. This field has been comprehensively reviewed by Stacey and Harris[18].

3. Mechanism of Radical Addition Processes.

The overall process by which a molecule AB adds across a double bond by a free radical mechanism to yield a 1:1 adduct (equation A) involves a chain reaction as indicated below[17].

$$A\text{-}B + RCH{=}CH_2 \longrightarrow RCHBCH_2A \qquad (A)$$

$$A\text{-}B \longrightarrow A^{\bullet} + B^{\bullet} \qquad \text{Initiation.}$$

$$A^{\bullet} + RCH{=}CH_2 \longrightarrow R\dot{C}H\text{-}CH_2A \qquad \text{Propagation} \qquad \text{(Addition)}$$

$$R\dot{C}H\text{-}CH_2A + A\text{-}B \longrightarrow RCHBCH_2A + A^{\bullet} \qquad \text{Transfer} \qquad \text{(Displacement)}$$

$$\left.\begin{array}{r} 2A^{\bullet} \longrightarrow A\text{-}A \\ 2R\dot{C}H\text{-}CH_2A \longrightarrow ACH_2CH(R)CH(R)CH_2A \\ A^{\bullet} + ACH_2\dot{C}HR \longrightarrow ACH_2CHAR \end{array}\right\} \text{Termination}$$

The initiation step to yield radical A• (B• is usually hydrogen or halogen) may take place using a chemical initiator, light or high energy radiation. The addition and displacement steps are important in determining the products since A• is consumed in the first step and regenerated in the second, and in some reactions this cycle may occur many thousands of times for every initiation step. As the chain termination steps merely destroy radicals, no more termination products are produced than the number of chains started and hence the overall result is essentially 1:1 addition i.e. reaction (A). The yield under a given set of experimental conditions however is determined by the

overall reaction rate and the kinetic chain length, (i.e. the number of molecules of product produced for each initiation step) and these depend on all three steps of initiation, addition, and displacement. As the chain termination steps are bimolecular reactions between radicals which always have very high rate constants, the time interval between the initiation and termination of a chain is only of the order of a second. Thus for a large number of addition steps to take place during that time they must be very rapid low activation energy reactions. A consequence of this is that small changes in the structure of the olefin or addend may have large effects on the overall rates and yields[17].

The overall kinetics of these processes may be treated by the usual steady state method[19]. If the addition and displacement steps are symbolized as follows,

$$A\bullet + M \xrightarrow{k_a} M\bullet \qquad (1)$$

$$M\bullet + A\text{-}B \xrightarrow{k_d} P + A\bullet \qquad (2)$$

with three possible termination steps, (either coupling or disproportionation gives the same kinetics).

$$2M\bullet \xrightarrow{k_{t_1}} M\text{-}M \qquad (3)$$

$$A\bullet + M\bullet \xrightarrow{k_{t_{12}}} A\text{-}M \qquad (4)$$

$$2A\bullet \xrightarrow{k_{t_2}} A\text{-}A \qquad (5)$$

Working from this the expression for the overall rate of reaction is complex. However in the cases where there are large excesses of olefin or addend reactions (3) or (5) can be made respectively the sole important termination steps and the expression for the rate of reaction in the first case becomes

$$\frac{-d[M]}{dT} = \frac{-d[AB]}{dT} = k_d[AB](Ri/2k_{t1})^{\frac{1}{2}}$$

while with excess addend the expression is

$$\frac{-d[M]}{dT} = \frac{-d[AB]}{dT} = k_a[M](Ri/2k_{t2})^{\frac{1}{2}}$$

i.e. first order in olefin or addend (Ri is the rate of initiation).

The effect of olefin/addend ratio on the yields of a number of halomethane additions have been investigated by Lewis and Mayo[20], the results of which appear to be quite general. At intermediate ratios termination may involve all three reactions (3, 4 and 5), and the general result is a rather pronounced maximum in yield for a given amount of initiator (i.e. rate of reaction) at a certain olefin/addend ratio. (Generally with a three to four fold excess of addend).

4. Effect of the Structure of the Olefin and Addend.

For both the addition and displacement steps to be rapid the ΔH of the overall reaction (which is usually about -20 K.cal/mole where A• is a hydrocarbon radical) must be suitably divided between the two

steps and the balance must not be so poor that one is significantly endothermic[17]. This balance is determined primarily by the effective resonance energies of the radicals A• and M• involved in the two steps. Resonance stabilization of the double bond also plays a minor role, but this may be neglected in this discussion. Although these two effects are parallel it has been shown from copolymerization studies that a given substituent is more effective at stabilizing a radical than the olefin from which that radical is formed,[21] suggesting that delocalization of an unpaired electron is easier than one forming a double bond.

In the addition step the resonance energy of A• is lost and that of M• is gained and hence if the radical A• is highly stabilized the exothermicity of the process is decreased, while it is increased by substituents on the olefins leading to a highly stabilized radical M• In the displacement step the resonance energy of M• is lost and that of A• is gained and hence the opposite situation results.

The ΔH's of the individual steps may be calculated as the difference between the energies of the bonds broken and formed during the reactions. In many cases it is thus possible to predict circumstances under which additions may or may not be possible. A series of such ΔH's for radical additions to ethylene derived from bond dissociation data are listed in table 2. The assumption is made that the β-substituent has a negligible effect on the resonance

stabilization of the ethyl radical.

Thus it may be seen with the hydrogen halides that only in the case of hydrogen bromide are both the addition and displacement steps exothermic, and this is the only one which undergoes radical addition by long chain processes though short chains have been observed with hydrogen chloride the next most favourable case.

The effects of changes in olefin structure may be seen by comparing the values in table 2 with those for radical additions to styrene set out in table 3[23]. These may be calculated from the difference in resonance energies of the substituted phenylethyl and ethyl radicals E_R (the same as the resonance energy of the benzyl radical 24.5 K.cal.), and the resonance energy of the vinyl group of styrene E_S (1.5 K.cal from heats of hydrogenation data). Where displacement occurs on halogen, correction must be made for the strengthening of the benzyl halogen bond E_X, obtained from bond dissociation energies of benzyl halides.

$$\Delta H_A(\text{styrene}) = \Delta H_A(\text{ethylene}) - E_R + E_S$$

$$\Delta H_D(\text{styrene}) = \Delta H_D(\text{ethylene}) + E_R - E_X$$

Thus it may be seen that in all cases the exothermicity of the addition step is increased while that of the displacement step is decreased.

The calculations above can give only a general picture of

TABLE 2. Energetics of Chain Steps in Radical Additions to Ethylene.[22]

(In K.cal./mole at 25°C)

B-A	ΔH_A $A\bullet + CH_2{=}CH_2$	ΔH_D* $A\text{-}CH_2CH_2\bullet + B\text{-}A$
H-SH	-16	-8
H-F		37
H-Cl	-26	5
H-Br	-5	-11
H-I	7	-27
Cl-Cl	-26	-19
Br-Br	-5	-17
I-I	7	-13
$H\text{-}COCH_3$	-16	-10
$H\text{-}CCl_3$	-14	-8
$Cl\text{-}CCl_3$	-14	-8

* For reactions in which B = halogen $D(ACH_2CH_2\text{-}B)$ has been taken as $D(CH_3\text{-}B)$ -4 K.cal, 4 K.cal/mole being the difference between $D(CH_3\text{-}H)$ and $D(C_2H_5\text{-}H)$

TABLE 3. Energetics in Chain Steps in Radical Additions to Styrene.[23]

(In K.cal./mole at 25°C)

B-A	ΔH_A $A\bullet + CH_2{=}CH\phi$	ΔH_D $A{-}CH_2{-}CH\phi + B{-}A$
H-SH	-39	16.5
H-Cl	-49	26
H-Br	-28	13.5
H-I	-16	-3.5
Cl-Cl	-49	-6 *
Br-Br	-28	0
I-I	-16	1
$H{-}COCH_3$	-39	14.5
$H{-}CCl_3$	-37	16.5
$Cl{-}CCl_3$	-37	5 *

* These values are probably low.

minimum possible activation energies required for radical processes, and these may be appreciable even for exothermic processes.[23] The rate of reactions may be significantly affected by small changes in activation energy or in pre-exponential factors, and these effects may be discussed in terms of steric or polar factors[17].

Radical additions are affected by steric hindrance particularly in the addition step, and non-terminal olefins generally undergo addition less readily than terminal ones[17]. This has been demonstrated for example by Szwarc and co-workers who have compared the methyl affinities of various substituted olefins and found the order of reactivity below.[24] The radicals were generated by the decomposition of acetyl peroxide, and may either add to the olefin or abstract hydrogen from the solvent (iso-octane) (equations 6 and 7). Chain termination occurs by radical coupling or reaction with a solvent radical (equations 8 and 9).

$$CH_3\cdot + M \longrightarrow CH_3M\cdot \qquad (6)$$

$$CH_3\cdot + \text{iso-}C_8H_{18} \longrightarrow CH_4 + \text{iso-}C_8H_{17}\cdot \qquad (7)$$

$$2CH_3M\cdot \longrightarrow \text{products} \qquad (8)$$

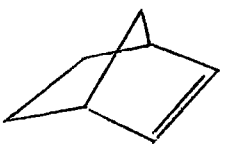
$$CH_3M\cdot + S\cdot \longrightarrow \text{products} \qquad (9)$$

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

It may be seen that substituents on the radical centre increase reactivity due to resonance stabilization, but substituents in the 2-position decrease it. Steric hindrance in the displacement step is apparently less important and not well established[17].

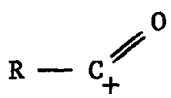
In their copolymerization studies Lewis and Mayo have compared the relative reactivities of various cis and trans isomers[25]. Cis-stilbene is only half as reactive as the trans form this being attributed to steric inhibition of resonance. The greater reactivity of dialkyl fumarates compared with the maleates has been accounted for in a similar manner.

Cadogan and Sadler have found that norbornene (I) is approximately 40 times as reactive as cyclohexene towards thiyl radicals, and have attributed this to relief of conformational strain in the bridged compound[26].

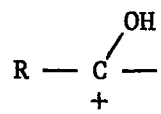


I.

Polar factors play an important role in determining the rates of both the addition and displacement steps in radical reactions.[17] Radicals with electron withdrawing groups, whose corresponding negative ions are reasonably stable add easily to olefins in which the π electrons are readily available. Thus the following order of olefin reactivity has been observed for the addition of the strongly electrophilic trifluoromethyl radical, $CH_2 = CH_2 > CF_2 = CH_2 > CF_2 = CF_2$.[27] Similarly radicals with stable corresponding carbonium ions add well to olefins bearing electron withdrawing groups. Aldehydes and alcohols give rise to radicals of the electron donor type since the corresponding carbonium ions (II) and (III) which would result from complete loss of an electron are fairly stable, and these compounds give high yields with fluoroölefins



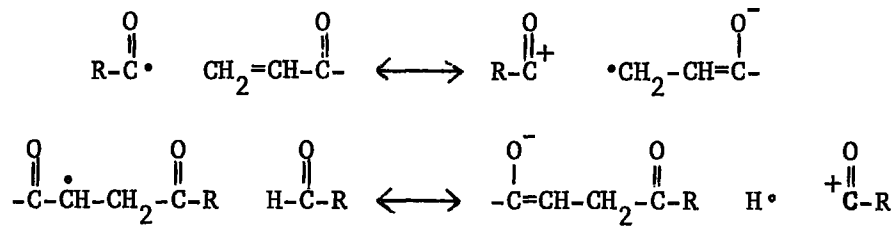
II.



III.

This effect has been interpreted in various ways. It has been suggested that a mutual polarization of the radical and olefin occurs as they approach the transition state[28]. Alternatively, the suggestion has also been put forward that at least in strongly alternating systems, the energy of the transition state may be lowered by the participation of resonance structures in which electron transfer has occurred between the

radical and olefin[29]. For example the easy addition of aldehydes to carbonyl-conjugated olefins may be explained by the transition states of the addition and displacement steps receiving stabilization through structures such as[30]



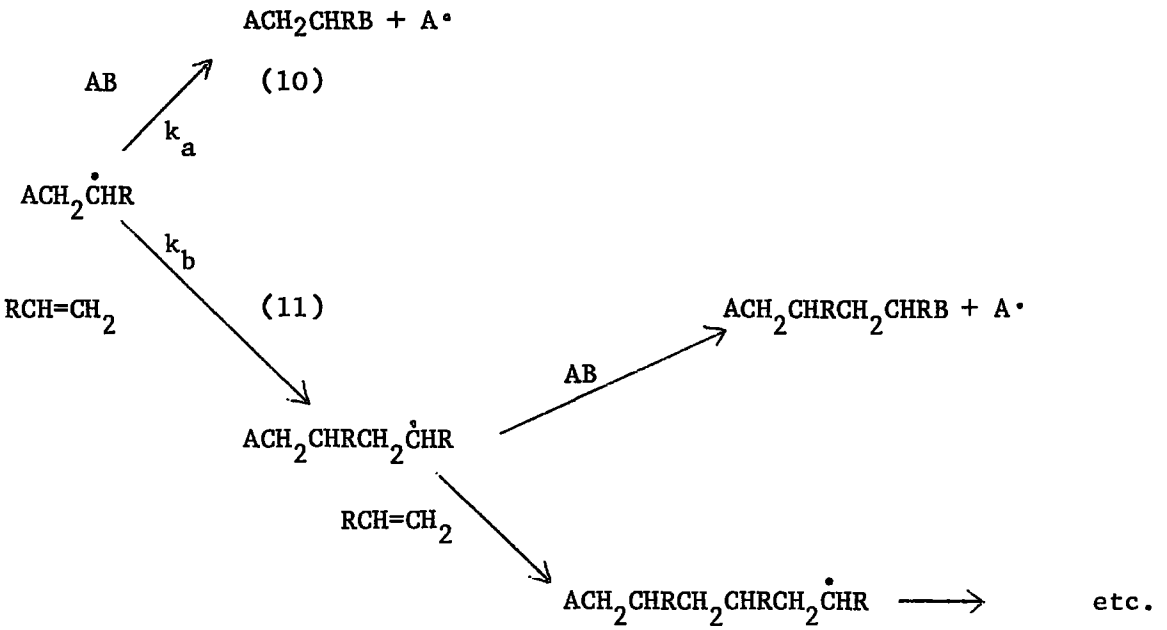
The participating acyl carbonium ion structure is one of considerable stability and has even been shown to exist as a stable entity in sulphuric acid solutions of highly hindered acids[31].

Thus it may be seen that no single factor is entirely responsible for the variation of olefin reactivity to free radical addition, but polar, steric, and other factors all play a part.

5. Processes Competing with Radical Addition

A. Telomer Formation

Polymerization often competes with 1:1 radical addition and the displacement step (reaction 10) whereby the intermediate radical reacts with a molecule of the addend always takes place in competition with another molecule of olefin (reaction 11)[17]. Thus a series of higher products $A(CH_2CHR)_nB$ i.e. telomers may be obtained in addition to the 1:1 adduct.



The transfer constant C, the ratio of the rate constants for reaction of the intermediate radical with AB or with another molecule of olefin gives a quantitative indication of the importance of telomer formation. Thus it may be shown that,

$$\frac{\text{Mole fraction 1:1 product}}{\text{Mole fraction telomers}} = \frac{k_a[AB]}{k_b[\text{olefin}]} = C_1 \frac{[AB]}{[\text{olefin}]}$$

In this case C_1 is the first transfer constant involving reaction of $ACH_2\dot{C}HR$, and a similar expression may be derived for all the other steps.

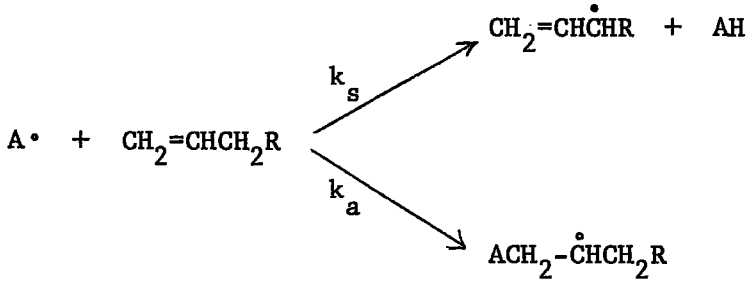
In cases where C > 1 good yields of the 1:1 adduct may be obtained with only a small excess of AB, but if C is very low good yields of the 1:1 adduct can only be obtained by using large excesses of AB.

Generally telomers are undesired by-products but in fluorine chemistry telomerization reactions offer a useful synthetic route to products with structures A(olefin)$_n$B, particularly in the case of the addition of fluorocarbon iodides.[32]

High transfer constants are favoured by substituents in the addend which increase resonance stabilization since this increases the ease of the displacement step. In the case of olefins however substituents which stabilize the intermediate olefin derived radical also increase olefin reactivity but decrease the rate of the displacement step so telomer formation is favoured. Non-terminal olefins show little tendency to telomerize since polymerization is retarded by steric hindrance. Polar effects are also important in determining transfer constants as illustrated by the fact that perfluoroölefins give good yields of 1:1 adducts with alcohols, whereas extensive telomerization may occur with hydrocarbon olefins such as ethylene[17].

B. Allylic Attack

In some cases hydrogen abstraction to form an allyl radical may compete with the addition step.



With non-terminal olefins with very reactive allylic hydrogen atoms, and cyclic olefins, allylic substitution may become quite significant but terminal olefins with reactive double bonds do not usually suffer allylic attack.

Ratios of k_s/k_a have been studied by a number of workers. Szwarc and co-workers have attributed the increased amount of allylic substitution with cis and trans-but-2-ene versus 2-methylpropene in the reaction with methyl radicals (k_s/k_a 0.95, 0.7 and 0.06 respectively) to the decreased rate of addition to a non-terminal double bond,[33] and Huyser has shown that the proportion of allylic attack for a series of olefins increases in the following order oct-1-ene, dec-1-ene $\ll$ pent-2-ene $<$ cyclopentene $<$ cycloheptene $<$ hept-3-ene $\ll$ 4-methylpent-2-ene $<$ cyclohexene.[34] Since the resulting allylic radicals are highly resonance stabilized they may fail to react with a further molecule of addend AB and merely disappear by bimolecular coupling or disproportionation. This results in chain termination, and together with the fact that the reaction competes with the addition step, may result in a reduction in overall yields.[17]

C. Rearrangements

Finally it may be noted that rearrangements may take place in radical addition processes. These involve 1,2 shifts and ring opening, together with some other types of reactions.[17]

6. Orientation of Addition

Except in the cases of symmetrical olefins two products are possible from free radical addition reactions owing to the possibility of attack at either end of the double bond. Addition to both ends of an unsymmetrical olefin has only been reported in comparatively few cases. It has generally been concluded that the most important factor in determining the point of attack is the relative stabilities of the two intermediate radicals formed as was first postulated by Mayo and Walling[6], (tertiary > secondary > primary), while steric and polar factors may become important in some cases.

Hazeldine and Steele studied the free radical addition of trifluoroiodomethane to a variety of olefins of the type $RCH{=}CH_2$, and showed that the direction of addition is independent of the direction of polarization of double bond, since in all cases adducts of the type $RCHICH_2CF_3$ were obtained regardless of whether the polarization is in the direction $\overset{\delta+}{R}CH{=}\overset{\delta-}{C}H_2$ ($R = CH_3Cl$, F), or $\overset{\delta-}{R}CH{=}\overset{\delta+}{C}H_2$ ($R = CF_3$, CN, COOMe).[35] Similarly Cadogan and co-workers found that in the addition of trichloromethyl radicals to substituted trans-stilbenes, the relative amounts of attack at the different ends of the double bond are little affected by polar effects, and are governed by the high stability of the intermediate benzyl-type radicals.[36] From spectroscopic studies of the corresponding iodides, Hazeldine also showed that the stabilizing powers of various substituents on a radical centre vary in the following order

I > Cl > F > H and C_2F_5 > CF_3 > F,[37] and Huang found the following order of stabilizing ability from the addition of bromotrichloromethane and aldehydes to unsymmetrical olefins:

$$Ph > CN \sim CO > COOEt \sim COOH > Me$$ [38,39]

In cases where the difference in stability between two possible intermediate radicals is not great polar factors may become importnat. This may be illustrated by considering some of the data available for hexafluoropropene shown in table 4. Radical attack on this olefin would be expected to occur on the CF_2 group, on the basis of radical stability and also on steric grounds. Nucleophilic attack on hexafluoropropene is exclusively on the CF_2 group[40] showing that the polarization of the double bond is in the direction $CF_3\overset{\delta-}{C}F=\overset{\delta+}{C}F_2$. The position of radical attack is affected by the nucleophilic or electrophilic nature of the attacking radical, as has been shown by Hazeldine and co-workers[40] and Harris and Stacey[41].

The most nucleophilic radical in the series $(CH_3)_3Si\cdot$ > $(CH_3)_2HSi\cdot$ > $(CH_3)H_2Si\cdot$ > $H_3Si\cdot$ or $CH_3S\cdot$ > $CF_3CH_2S\cdot$ > $CF_3S\cdot$ shows the greatest tendency to attack the positive end of the double bond. LaZerte and Koshar[44], and Kisby[45] have shown that in the case of additions of alcohols and aldehydes which yield the strongly nucleophilic α-hydroxyalkyl and acyl radicals, attack occurs exclusively on the CF_2 group as in these cases radical stability, polar, and steric factors reinforce each other. It has also been shown that this occurs in the attack by

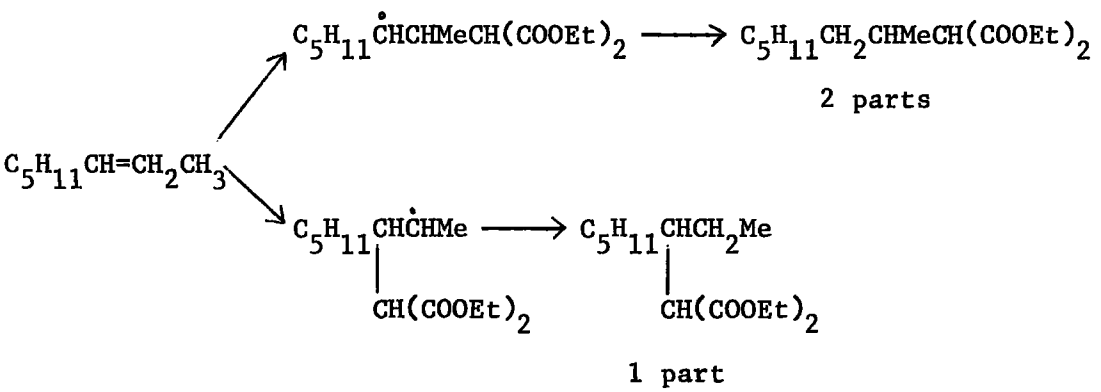
TABLE 4. The Direction of some Radical Additions to Hexafluoropropene.

Radical	Attack % on starred carbon atom $CF_3CF{=}\overset{*}{C}F_2$	$CF_3\overset{*}{C}F{=}CF_2$	Reference
$(CH_3)_3Si\bullet$	96	4	40
$(CH_3)_2HSi\bullet$	95	5	40
$(CH_3)H_2Si\bullet$	76	24	40
$H_3Si\bullet$	60	40	40
$CF_3\bullet$	85	none detected	42
	80	20	40
$CH_3S\bullet$	91	9	41
$CF_3CH_2S\bullet$	70	30	41
$CF_3S\bullet$	45	55	41
$PH_2\bullet$	66	34	40
$Br\bullet$	60	40	43
$\cdot\bullet CH_2OH$	100		44
$CH_3CH_2CH_2\dot{C}O$	100		44
$CH_3\dot{C}HOH$	100		45
$CH_3CH_2\dot{C}HOH$	100		45
$(CH_3)_2\dot{C}OH$	100		45
$CH_3CH_2CH_2\dot{C}HOH$	100		45
$CH_3\dot{C}O$	100		45
$CH_3COO\dot{C}HCH_3$	100		45

the $CH_3COO\dot{C}HCH_3$ radical derived from ethyl acetate[45].

With most fluoroölefins studied so far radical attack has been found to take place exclusively in one direction, but attack at both ends of the molecule has been noted in additions to trifluoroethylene where the difference in stabilities of the intermediate radicals is not great, i.e. $RCFH\dot{C}F_2$ and $RCF_2\dot{C}FH$,[46] and in some other cases.

An example of a reaction where the ratio of the two products has been attributed to steric factors is the addition of diethyl malonate to oct-2-ene, since the two possible intermediate radicals are of similar stability[47].



A new theory regarding the factors controlling the orientation of free radical addition has been put forward by Tedder and Walton[48,49], who have investigated the addition of trichloromethyl radicals to ethylene and some of its derivatives. The reactions were carried out in the gas phase over a wide range of temperatures and the activation energies and Arnhenius parameters were measured, the results of which are summarized on page 24.

Addition to CH_2	log A_1	E_1	Addition to $\dot{C}$	log A_1	E_1
$H_2C{=}CH_2$	5.6	3.2 ± 0.3	$H_2\dot{C}{=}CH_2$	5.6	3.2 ± 0.3
$FHC{=}CH_2$	5.5	3.3 ± 0.2	$FH\dot{C}{=}CH_2$	5.4	5.3 ± 0.2
$F_2C{=}CH_2$	5.6	4.6 ± 0.3	$F_2\dot{C}{=}CH_2$	5.5	8.3 ± 0.5
			$F_2\dot{C}{=}CF_2$	7.1	6.1 ± 0.4

The authors found that except in the case of tetrafluoroethylene log A_1 is constant within experimental error, and hence the rate of the reactions depends on the activation energies. The first column of the table shows that when attack occurs on the CH_2 group of ethylene, vinyl fluoride, and vinylidene fluoride the activation energies show only a small variation but the site of the odd electron varies, whereas for attack on the CFH and CF_2 groups of the latter two olefins there is a vast change in the activation energy but the odd electron is always on a CH_2 group. It has therefore been suggested that for trichloromethyl radicals at least, the rate of addition is determined principally by substituents on the carbon atom attacked and only to a lesser extent by substituents on the carbon atom at which the unpaired electron is sited. Thus the orientation of radical addition is determined principally by the relative strengths of the two possible bonds initially formed. At present assessing the relative strengths of the bonds can only be done in a qualitative manner by examining sites for the odd electron and then assuming that the new bond is formed at the carbon atom which would give

the least stabilized radical. This must lead to exactly the same predictions as the previous theory.

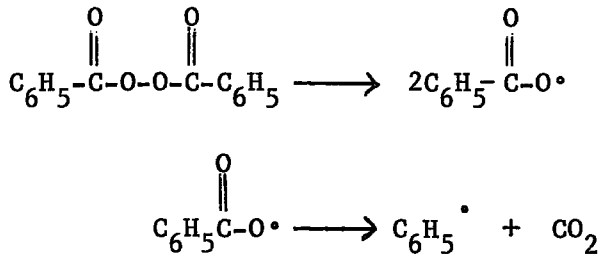
Tedder and Walton also point out that in the first column the change in activation energy is the reverse of that predicted by the old theory (radical stabilization by F), and that the new model can only account for this if polar forces in the transition state are invoked since attack by electrophilic trichloromethyl radicals should be less favourable with fluorine-substituted olefins.

7. Methods of Initiation

Three general methods have been used to initiate free radical addition reactions (1) chemical initiation (2) high energy radiation (3) photoinitiation. Thermal initiation has also been used in some specialized cases[17].

Chemical initiators which have been employed may be divided into two chief types, organic peroxides and azobis(nitriles). Both these types of materials in the absence of any induced reactions decompose thermally into free radicals in a first order reaction.

Benzoyl peroxide has been reported to be a very satisfactory initiator for the addition of alcohols and aldehydes to perfluoroölefins when used in quantities of 0.5-1% by weight of reactants[44,45]. In general the best reaction temperature has been found to be 115°-120°. Benzoyl peroxide is decomposed as follows.



The amount of secondary elimination is dependent on the nature of the reagents with which the benzoyl peroxide may react. Muramatsu and co-workers have used t-butyl perbenzoate to initiate addition reactions of alcohols, aldehydes, and ethers to perfluorocyclobutene[50].

High energy radiation, particularly γ-rays, but also α and β particles and X-rays, have been used to initiate free radical chain reactions. While such radiation mainly strips electrons from organic compounds to form ions, up to approximately 20% of the total energy absorbed may go into homolytic bond cleavage to form radicals[17]. γ-Radiation has been extensively used by Kisby[45], and Muramatsu and co-workers[50-56] in the addition of aldehydes, alcohols, ethers, esters and thiols to fluoroolefins.

Ultraviolet light has principally been used for the addition of hydrogen bromide, thiols, and polyhaloalkanes, together with certain alcohols and amines, but there is always the possibility of photochemical reactions other than the desired process occurring.

8. Aldehyde Additions

Kharasch and co-workers first noted the free radical addition of aldehydes to olefins to yield 1:1 products in 1949[57]. They reported that the highest yields were obtained from the addition of long chain aldehydes to long chain terminal olefins, while telomerization and hydrocarbon

formation by loss of carbon monoxide from the acyl radical were also noted in some cases. Non-terminal hydrocarbon olefins such as cyclohexene do not generally give good yields[57].

Aldehydes add to carbonyl-conjugated olefins in high yields however,[58,59] and LaZerte and Koshar have reported the addition of acetaldehyde to octafluorobut-1-ene, and butanal to hexafluoropropene in yields of 76% and 70% respectively, using benzoyl peroxide as initiator[44].

$$RCHO + RfCF{=}CF_2 \longrightarrow RfCFHCF_2COR$$

(R = alkyl group, Rf = perfluoroalkyl group).

This ease of addition can be attributed to polar factors as the aldehyde and acyl radical act as electron donors, and the transition states of the addition and displacement steps are stabilized in olefins in which the π electron density is reduced.

Kisby has obtained 90% yields in the peroxide initiated addition of acetaldehyde to hexafluoropropene and decafluorocyclohexene, while octafluorocyclohexa-1,4-diene gave a 25% yield of the 1:1 adduct under the same conditions[45]. Muramatsu and Inukai have reported peroxide initiated aldehyde additions to 1,2-dichloro-1,2-difluoroethylene and 1,1-dichloro-2,2-difluoroethylene[60] in 15-40% yields, and also γ-ray initiated additions to 1,2,2-trichloro-1-fluoroethylene[53].

$$RCHO + CFCl{=}CFCl \longrightarrow RCOCFClCFClH$$

$$RCHO + CF_2{=}CCl_2 \longrightarrow RCOCF_2CCl_2H$$

$$RCHO + CFCl{=}CCl_2 \longrightarrow RCOCFClCCl_2H$$

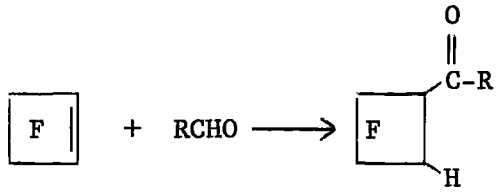
In all additions to unsymmetrical fluoroölefins so far reported in the literature all three factors influencing the orientation of addition, i.e. radical stability, polar and steric factors favour the product formed, and no case of addition at both ends of the double bond has been reported. Additions of 2-methylpropanal to 1,2-dichloro-1,2-difluoroethylene and 1,1-dichloro-2,2-difluoroethylene give 3-methylhalobutanes as the major products in 15% and 26% yields respectively. These are formed by loss of carbon monoxide from the acyl radical followed by a normal chain reaction.

$$\text{i-}C_3H_7\dot{C}O \longrightarrow \text{i-}\dot{C}_3H_7 + CO$$

$$\text{i-}\dot{C}_3H_7 + CF_2{=}CCl_2 \longrightarrow \text{i-}C_3H_7CF_2\dot{C}Cl_2$$

$$\text{i-}C_3H_7CF_2\dot{C}Cl_2 + \text{i-}C_3H_7CHO \longrightarrow \text{i-}C_3H_7CF_2CCl_2H + \text{i-}C_3H_7\dot{C}O$$

Little work has been done on the stereochemistry of aldehyde additions, but the product of the addition of acetaldehyde to decafluorocyclohexene (2H-decafluorocyclohexyl)methyl ketone consists of two isomers one vastly in excess of the other[45]. N.M.R. studies indicated that the major isomer results from cis addition. By contrast the spectrum of the adduct of acetaldehyde and octafluorocyclohexa-1,4-diene, (2H-octafluorocyclohex-4-enyl)methyl ketone, indicates that it consists of both cis and trans forms. Muramatsu and co-workers have reported the following isomer ratios for the addition of aldehydes to perfluorocyclobutene.[50]

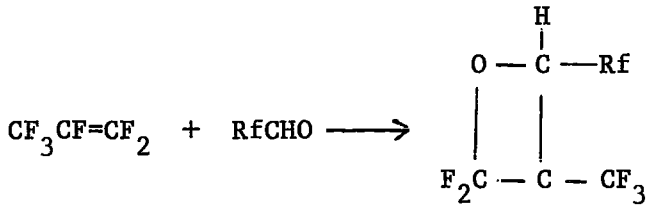


cis and trans

Aldehyde	Molar ratio aldehyde/olefin	Total yield 1:1 adduct	Trans/cis
CH_3CHO	3.04	25.4%	4.0:1
C_2H_5CHO	2.74	62.4%	5.1:1
nC_3H_7CHO	2.37	63.4%	4.8:1

No explanation has been put forward for these results.

Harris and Coffman have reported that the ultraviolet initiated addition of polyfluoroaldehydes to fluoroölefins results in cyclo-addition giving polyfluoroöxetanes rather than the normal addition products[61].

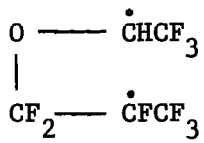


$Rf = CF_3$ Yield 32% cis and trans

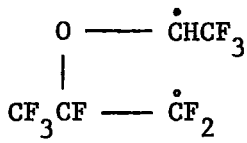
$Rf = H(CF_2)_4$ Yield 59%

Similar reactions were reported for the addition of fluoroketones and fluoroacyl fluorides. These workers also reported that an attempted reaction between perfluorobutyraldehyde and hexafluoropropene using benzoyl peroxide for initiation gave no detectable product and suggested that abstraction of hydrogen from a polyfluoroaldehyde is very much more

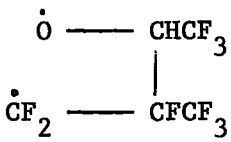
difficult than from an aliphatic aldehyde, thus allowing non-chain cycloaddition to occur rather than ketone formation by a chain reaction. The mechanism for these reactions may be a two step process initiated by the carbonyl compound in a diradical triplet state, as first suggested by Büchi and co-workers[62] who pointed out that this concept is useful in predicting the product by assuming that the intermediate radical is the most stable of those possible. Thus in addition of trifluoroacetaldehyde to hexafluoropropene the most stable intermediate diradical (1) is congruent with the oxetane formed.



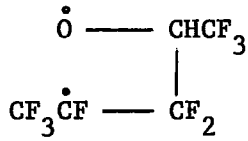
(1)



(2)



(3)



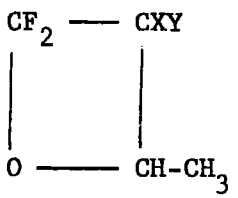
(4)

Harris and Coffman have also suggested that a four-centre concerted mechanism is a possibility for these reactions.

Bissell and Fields obtained both the oxetane and the normal addition compound simultaneously from the ultraviolet irradiation of acetaldehyde and tetrafluoroethylene, chlorotrifluoroethylene and 1,1-dichlorodifluoro-

ethylene in the gas phase[63]. In all cases the ketone was the major product and the structures of it, and the oxetane were those which would be predicted from the principles already discussed.

e.g. $CH_3CHO + CF_2{=}CXY \xrightarrow[\text{gas phase}]{\text{u.v.}} CH_3COCF_2CHXY +$



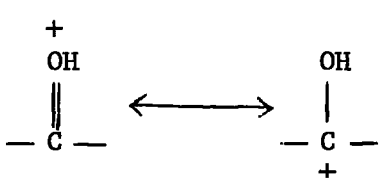
cis and trans

(X = Cl or F, Y = Cl or F).

9. Alcohol Additions

The free radical addition of alcohols to olefins to yield 1:1 adducts was first reported by Urry and co-workers[64] who found that primary and secondary alcohols added to oct-1-ene in the presence of t-butyl peroxide or light. Large excesses of alcohol were necessary owing to the fact that transfer constants are low. Displacement always occurs on a hydrogen attached to the carbon bearing the hydroxyl group hence tertiary alcohols are excluded.

Although the scope of the reaction is rather limited with hydrocarbon olefins, good yields have been reported in the case of fluoroölefins. This effect can be attributed to polar factors since alcohols and the resulting α-hydroxyalkyl radicals behave as electron donors in radical processes, since the corresponding carbonium ion (the conjugate acid of a carbonyl compound) is relatively stable[65].



Methanol and tetrafluoroethylene yield telomers of the type $H(CF_2)_nCH_2OH$ in addition to the 1:1 adduct[66], but LaZerte and Koshar have reported the free radical addition of several alcohols to terminal perfluoroölefins in yields ranging from 55-90% using benzoyl peroxide for initiation[44]. The latter workers also found that methanol added to octafluorobut-2-ene at least as readily as to octafluorobut-1-ene. Kisby reported the addition of various alcohols to hexafluoropropene and has reviewed alcohol addition to fluoroölefins up to 1964[45].

e.g. $RfCF{=}CF_2 + RR'CHOH \longrightarrow RfCFHCF_2CH(OH)RR'$

(Rf = perfluoroalkyl, R and R' = alkyl).

Muramatsu has found the following order of reactivity in his studies of the γ-ray initiated addition of alcohols to 1,1-dichloro-2,2-difluoroethylene and 1,2-dichloro-1,2-difluoroethylene, i-PrOH > n-PrOH, EtOH > MeOH.[51] These results are in agreement with the relative ease of chain transfer found for telomerization reactions with hydrocarbon olefins[67] and can be explained on the grounds of increasing resonance stabilization and hence ease of formation of the α-hydroxyalkyl radicals. Ethanol however gives better yields than propan-1-ol or propan-2-ol in the case of 1-fluoro-1,2,2-trichloroethylene this being attributed to steric hindrance with the large chlorine atoms.[51] All alcohol additions to asymmetric acyclic fluoroolefins reported have resulted in addition to one end of the double bond only.

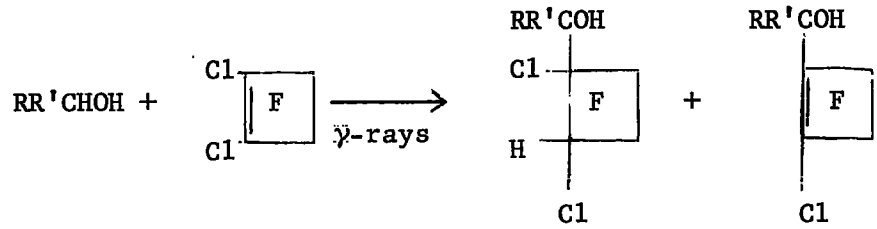
Alcohol additions to cyclic perfluoroölefins also take place in good

yield. Kisby has reacted a series of alcohols with decafluorocyclohexene and has found that the products are mixtures of trans and cis isomers from ^{19}F N.M.R. spectroscopy. Octafluorocyclohexa-1,4-diene yields both the 1:1 and 2:1 adducts with methanol in 68% and 22% yields respectively, while ethanol gives the 1:1 adduct in 56% yield. The presence of both cis and trans isomers of the 1:1 adducts was again shown by ^{19}F N.M.R. spectroscopy[45]. Muramatsu has added four different alcohols to hexafluorocyclobutene and has obtained the following trans and cis isomer ratios[50]

Alcohol	Molar ratio alcohol/olefin	Yield%	Trans/cis
CH_3OH	3.01	84.7	5.0
C_2H_5OH	3.00	69.7	2.6
n-C_3H_7OH	2.99	67.0	1.8
i-C_3H_7OH	3.04	79.9	5.0

Here it is sufficient to note the production of cis and trans isomers and this factor will be dealt with in more detail later.

The radiation induced addition of alcohols to 1,2-dichlorotetrafluorocyclobutene has been reported by Muramatsu and co-workers to yield both the 1:1 adducts and the cyclobutenyl compounds[52].



R = H or CH_3

R' = H, CH_3, or C_2H_5

cis and trans

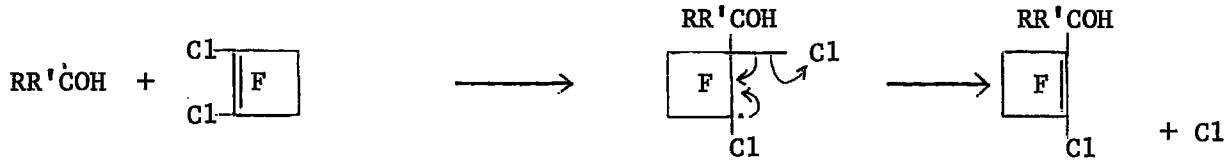
II III

Though the structures of the stereoisomers were not proved, these workers showed by molecular models that when R and R' in (II) are bulky groups steric interference with neighbouring groups is larger in the isomer where the chlorine atoms are trans, and hence suggested that in the table below isomer A is the trans form and isomer B the cis form.[52]

	Composition 1:1 adducts%			
Alcohol	II	III	Isomer A	Isomer B
CH_3OH	57	43	51	49
C_2H_5OH	74	26	33	67
C_2H_5OH	75	25	36	64
nC_3H_7OH	54	46	32	68
nC_3H_7OH	52	48	36	64
$i\text{-}C_3H_7OH$	7	93	7	93
$i\text{-}C_3H_7OH$	7	93	5	95

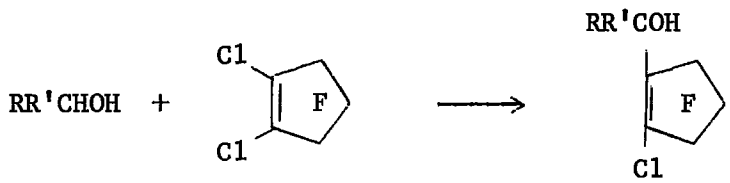
(Where two results have been included these are for different experiments using different times of irradiation).

The dehydrochlorinted adducts are thought to be formed by the mechanism shown below



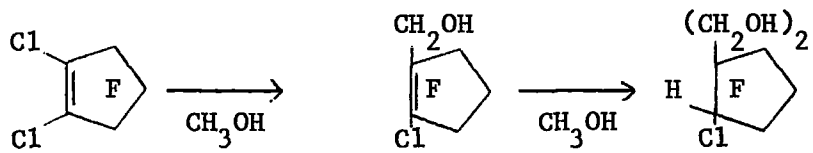
The radical dechlorination reaction competes with the abstraction of hydrogen and hence the more reactive alcohols give a greater proportion of the 1:1 adduct, as illustrated by the difference in the proportions of (II) to (III) between methanol and ethanol. The decrease in the ratio between ethanol and propan-2-ol has been attributed to the steric effect of the alkyl group in the alcohols.[52]

The addition of alcohols to 1,2-dichlorohexafluorocyclopentene gives almost exclusively the corresponding dehydrochlorinated 1:1 adducts



$R = H$ or CH_3 $R' = H, CH_3$ or C_2H_5

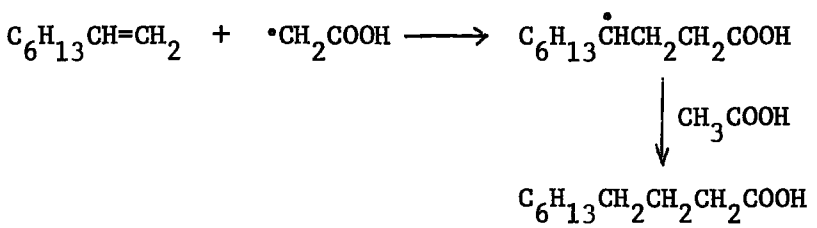
A small amount of what was tentaively identified as 1,1-bis(hydroxymethyl)-2-chloro-3,3,4,4,5,5-hexafluorocyclopentane was reported to be formed in the addition of methanol to 1,2-dichlorohexafluorocyclopentene.[52]



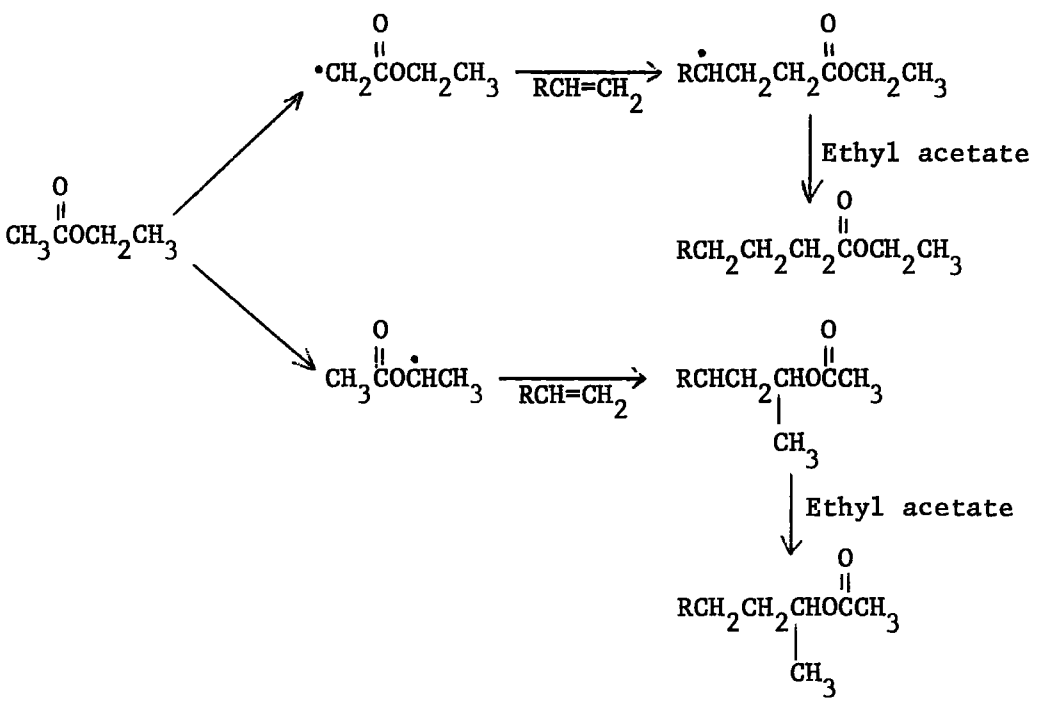
10. <u>Ester and Acid Additions</u>

Rather specialized conditions are required for the free radical

addition of esters and carboxylic acids to olefins. The peroxide induced reaction of acetic acid with ethylene was reported to yield telomers of the type $CH_3(CH_2)_nCOOH$ in 1952[68]. Allen, Cadogan and Hey reported that very high acid/olefin ratios were necessary for the addition of acetic acid to oct-1-ene using initiation by di-t-butyl peroxide[69].



These workers reported similar reactions with acetic anhydride and acetonitrile, while ethyl acetate gives a mixture of products owing to abstraction of an α-hydrogen from the ethyl group of the ester in addition to abstraction from the acyl group[69].



Diethyl malonate, acetylacetone, ethyl acetoacetate, ethyl cyanoacetate and other related compounds also give 1:1 adducts with suitable olefins[47,70]. Abstraction of hydrogen takes place at the methylene groups in these cases. Kharasch and co-workers have reported the addition of bromoesters to olefins in good yield using diacetyl peroxide as initiator. Displacement occurs on a bromine atom, cleavage of this bond being easier than a carbon-hydrogen one[71].

e.g.

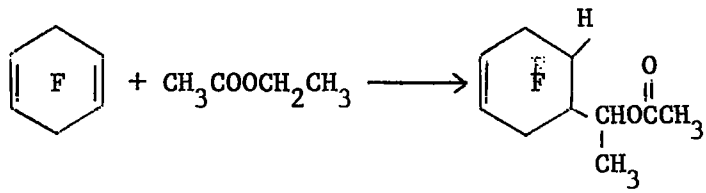
$$\cdot CH_3 + BrCH_2COOC_2H_5 \longrightarrow CH_3Br + \cdot CH_2COOC_2H_5$$

$$\cdot CH_2COOC_2H_5 + n\text{-}C_6H_{13}CH{=}CH_2 \longrightarrow n\text{-}C_6H_{13}\dot{C}HCH_2CH_2COOC_2H_5$$

$$n\text{-}C_6H_{13}\dot{C}HCH_2CH_2COOC_2H_5 + BrCH_2COOC_2H_5 \longrightarrow n\text{-}C_6H_{13}CHBrCH_2CH_2COOC_2H_5 + \cdot CH_2COOC_2H_5$$

There have been few reports of free radical additions of esters to fluoroölefins. Hanford reported the telomerization of tetrafluoroethylene by such reactions,[72,73] while Kisby added ethyl acetate to hexafluoropropene and octafluorocyclohexa-1,4-diene. In both cases displacement occurred on an α-hydrogen atom in the ethyl group of the ester[45].

$$CF_3CF{=}CF_2 + CH_3COOCH_2CH_3 \longrightarrow CF_3CFHCF_2\underset{\underset{CH_3}{|}}{CH}OC(=O)CH_3$$

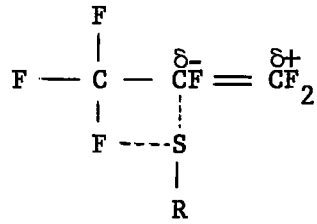


11. Thiol Additions

Although the free radical additions of thiols to hydrocarbon olefins

has received intensive study particularly with regard to the stereochemistry involved, there are few reports of addition to fluoroölefins. Harris and Stacey[41,74] and Muramatsu and co-workers have reported the addition of a variety of thiols to fluoroolefins to yield 1:1 adducts[56]. X-rays, and ultraviolet light have been used to initiate these reactions.

Cleavage of the S-H bond takes place in the case of thiols and the products of addition reactions are thioethers. Owing to the electrophilic nature of the thiyl radical, thiols are less reactive towards fluoro-olefins. This is reflected in the additions CF_3SH, CF_3CH_2SH and CH_3SH to hexafluoropropene, each of which gives two products in which the relative proportions of attack at C1 and C2 can be correlated with the electro-philicities of the radicals as has already been discussed. It has also been suggested that attack at the 2-carbon atom in addition to being favoured on electronic grounds ($CF_3\overset{\delta-}{C}F{=}\overset{\delta+}{C}F_2$), may be assisted by the negative screen afforded by the trifluoromethyl group. Thus in the transition state interaction of the thiyl radical may be envisaged as shown below[41]



In the addition of trifluoromethanethiol and methanethiol to trifluoro-ethylene the proportion of attack on the CFH group, (favoured on radical

stability and polar grounds, $\overset{\delta+}{CF_2}=\overset{\delta-}{CFH}$), is 98% and 75% respectively[41]. Harris and Stacey pointed out that these results could also be explained on steric grounds as a $CF_3S\cdot$ radical would have more difficulty in approaching the CF_2 group, but did not consider that the steric effect is predominant in view of the results obtained with hexafluoropropene.

12. Other Additions

Only additions of the types of molecules which have been used in the present work have been discussed in detail in the previous sections. Free radical additions of several other classes of compounds to fluoroolefins have also been studied however.

Ethers have been reported to react with tetrafluoroethylene[75] and also 1,1-difluoroethylene and hexafluoropropene[76] to yield telomers, and Muramatsu and co-workers have reported the addition of several ethers to cyclic,[55] and acyclic fluoroölefins[54].

The free radical addition of halogens, hydrogen bromide, silanes, phosphines, and other compounds to fluoroölefins have also been extensively studied but this work is beyond the scope of the present discussion.

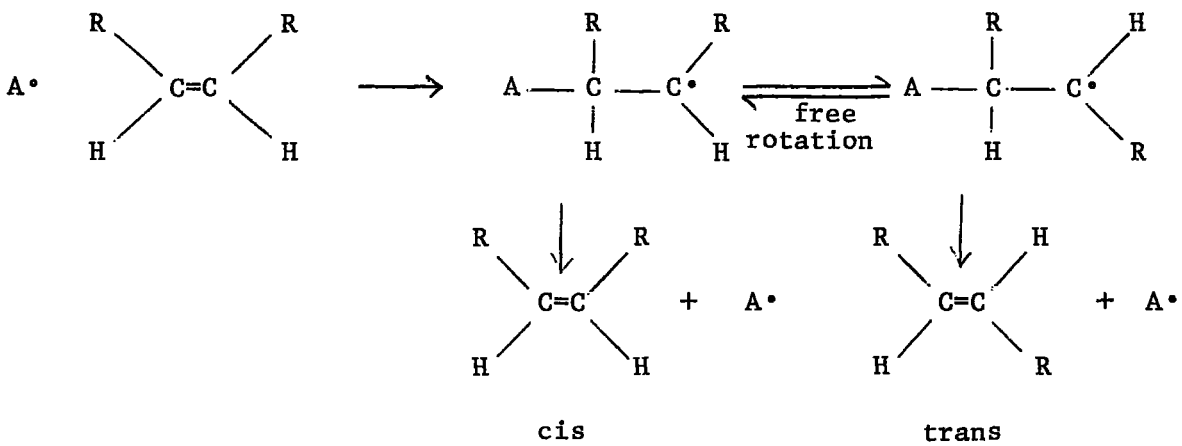
CHAPTER 2.

INTRODUCTION PART 2.

THE STEREOCHEMISTRY OF FREE RADICAL ADDITION REACTIONS.

1. Introduction

Interest in the stereochemistry of free radical addition reactions dates from the early 1950's when the first results of additions to cyclic olefins were reported. Although the stereochemical aspects of results obtained for additions to acyclic olefins have sometimes been obscured by cis-trans isomerization of the olefin, owing to reversible radical addition, these systems have also received attention

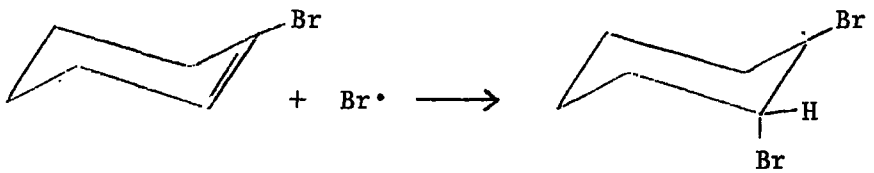


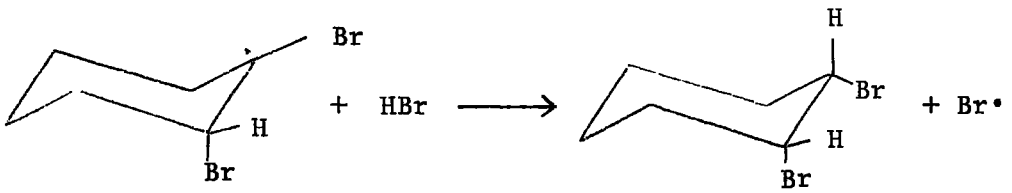
The stereochemistry of the free radical addition of hydrogen bromide and thiols has been widely studied, but there are only a few reports of the stereochemistry of the addition of other addenda.

2. Addition of Hydrogen Bromide

The first study of the stereochemistry of the addition of hydrogen bromide to cyclic olefins was reported by Goering, Abell and Aycock in 1952[77], who found that the ultraviolet light, or peroxide catalyzed

addition of hydrogen bromide to 1-bromocyclohexene in pentane gave almost exclusively cis-1,2-dibromocyclohexane[77,78]. As this isomer is less thermodynamically stable than the trans, a trans addition process was in operation





The addition of hydrogen bromide to 1-methylcyclohexene under the same conditions gave cis-1-methyl-2-bromocyclohexane, and 1-methyl-1-bromocyclohexane, the latter formed by ionic addition.

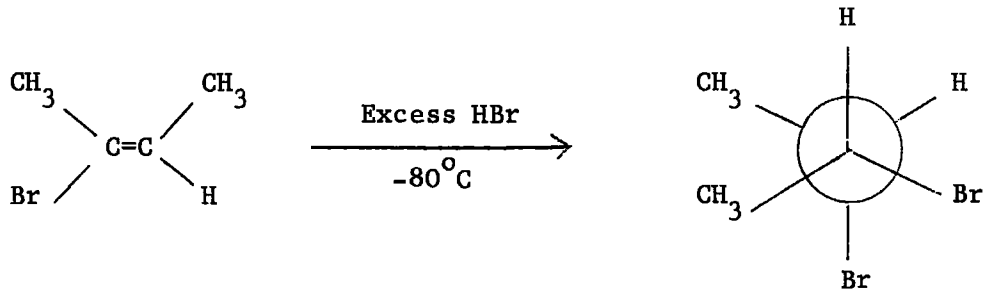
The authors noted that no interconversion of these compounds took place under the conditions of the reaction, indicating that they were the initial products formed. Since this paper was published hydrogen bromide has been added to a variety of monocyclic olefins by a free radical mechanism and the results are summarized in table 5.

It may be seen that in all cases trans addition is preferred. High degrees of stereospecificity have been reported for the addition of hydrogen bromide to acyclic olefins under certain conditions. Goering

TABLE 5. The Free Radical Addition of Hydrogen Bromide to some Monocyclic Olefins

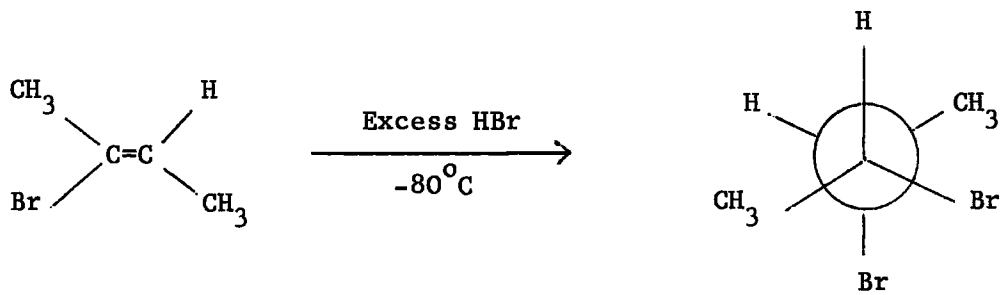
Olefin	Product from Addition	%Trans Addn.	%Cis Addn.	Ref.
1-Bromocyclohexene	1,2-Dibromocyclohexane	100	0	77
		99.5	0.5	78
1-Methylcyclohexene	1-Methyl-2-bromocyclohexane	100	0	77
1-Chlorocyclohexene	1-Chloro-2-bromocyclohexane	99.7	0.3	78
3-Bromocyclohexene	1,3-Dibromocyclohexane	100	0	79
1-Methylcycloheptene	1-Methyl-2-bromocycloheptane	At least 95	-	80
1-Bromocyclobutene	1,2-Dibromocyclobutane	79	21	81
1-Bromocyclopentene	1,2-Dibromocyclopentane	94	6	81
1-Bromocycloheptene	1,2-Dibromocycloheptane	91	9	81
1-Chloro-4-t-butyl-cyclohexene	1-Bromo-1-chloro-4-t-butyl-cyclohexane	95-98	3-5	82

and Larsen found that hydrogen bromide or deuterium bromide add to cis- and trans-2-bromobut-2-ene by a stereospecific trans mechanism at low temperatures and with a large excess of the addend present[83,84].



cis

Meso



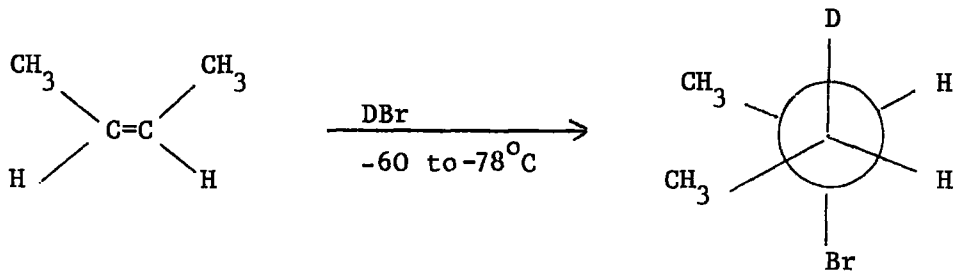
Trans

dl.

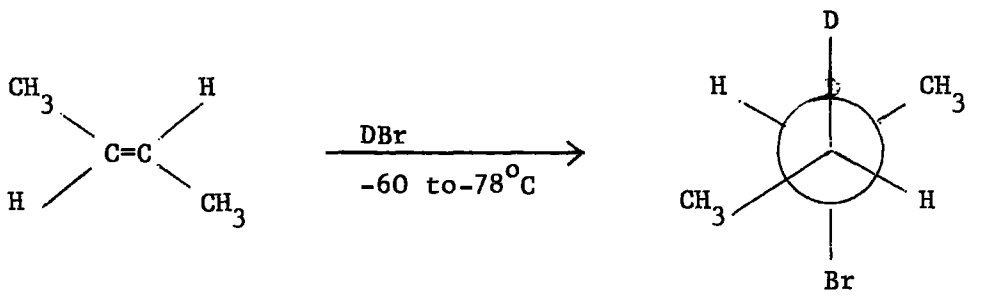
Raising the temperature of the reaction and lowering the proportion of the hydrogen bromide present decreases the stereochemical preference for trans addition until at 25°C the same mixture of products is obtained from either the cis or the trans olefin.

The stereospecific addition of deuterium bromide to cis- and trans-

but-2-ene in the temperature range -60 to -78°C has been reported by Skell and Allen[85]. Cis-but-2-ene gives pure threo-3-deuterio-2-bromobutane, while the trans isomer gives the erythro product.



cis Threo

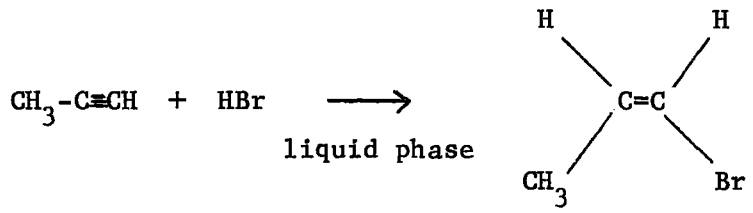


Trans Erythro

Similarly the free radical addition of deuterium bromide to cis- and trans-1-deuteriohex-1-ene is stereospecific in the same temperature range, trans addition being postulated on the basis of previous evidence[86].

Skell and Allen also found that the addition of hydrogen bromide to propyne in the liquid phase using approximately equimolar amounts of

reactants and a temperature in the range -60° to -78°C gave exclusively cis-1-bromoprop-1-ene (radical addition), and 15-20% 1,2-dibromopropane, indicating a trans addition process in the first step[87].



As early as 1939 Walling, Kharasch, and Mayo had reported that dl-2,3-dibromobutane was the sole product from the free radical addition of hydrogen bromide to but-2-yne, (2,2-dibromobutane was also produced from the ionic reaction)[88]. This could have resulted from two successive trans or cis additions[89], but the authors did not interpret their results in this light.

Bergel'son however reports that the free radical addition of hydrogen bromide to 1-bromoprop-1-yne at -78°C in pentane gave a 92% yield of 1,2-dibromoprop-1-ene of which about 75% was the trans isomer, while 1-bromo-3,3-dimethylbut-1-yne gave 1,2-dibromo-3,3-dimethylbut-1-ene of which 95% was the trans isomer indicating that cis addition takes place predominantly[90].

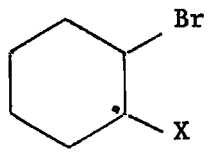
Three main theories have been put forward to account for the preferred trans addition of hydrogen bromide under certain conditions.

1. Participation of a bridged intermediate radical similar to the bromonium ion.

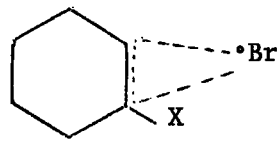
2. π-Complexing between the hydrogen bromide and the olefin during the addition process.

3. A very rapid displacement step involving transfer of a hydrogen atom before inversion of the radical centre takes place.

The idea of a bridged intermediate radical was first proposed by Goering and co-workers in 1952 to account for the trans addition of hydrogen bromide to 1-bromocyclohexene and 1-methylcyclohexene[77]. It was suggested that the intermediate radical does not have the classical structure (a) but that the bromine is centrally located between the two carbon atoms (b). This means that transfer of a hydrogen atom has to take place on the opposite side of the molecule to the bromine bridge, leading to trans addition

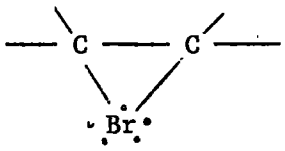


a

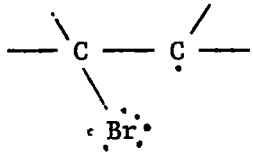


b

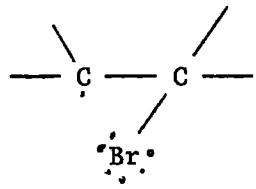
The following forms can be written for the intermediate.



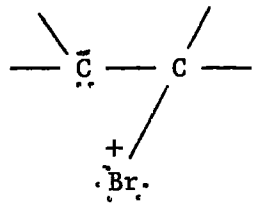
1



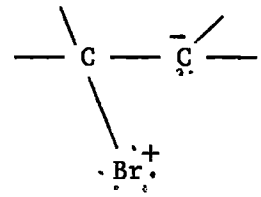
2



3



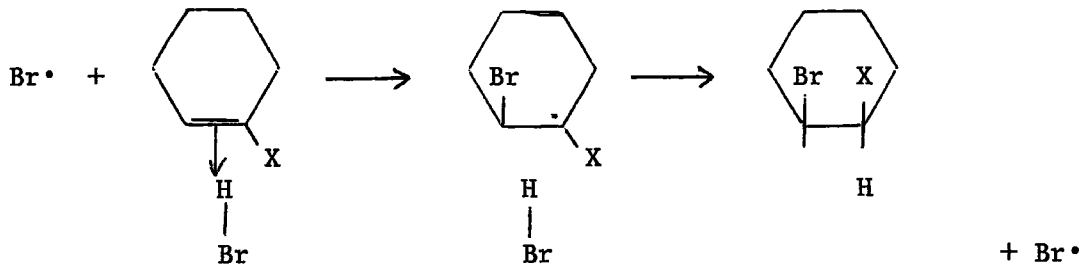
4.



5.

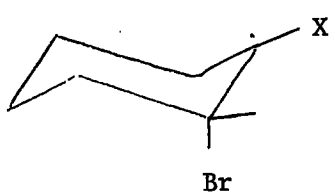
In structure (1) the bromine atom contains nine electrons in its outermost shell and hence is unlikely. The rest contain three electron bonds but it has been pointed out that there is some justification for this type of structure [91], as according to Pauling for a three electron bond to exist the atoms involved must be identical or have a difference in electronegativities of 0.5 unit or less. Carbon and bromine whose electronegativities differ by 0.3 unit satisfy this condition.

In a later paper Goering and Sims discussed the two other possible explanations[78]. It was suggested that the olefin and hydrogen bromide formed a π-complex and that the bromine atom added to the double bond on the side opposite to the complexed hydrogen bromide molecule, from which hydrogen was then abstracted in a concerted process as shown below

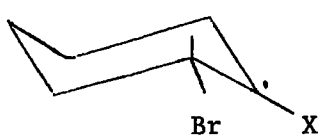


To test this theory they did the reaction in the presence of a large excess of anhydrous ether which would be expected to complex the hydrogen bromide in preference to the olefin, but no loss of stereospecificity of addition occurred. A similar result was obtained when the reaction was carried out in the presence of a large excess of hydrogen chloride. Although hydrogen bromide shows more tendency to complex with olefins than hydrogen chloride it was argued that the latter would be mainly complexed owing to the vast excess present and hence would prevent a rapid transfer reaction of the type shown in the equation above. In view of these two pieces of evidence the π-complex theory was not favoured.

In the same paper however Goering and Sims pointed out that the results could be explained purely in terms of classical radicals.[78] Considering the case with cyclohexenes, the intermediate radical may have two possible chair conformations (I) and (II).



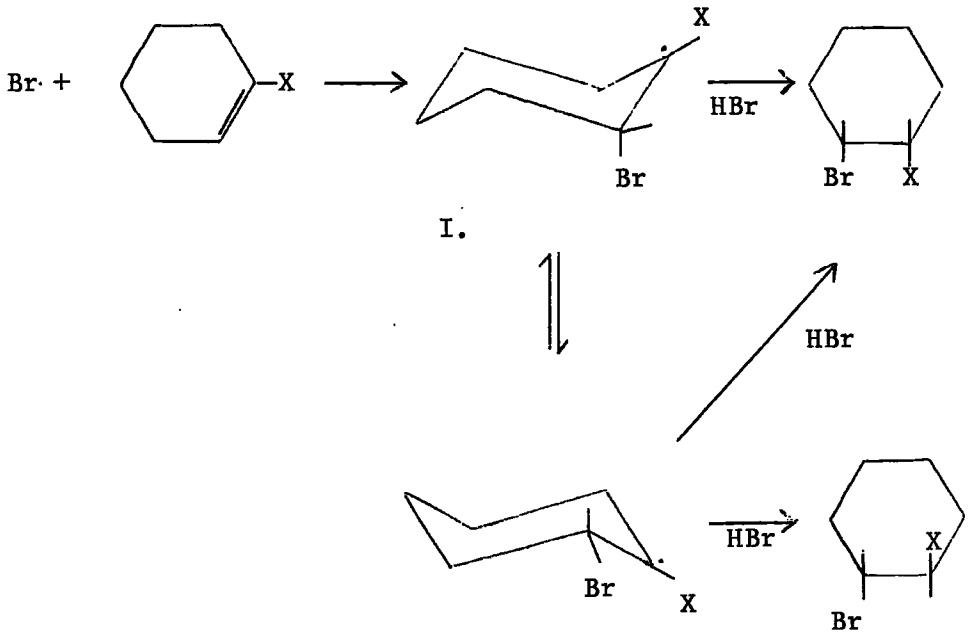
I.



II.

Structure (II) is sterically less strained than (I), but the latter is favoured on electrostatic grounds. In (II) the carbon-halogen bonds are nearly co-planar and this form is thus destabilized by electrostatic

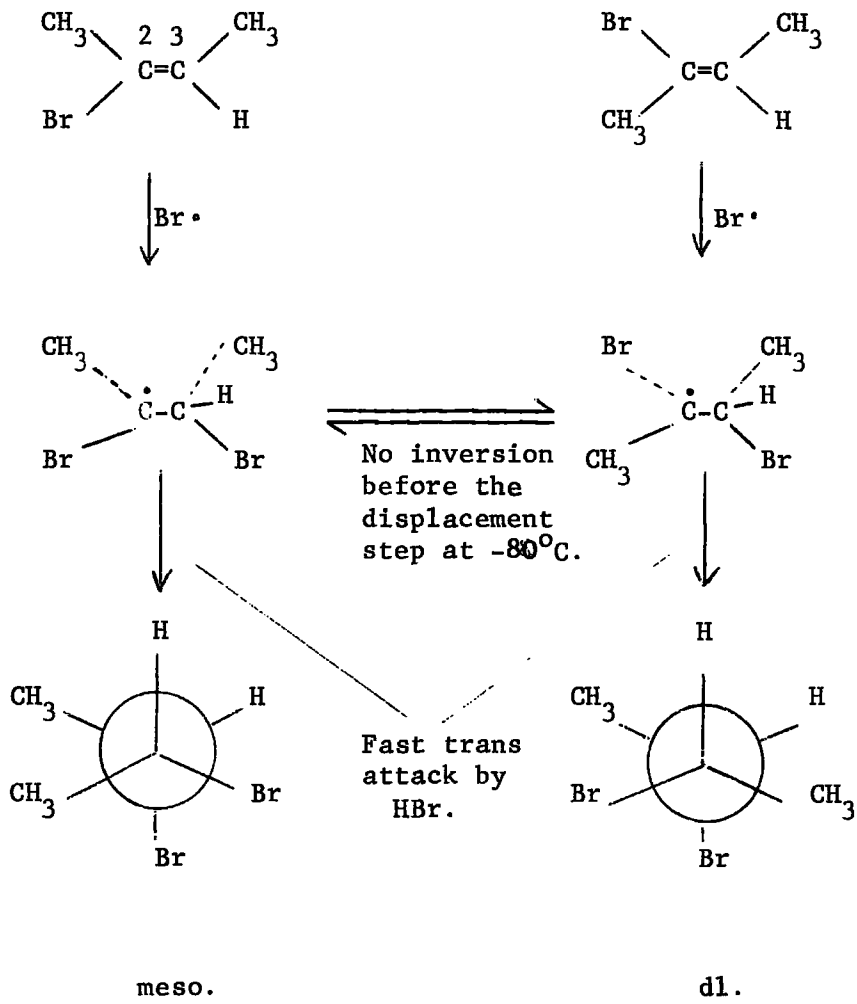
interactions (carbon-halogen dipole repulsion). Because the steric and electrostatic effects oppose each other it is difficult to say which form is the more stable, but Goering and Sims argued that even if (II) was more stable than (I), the latter could be involved in radical additions. It is likely that the chain carrying radical approaches a double bond perpendicular to the plane of the sigma bonds of the ethylenic linkage, and hence the bromine atom goes into an axial position. This results in the formation of (I). If the displacement step occurs before inversion of the cyclohexane ring, trans addition takes place since approach of a hydrogen bromide molecule on the side opposite to the bromine atom is sterically favoured. If ring inversion to (II) takes place however, trans or cis addition can result, hence for stereospecific addition the displacement step must be rapid.



This explanation involving classical radicals has the advantage that it allows for approach of the hydrogen bromide from either side of the free radical carbon in the displacement step, but with a substantial preference for the less hindered side, thus explaining cases in which complete stereospecificity is not observed. Abell and Chiao explained the results with 1-bromocyclobutene, 1-bromocyclopentene and 1-bromocycloheptene on this basis[81], (See Table 5). The variation of stereospecificity with ring size was attributed to the availability of unhindered approach to the free radical carbon coupled with the degree of reluctance to force the bromines into a cis configuration. The cyclobutane ring is quite rigid in its bond angles, and forcing the bromines into a true unskewed cis configuration (trans addition) may be expected to be difficult, and hence a fair degree of cis addition is observed. The cyclopentane ring has more flexibility, but only with the cyclohexane ring is crowding of the two cis bromines negligible and only in this case is almost exclusive trans addition observed. Similar arguments were used with 1-bromocycloheptene, but the situation in this case is rather more complicated.

Additions to acyclic olefins have been explained in terms of these theories; both classical and bridged radicals have been invoked. Goering and Larsen's results with 2-bromobut-2-ene have shown that the preference for trans addition decreases at higher temperatures and lower hydrogen bromide concentrations, suggesting that the addition to

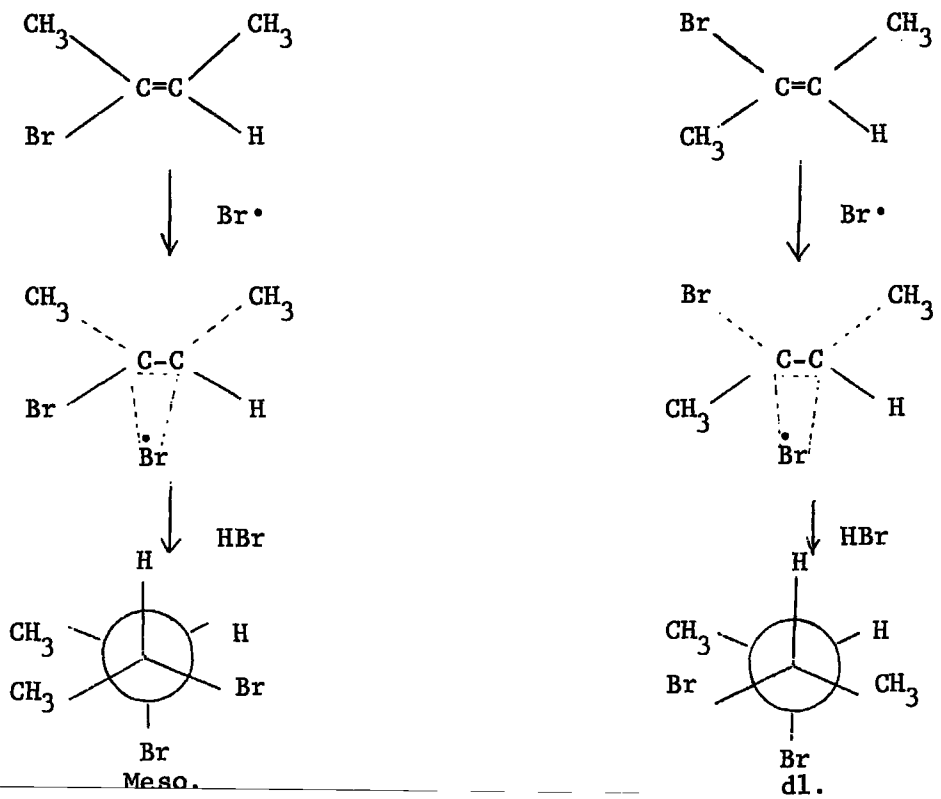
the two geometric isomers of the olefin involves two different conformations of the intermediate radical which may or may not equilibrate before the displacement step[83,84].



Present indications are that a typical organic radical centre is either planar or slightly pyramidal[92], but if the radical centre is non-planar

and inverts rapidly then the planar configuration represents the average state. In any case the two isomeric radicals can only interconvert, (without breaking a bond), by rotation about the C2-C3 bond. Trans addition is preferred because it avoids interaction with the C3 bromine, and permits a smooth transition to the product without eclipsing of the bonds in the displacement step. At 25°C the reaction is non-stereospecific both isomers of the olefin giving approximately 25% meso- and 75% dl-2,3-dibromoethane.

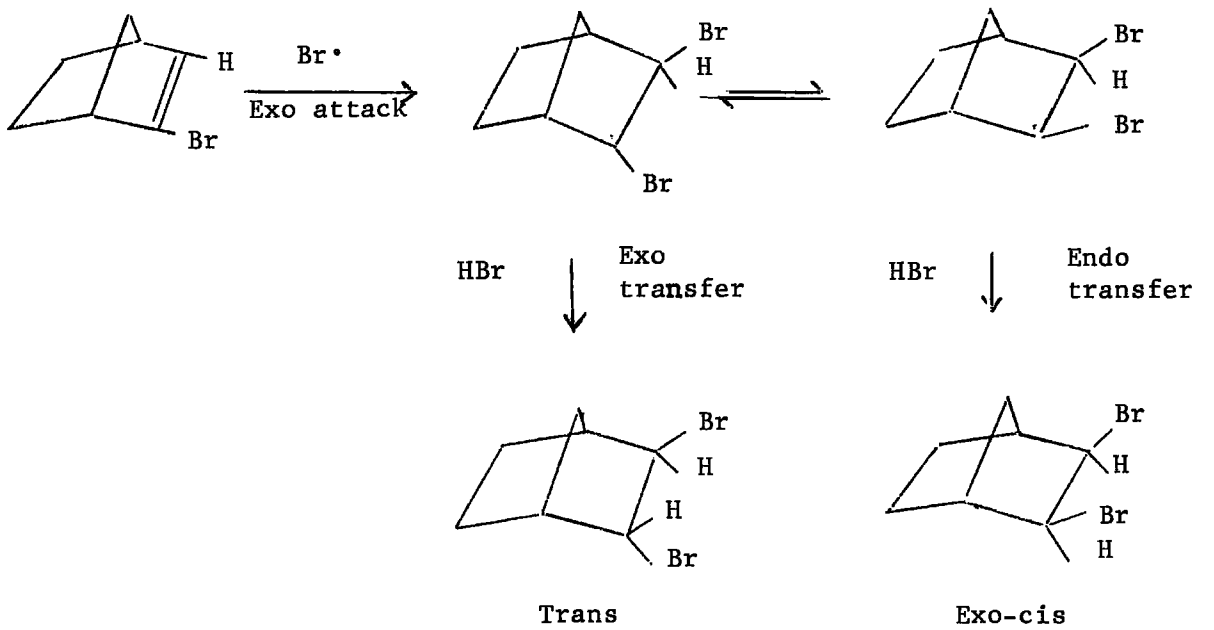
In the picture above the transfer step competes successfully with rotation about the C2-C3 bond, and its activation energy must be very low. It has been suggested that the barrier to rotation about this bond could be increased by bridging by the C3 bromine[84], and a bridged intermediate radical offers an alternative explanation.



It can be postulated that transfer of the hydrogen atom takes place trans to the bromine bridge leading to stereospecific trans addition, and that at higher temperatures and lower hydrogen bromide concentrations the two bridged forms invert via open chain radicals[93]. Skell has interpreted the stereospecific trans addition of hydrogen bromide to unsaturated linkages in this manner[94].

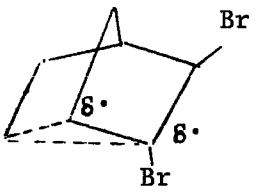
Goering and Larsen also considered the possibility of complexing of the olefin and addend prior to addition[84]. According to this scheme the displacement step would be a first order process and would not require that the two species diffuse together, thus enabling it to compete successfully with rotation about the C2-C3 bond. This also accommodates their observation that deuterium bromide and hydrogen bromide show about the same stereospecificity, a fact which is difficult to rationalize in terms of competition between displacement and rotation since hydrogen bromide apparently transfers about 2.4 times as fast as deuterium bromide. (In this picture the relative rates would depend in part on the relative tendencies to complex with the limited amount of olefin available).

The addition of hydrogen bromide to 2-bromonorbornene yields 71% trans-2,3-dibromonorbornane (cis addition) and 29% exo-cis-2,3-dibromonorbornane (trans addition)[95].

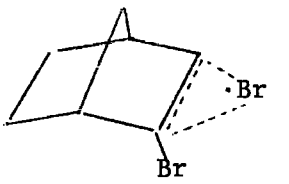


Initial approach of the bromine atom would be expected to be from the least hindered exo side of the molecule (i.e. adjacant to the methylene bridge) and this is the case as no endo-cis-2,3-dibromonorbornane was detected. Owing to steric repulsions in the molecule the transfer step is very much slower than in acyclic and monocyclic olefins, allowing time for inversion of the radical centre to occur giving a mixture of products. Hence in this case the ratio of the products formed represents a balance amongst the steric repulsions in the molecule. In his paper Lebel also pointed out that a non-classical radical such as (III) cannot be involved because no rearranged products were obtained, and that the preponderance of cis addition rules against the participation of a bridged radical (IV) [95]. In his review however

Skell attributes this to steric strain reducing the stability of the bromine bridged radical relative to the classical intermediate thus allowing ring opening to become faster than trapping with hydrogen bromide[94].

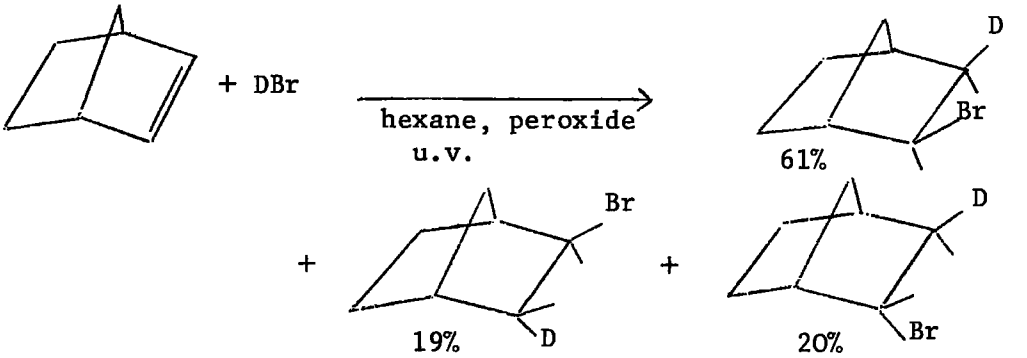


III



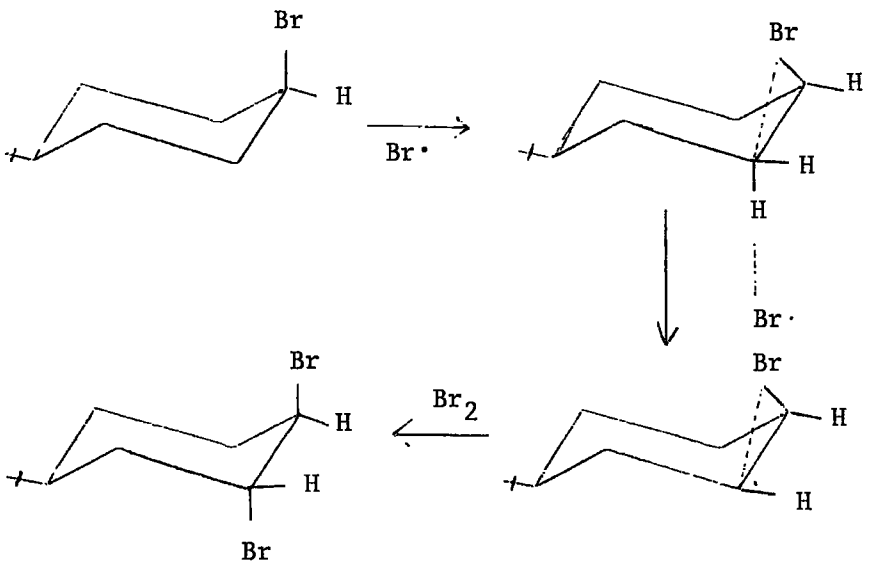
IV

The addition of deuterium bromide to norbornene has been reported to give three products as shown below. Again a preponderance of exo-cis addition was obtained, this being attributed to steric control.[96]



The problem of whether bridged or open-chain radicals are more stable has received wide attention. Evidence supporting the idea that bromine atoms bridge to radicals of lower energy than the analogous open-chain radicals was put forward in 1964 by Skell and Readio who

found that the bromination of cis-1-bromo-4-t-butylcyclohexane (the bulky t-butyl group holds the molecule in a conformation in which the bromine is axial) gives ax,ax-1,2-dibromo-4-t-butylcyclohexane as the almost exclusive product.[97] The formation of this product was accounted for by bridging in the transition state for hydrogen abstraction, (anchimeric assistance) attack by bromine taking place in the axial direction at the 2-position only. The alternative equatorial attack at the 1-position is a higher energy reaction path as it does not involve a diaxial transition state (diaxial rule)[97].



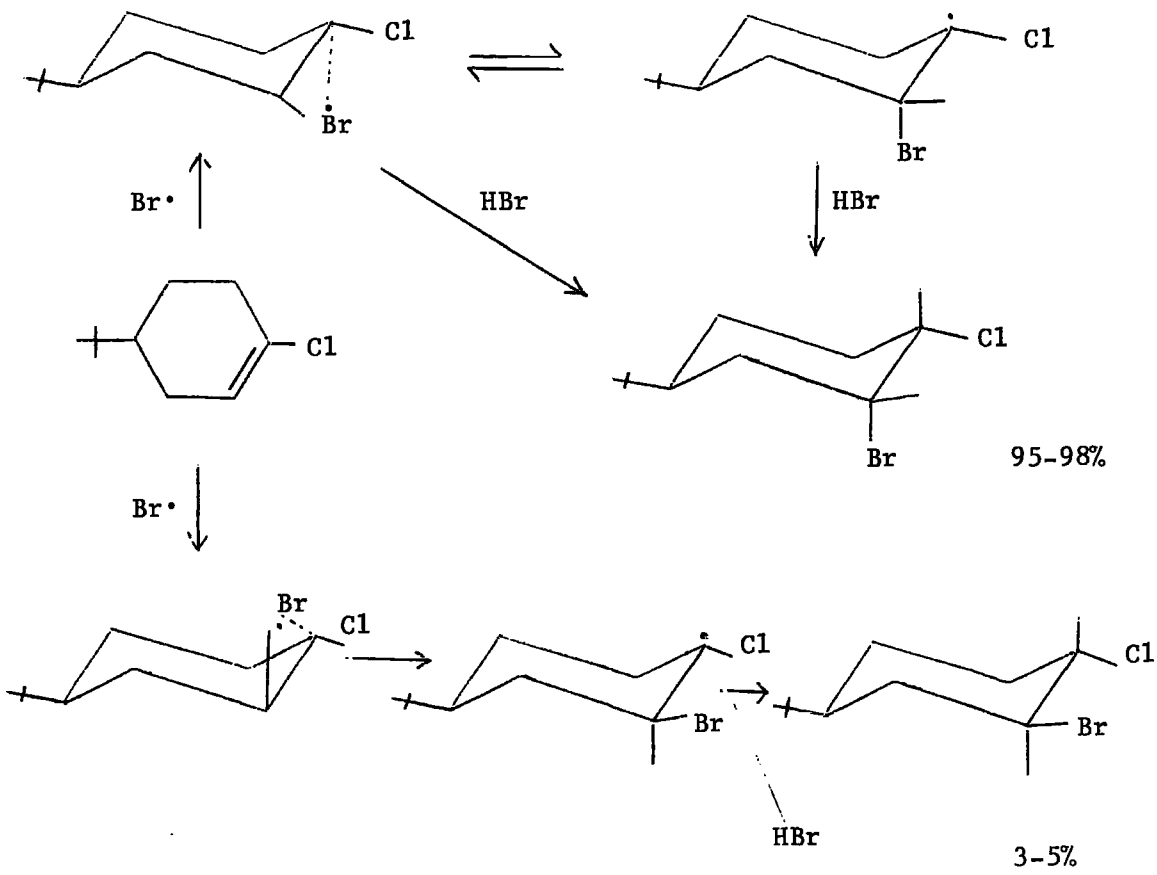
Transition state for hydrogen abstraction

Intermediate radical.

Photobromination of trans-1-bromo-4-t-butylcyclohexane in which the bromine is in the equatorial position occurs less than one fifteenth as fast resulting in a mixture of isomeric dibromides. This was explained by anchimeric assistance not taking place in this case because

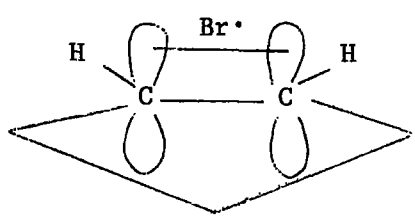
a trans-diaxial arrangement of hydrogen and bromine could be obtained only after conversion to the cyclohexane boat form, and unassisted abstractions thus follow lower energy paths.[97]

On the basis of these results, Skell and Readio have recently accounted for the trans addition of hydrogen bromide to 1-chloro-4-t-butylcyclohexene to give 95-98% trans-3-bromo-trans-4-chloro-t-butylcyclohexane in terms of bridged intermediate radicals by the scheme below[82].



Skell and co-workers have pointed out[98] that a bridged intermediate radical is consistent with the facile 1,2 migrations by bromine which have been observed[99].

The question of whether stereospecific additions of hydrogen bromide are due to bridged or classical intermediates remains a matter of speculation. In 1962 Abell and Piette reported the results of a study of the addition of hydrogen bromide to various olefins at 77°K using electron spin resonance spectroscopy[100]. It was claimed that with symmetrical olefins spectra were obtained which could be interpreted as arising from a symmetrical intermediate radical. For example the spectrum from hydrogen bromide and cyclopentene was attributed to an intermediate radical with the structure below

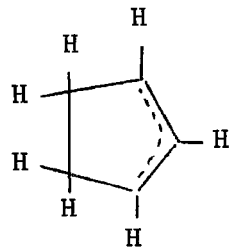


The spectra obtained from hydrogen bromide and but-2-yne, hex-3-yne, cis- and trans-but-2-ene, cis-hex-3-ene and cyclohexene were attributed to similar structures, but unsymmetrical olefins did not give the same type of spectra and were not interpreted.

Although these results were widely quoted, they have been disputed by Symons who has postulated that the radicals detected by Abell and Piette were allylic[101]. The spectra of the radicals obtained

from but-2-ene and cyclopentene were dealt with in detail and it was shown that they could arise from the radicals resulting from allylic abstraction of hydrogen as shown below. (The possibility of addition of a hydrogen atom was eliminated in these two cases since Abell and Piette showed that the same spectra were obtained from deuterium bromide and the olefins).

$\dot{C}H_2$-CH=CH-CH_3

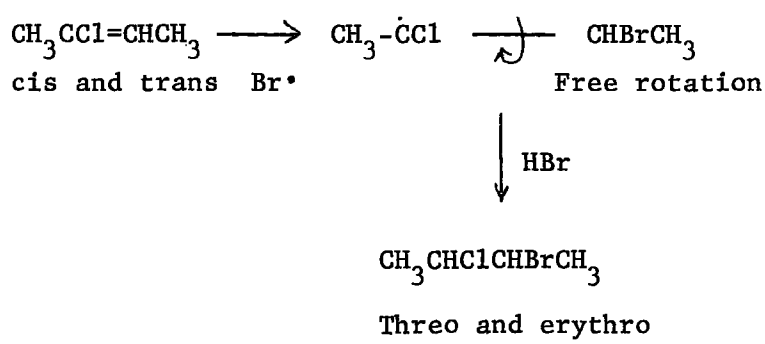


Thus these results cannot be taken as evidence for bromine bridging.

The idea of a bridged intermediate radical was first put forward to explain early stereospecific additions of hydrogen bromide, but with the discovery of several cases where addition is only partially stereospecific, the theory of a classical intermediate was advanced, the degree of stereospecificity depending on the rate of the displacement step. The bridged model can accommodate this in terms of opening of the bridge before hydrogen abstraction[94], but several authors have concluded that it offers no advantage over a classical intermediate[91,102,103].

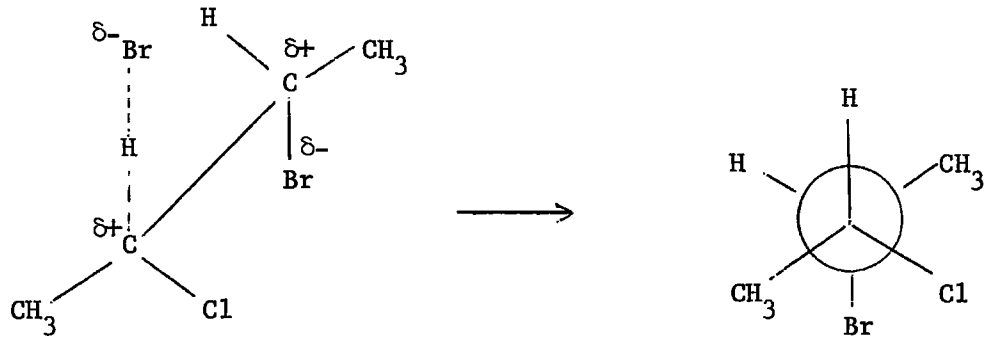
In cases where cis and trans isomers of acyclic olefins have given the same products due to isomerization of the intermediate radical, the stereochemistry of the free radical addition of hydrogen bromide has been accounted for in terms of conformational effects. Neureiter and

Bordwell investigated the addition of hydrogen bromide to 2-chlorobut-2-ene and found that the olefin was rapidly isomerized to a mixture containing 80% trans and 20% cis at all temperatures between -78° and 25°C.[104]. The addition of hydrogen bromide to both trans and cis-2-chlorobut-2-ene at -20° and at 25° to 30°C yielded about 70% threo- and 30% erythro-2-chloro-3-bromobutane. Equilibration of the olefins with hydrogen bromide and equilibration of the intermediate radicals preceeded addition.



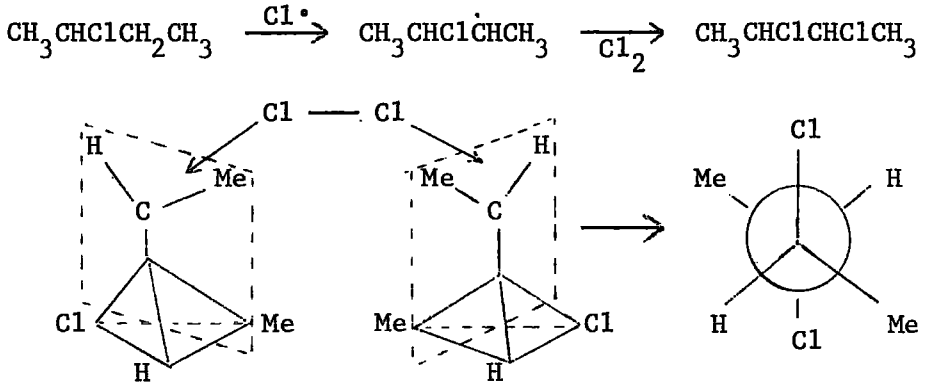
This preferential reaction of the intermediate radical via one of two competing transition states in the final transfer step, was attributed to the development of a dipole in the transition state which is preferentially orientated away from the largest permanent negative dipole on the saturated carbon atom. This means that in the displacement step the hydrogen bromide preferentially approaches the radical centre trans to the bromine on the saturated carbon. At the same time steric interactions must be minimised and this results in the transition state

below which gives the threo isomer. The authors pointed out that this scheme can be applied to any comparable case, involving other addenda.



Threo.

Fredricks and Tedder have attributed the preferential formation of erythro- over threo-2,3-isomers during the halogenation of 2-halobutanes to conformational effects in the intermediate 2-halo-1-methylpropyl radicals $CH_3CHX\dot{C}HCH_3$ (X = Br, Cl, F)[105]. It was assumed that the bonds on the tervalent carbon atom approximate to Sp^2 and are nearly planar, and that the other three bonds on the tetrahedral carbon atom can rotate relatively to this plane. A preferred conformation for the two such radicals, both of which favour substitution from one direction was postulated. In these the methyl group of the tervalent carbon atom is closely above the hydrogen atom of the tetrahedral carbon. The approach of the incoming halogen molecule (which must be approximately perpendicular to the free radical plane), is easier on the side away from the substituent halogen atom, yielding in both cases the erythro-compound.



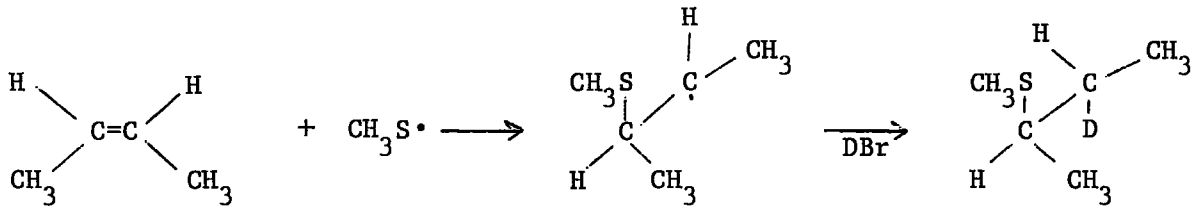
Erythro (meso).

3. Addition of Reagents Containing Sulphur.

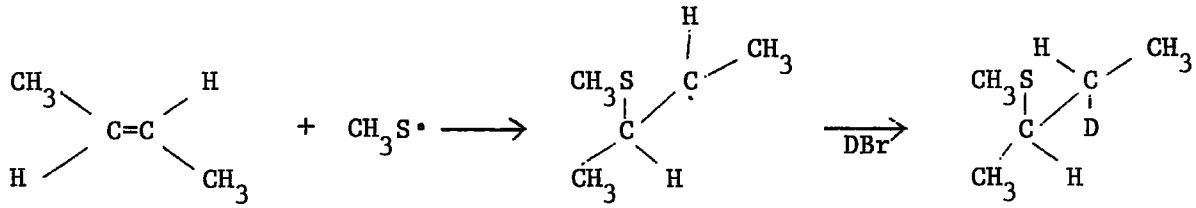
Apart from hydrogen bromide the stereochemistry of the addition of thiols and other compounds containing sulphur have received most attention. The addition of thiols to acyclic olefins is non-stereospecific. Neureiter and Bordwell found that the addition of thiolacetic acid to cis- and trans-2-chlorobut-2-ene at -78°C gave identical mixtures of products consisting of 90% threo- and 10% erythro-2-acetylmercapto-3-chlorobutane, indicating that radical inversion occurs before transfer[104]. This was rationalized in a similar way to the addition of hydrogen bromide (Page 60).

Skell and Allen have shown that the addition of methanethiol (CH_3SD) to cis- and trans-but-2-ene is non-stereospecific, but that stereospecific trans addition occurs when the reaction takes place at -78°C in the presence of deuterium bromide[106]. Thus cis-but-2-ene gives threo-3-deuterio-2-bromobutane and 3-deuterio-2-methylthiobutane,

while the trans olefin gives the erythro isomers.



Threo



Erythro

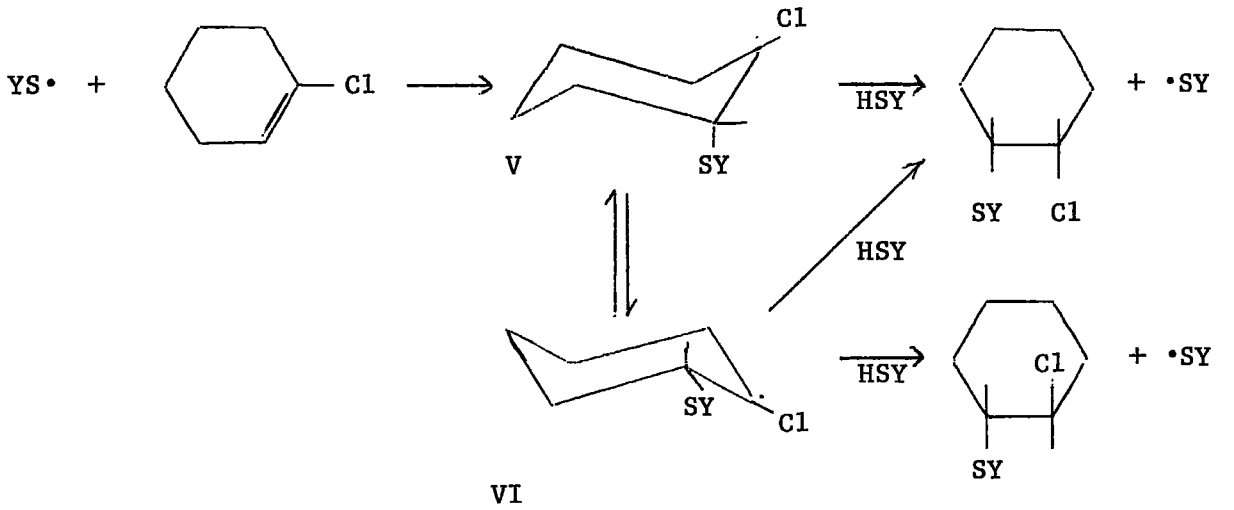
Hence in this case rapid transfer with deuterium bromide takes place before equilibration of the intermediate radicals. A bridged sulphur intermediate has also been postulated to explain this result, the hydrogen bromide trapping this radical before ring opening occurs[94].

Addition of thiols to cyclic olefins is stereoselective, trans addition mainly occurring together with a little cis addition. Some of the results are summarized in table 6.

TABLE 6. Free Radical Addition of Thiols to Some Monocyclic Olefins.

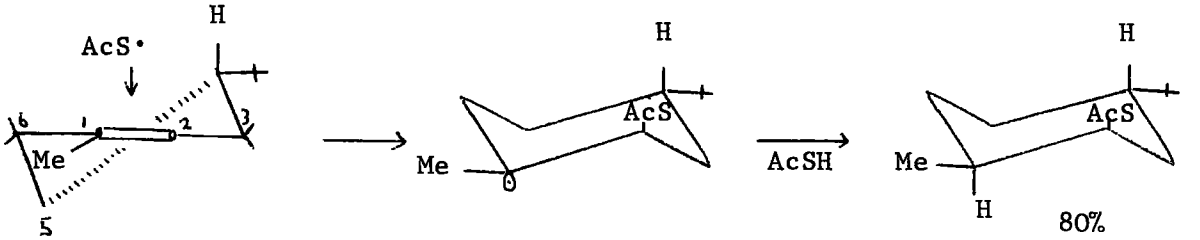
Olefin	Addend	%Trans addn.	%Cis addn.	Ref.
1-Chlorocyclohexene	Thiophenol	94-99	1-6	107
1-Chlorocyclohexene	Thiolacetic acid	66-73	27-34	107
1-Methylcyclohexene	Thiolacetic acid	85	15	108
1-Methylpentene	Thiolacetic acid	70	30	108
1-Methylcyclohexene	Thiophenol	Predominantly		108
1-Methyl-4-t-butyl-cyclohexene	Thiolacetic acid	SAc ax. 80	SAc eq. 20	109
1-Chloro-4-t-butyl-cyclohexene	Methanethiol	SCH_3 ax. H ax. 88 SCH_3 eq. H ax. 8	SCH_3 eq. H eq. 2 SCH_3 ax. H eq. 2	110

It has generally been concluded that with thiols the displacement step takes place more slowly than with hydrogen bromide, thus allowing time for some isomerization of the intermediate radical to take place leading to cis addition[91]. Thus Goering and co-workers accounted for the preferred trans addition to 1-chlorocyclohexene in terms of initial axial attack by the radical to give (V) to which transfer could take place axially to give the cis product (trans addition)[107]. Alternatively ring inversion could occur to give (VI) from which both addition products would be expected since there is no steric advantage in trans addition. This picture is consistent with the observation that the stereospecificity increases with thiol/olefin ratios.



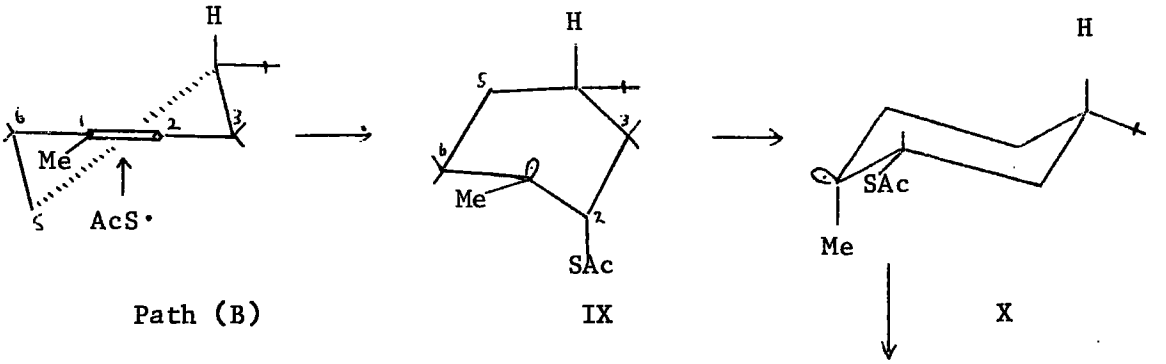
Bordwell and co-workers have recently looked at this problem in more detail[109]. In the addition of thiolacetic acid to 1-methyl-4-t-butylcyclohexene, the formation of about 80% trans product with the SAc group

axial was accounted for in terms of axial attack by the AcS• radical by path (A). This is sterically favoured since only the hydrogen atom at C4 offers any appreciable interference and the chain intermediate (VII) can be formed with little molecular readjustment of the original alkene conformation. Abstraction of a hydrogen atom by path (A) into an axial position then gives overall trans-diaxial addition

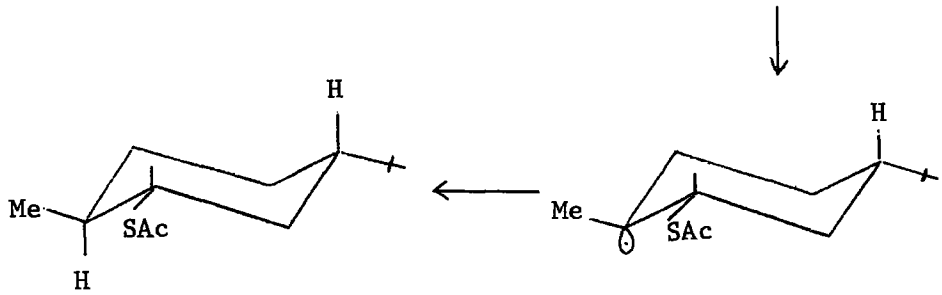


Path (A) VII VIII

It was shown that axial attack by the AcS• radical on the opposite side of the molecule is opposed by the pseudo-axial hydrogen atom at C3. For the addition to follow a path comparable to that shown for the formation of (VIII), it has to go through a twist-boat intermediate (IX) and then through (X) and (XI) to (XII). Thus path (B) is opposed both on the grounds of steric accessibility, and the relative stability of the intermediates.



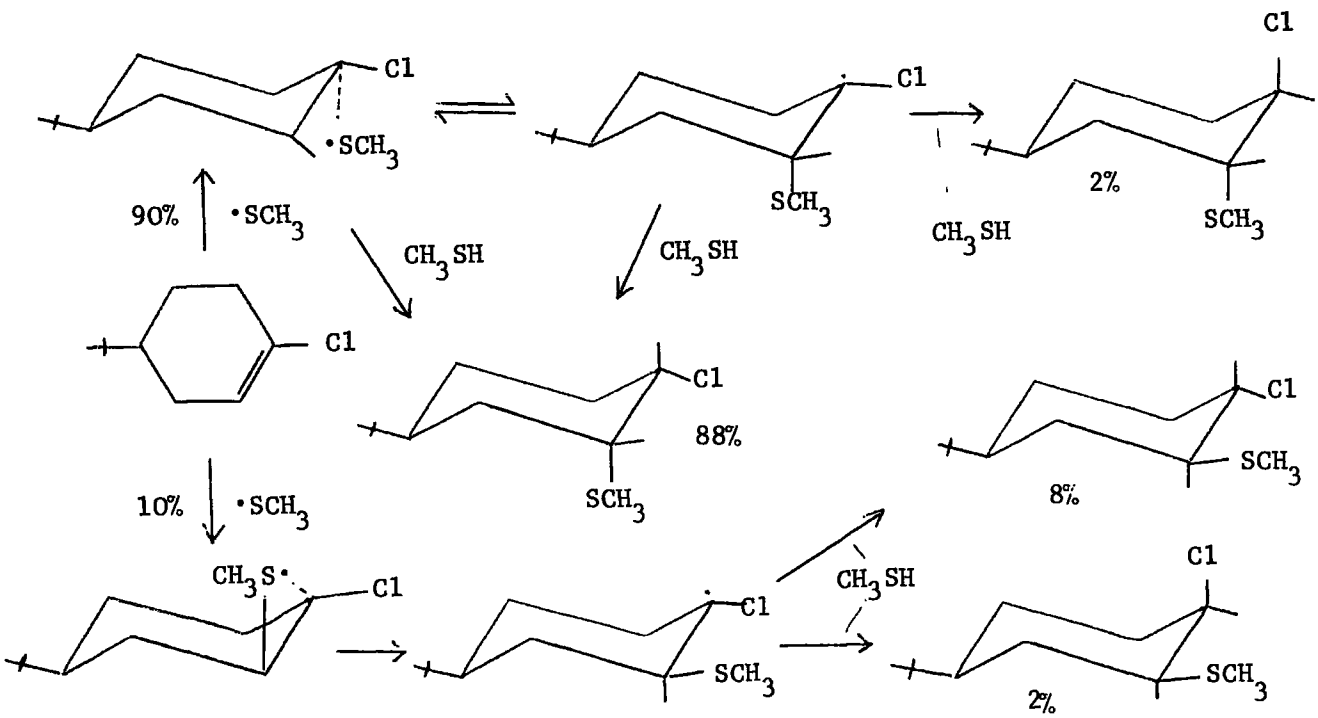
Path (B) IX X



20% XII XI

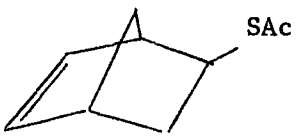
The authors found it difficult to rationalize the preferential abstraction of a hydrogen atom into an axial position using a planar radical centre, since the preferred steric approach of a thiolacetic acid molecule would lead to equatorial abstraction. For this reason a representation showing a pyramidal radical was preferred.

Readio and Skell however have accounted for their results of the addition of methanethiol to 1-chloro-4-t-butylcyclohexene in terms of bridged radicals, by the scheme below[110].

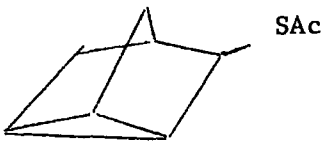


It was found that isomer composition did not vary with the thiol to olefin ratio, supporting this interpretation. These workers have also cited the results of the co-oxidation of indene and thiophenol by Ford, Pikethly and Young[111], as evidence for sulphur bridging although the latter interpreted their results in terms of classical radicals.

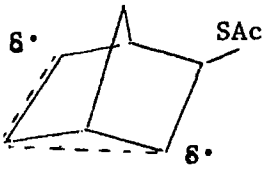
There have been several reports of additions of sulphur compounds to bridged bicyclic olefins by Cristol and co-workers[112-114], the results being interpreted in terms of steric control and classical radical intermediates rather than a sulphur-bridged structure. The addition of aromatic thiols to norbornadiene gives aryl exo-norborn-5-en-2-yl sulphides (XIII) formed by 1,2 addition and aryl 3-nortricyclo-enyl sulphides (XIV) by homoconjugative addition[115,116]. As the product ratios varied with concentration it was postulated that classical radicals were involved rather than the non-classical intermediate (XV)



XIII



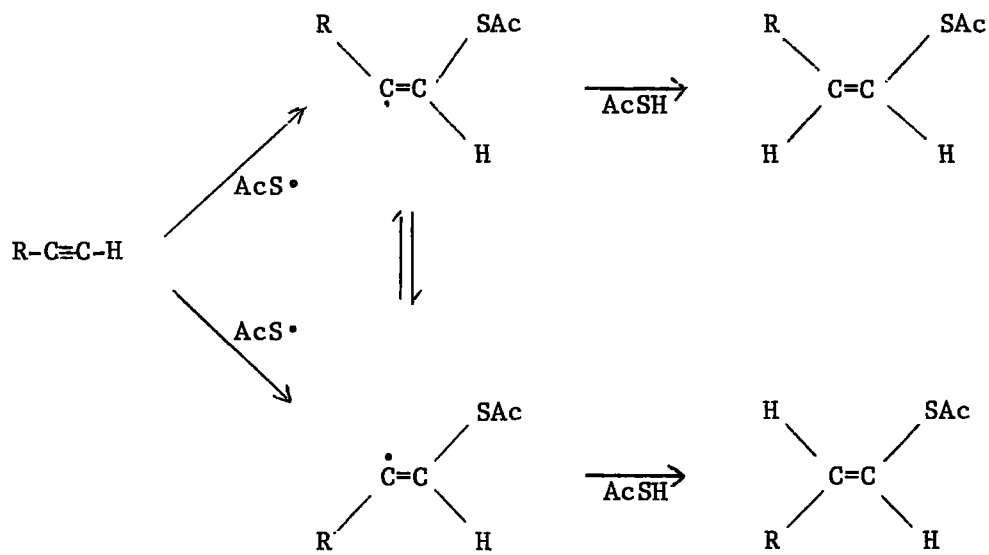
XIV



XV

Similar results have been obtained with benzene sulphonyl halides[117], while Claise and co-workers have recently reported a different type of rearrangement in the free radical addition of thiols to hexachloronorborn-adiene[118].

Free radical additions of thiols to acetylene have also been studied. Kampmeier and Chen have found that the addition of thiolacetic acid to hex-1-yne gives approximately 82% cis-hex-1-enyl thiolacetate when there is a large excess of the acetylene, but this shifts to approximately 75% when the ratio of reactants is 1:1[119]. These workers point out that it is difficult to interpret these results owing to the lack of knowlege about the relative rates of the displacement step and the isomerization of the intermediate vinyl radicals

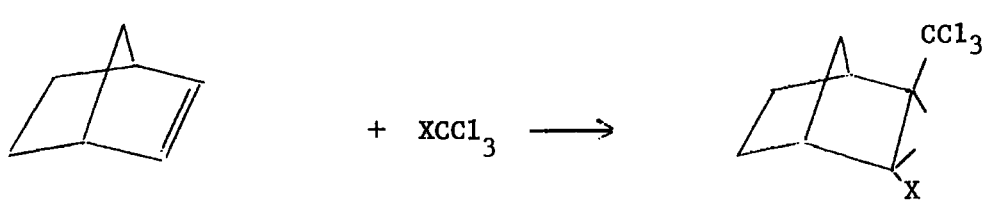


Similarly Oswald and co-workers have noted a preponderance of trans addition with phenylacetylene and various thiols.[120] It may thus be concluded that owing to a slower rate of transfer than with hydrogen bromide,thiols only undergo stereospecific free radical addition under certain specialized conditions, and that generally the course of addition

is determined by steric and conformational factors. Stereospecific addition has not been observed with other sulphur compounds; the addition of benzene sulphonyl iodide to cis- and trans-but-2-ene has been shown to be non-steroeospecific[121] while the copolymerization of these two olefins with sulphur dioxide yields identical products, indicating a non-stereospecific addition process[122].

4. Addition of Polyhalomethanes.

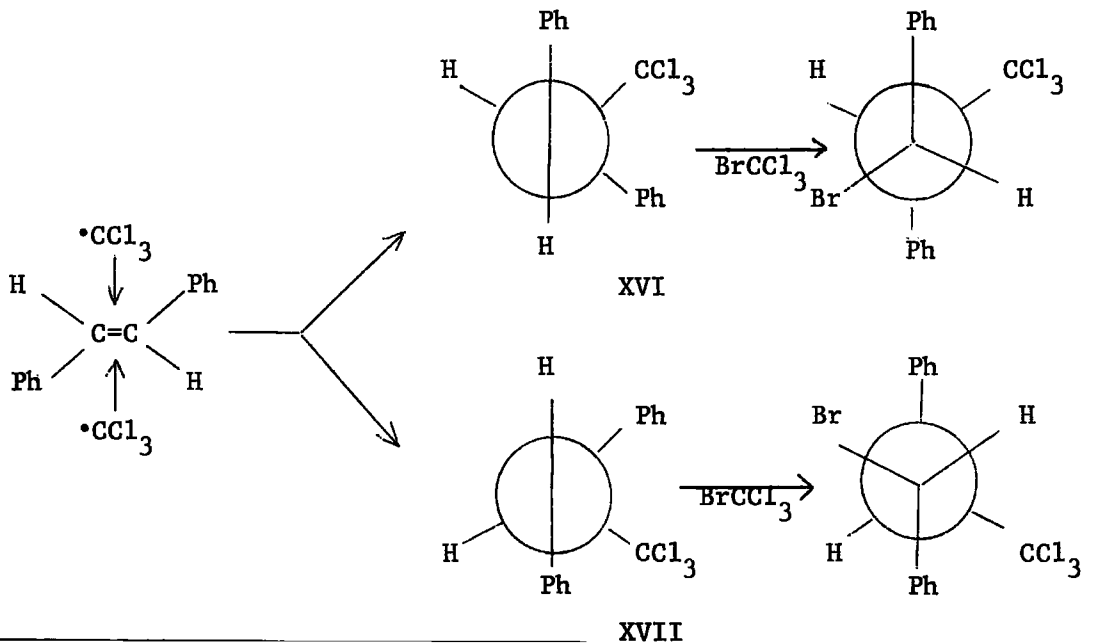
The free radical addition of bromotrichloromethane to several cyclic and bicyclic was reported by Kharasch and Friedlander in 1949[123]. It was noted that the adducts from some bicyclic olefins were resistant to dehydrohalogenation, and the results were interpreted by Fawcett in terms of a trans addition process, with the bromotrichloromethane molecule approaching the intermediate radical from the side opposite to the trichloromethyl group in the displacement step[124]. A recent re-investigation of this has confirmed that bromotrichloromethane and carbon tetrachloride add to norbornene in a trans manner[125].



(X = Cl or Br).

Skell and Woodworth reported in 1955 that the light initiated addition of bromotrichloromethane to cis- and trans-but-2-ene gave the same mixture of diastereomeric products[126]. As there was no detectable isomerization of the olefin under the conditions of the reaction, the result was interpreted in terms of open-chain intermediate radicals which interconvert by rotation about the C2-C3 bond before transfer of a bromine atom takes place.

By contrast, Cadogan and Duell found that the addition of this reagent to cis- and trans-stilbene gave only one racemic 1:1 adduct[127]. These workers accounted for this by suggesting that the chain transfer reactions of the intermediate radicals (XVI) and (XVII) are stereospecific, proceeding through preferred conformations in which the bulky phenyl and trichloromethyl groups are as far apart as possible. The bromotrichloromethane molecule approaches the radicals from the least hindered side in each case, giving the same single racemic 1:1 adduct.

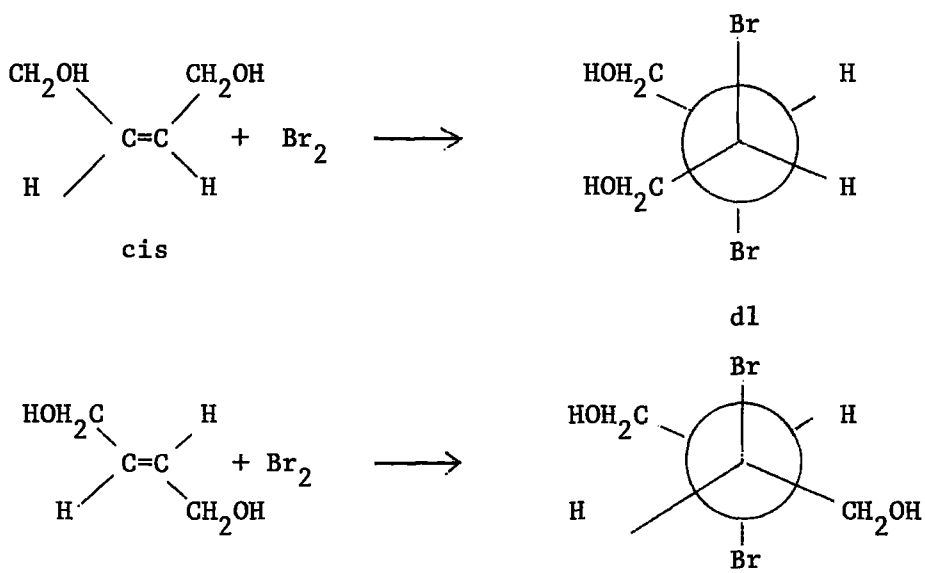


There is thus no evidence for a three-membered ring intermediate in these reactions, and the results can be explained in terms of steric and conformational effects.

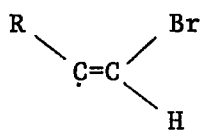
5. Addition of Bromine and Iodine.

There have been few reports of the stereochemistry of the free radical addition of bromine to double bonds. Bergel'son and Badenkova have reported that the u.v. catalyzed addition of bromine to cyclohexene gave a 90% yield of trans 1,2-dibromocyclohexane, and stereospecific trans addition to cis- and trans-but-2-ene-1,4-diol was also noted[128]. The trans isomers of the corresponding diacetate and 2,5-dimethylhex-3-ene-2,5-diol underwent trans addition similarly, but the cis isomers were reported to yield unidentified oils.

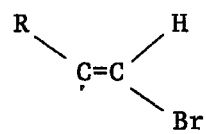
e.g.



The course of the addition of bromine to monosubstituted acetylenes is influenced by the nature of the alkyl substituents, and cis addition tends to occur when the alkyl group is large[129-131]. It has been postulated that as the size of the alkyl group R increases, interaction between it and the bromine atom increases making intermediate (XVIII) less stable than (XIX), and hence a major proportion of the product is formed from attack on the latter resulting in cis addition[91].



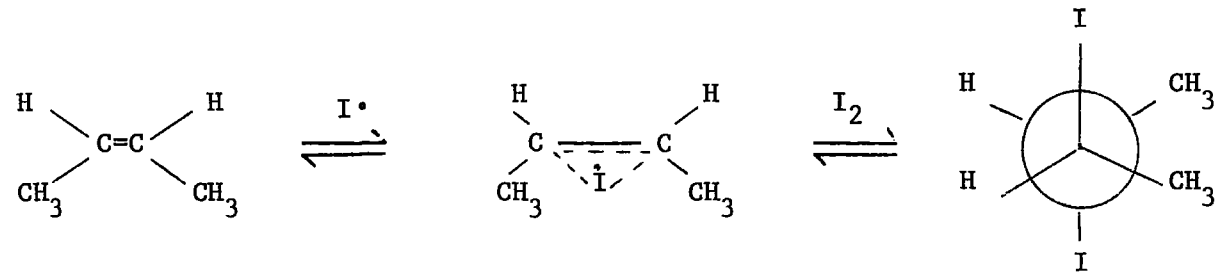
XVIII



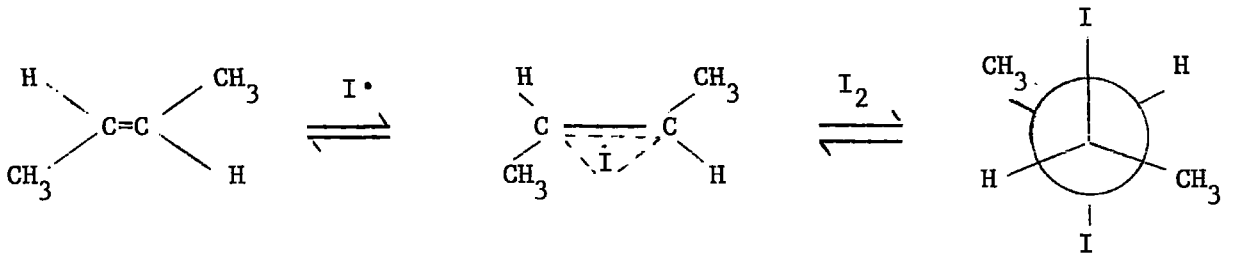
XIX

A similar experiment has been used to explain the course of addition to disubstituted acetylenes, but the results are not so clear-cut.

The photoinitiated radical chain addition of iodine to olefins has been reported by Skell and Pavlis[132]. Addition to cis and trans-but-2-ene occurs readily in boiling propane (-45°C) and is trans-stereospecific. The results were explained in terms of bridged iodoalkyl radicals.



dl

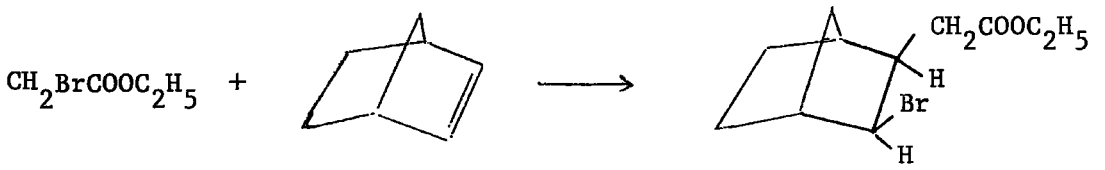


Meso

Non-stereospecificity has been observed with iodine concentrations below 10^{-5} m and this was attributed to ring opening before abstraction[94].

6. Other Additions and Conclusion.

Apart from the work on polyhalomethanes, very little study has been made of the stereochemistry of free radical addition reactions in which displacement takes place on a carbon atom. The addition of ethyl bromoacetate to norbornene gives the exo-cis product this being attributed to steric effects[92].

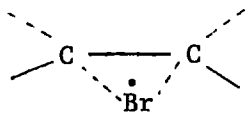


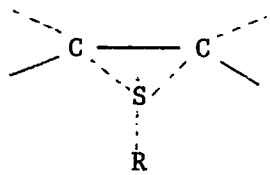
The only data at present available on the stereochemistry of the free radical addition of aldehydes, alcohols and ethers to olefins comes from the work of Muramatsu and co-workers and Kisby on cyclic fluoroölefins. The variation of cis and trans isomer ratios found in the addition of alcohols to 1,2-dichlorotetrafluorocyclobutene has been attributed to steric effects, but in general the results have not been interpreted in detail. No study of the stereochemistry of the addition of these addenda to acyclic olefins has been reported.

Walling and Huyser point out that in all additions to acyclic olefins involving displacement on a carbon atom so far investigated (i.e. polyhalomethanes) the same ratio of diastereomeric products has been obtained from both the cis and trans isomers, indicating that isomerization of the intermediate radicals by rotation about the former carbon-carbon double bond is rapid compared with the displacement step.[17]

It may be concluded therefore that stereospecific trans addition by hydrogen bromide, and thiols takes place under conditions in which

the displacement step is rapid. These results may be interpreted either in terms of classical radicals, or by invoking the bridged species below[94].





Stereospecific trans addition has also been observed with bromine and iodine, but it has not been established with other addenda as the displacement steps appear to be less rapid. In cases where the displacement step is slow, the stereochemistry of the reaction is controlled by conformational and polar effects.

CHAPTER 3.

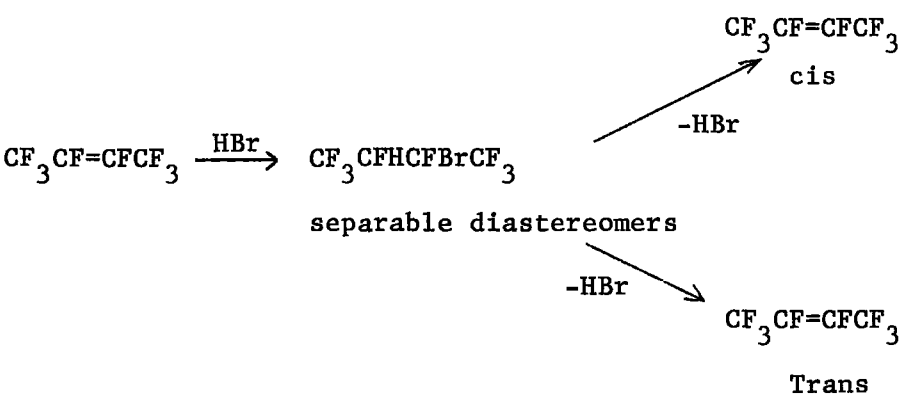
DISCUSSION OF EXPERIMENTAL WORK

PART 1.

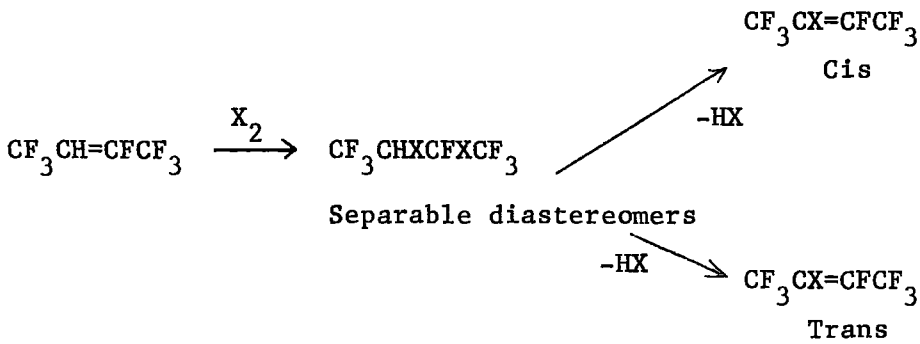
PREPARATION OF PURE GEOMETRICAL ISOMERS OF OCTAFLUOROBUT-2-ENE AND 2H-, 2-CHLORO-, AND 2-BROMOHEPTAFLUOROBUT-2-ENE.

1. Introduction

The study of the stereochemistry of the free radical addition of organic molecules to acyclic fluoroölefins described in this thesis, necessitated the preparation of pure geometrical isomers of the olefins. A survey of olefins which could possibly be used showed that octafluorobut-2-ene was the most suitable on account of its simple structure and ready availability. The most convenient method of obtaining pure geometrical isomers of this olefin was found to be the dehydrobromination of pure diastereomers of the hydrogen bromide adduct.



Pure geometrical isomers of 2-chloroheptafluorobut-2-ene and 2-bromoheptafluorobut-2-ene were obtained in a similar manner, the separable diastereomers of the precursors being obtained by addition of the halogen to 2H-heptafluorobut-2-ene.



(X = Cl, Br).

2. Separation of Cis and Trans Isomers of Octafluorobut-2-ene

Octafluorobut-2-ene was chosen initially for this study since it is commercially available, and the free radical addition of methanol had already been reported to take place in good yield. The ^{19}F N.M.R. spectrum of a sample of the commercial material indicated that the cis and trans isomers were present in a ratio of approximately 30:70 respectively. These showed on analytical V.P.C. as two partially overlapping peaks when a 2 metre column of acetonylacetone at -8°C was used. (The trans form is the lower boiling and had the lower retention time). Since a mixture of these olefins is reported to boil in the range 0.4-3°C [133] it became apparent that separation of the cis and trans forms using preparative scale V.P.C. would be likely to encounter difficulties. Schlag and Kaiser have however reported the separation of geometrical isomers of octafluoro-2-ene using a 35ft.

column with Kel-Fl polymer oil ($\left(CF_2\text{-}CFCl\right)_n$) as stationary phase at $-35^{o}C$.[134]

The problem of separating cis- and trans-octafluorobut-2-ene was overcome by preparing 2H-3-bromoöctafluorobutane by the addition of hydrogen bromide

$$CF_3CF{=}CFCF_3 \xrightarrow{HBr} CF_3CFHCFBrCF_3$$

This compound is a liquid at room temperature and the two diastereomeric forms are separable in preparative scale V.P.C. using a di-n-decylphthalate column. Dehydrobromination of the pure diastereomers yielded pure geometrical isomers of octafluorobut-2-ene since the elimination is stereospecifically trans. The presence of the single hydrogen atom in 2H-3-bromoöctafluorobutane causes a large difference in the polarities of the two forms rendering them separable on a polar chromatographic column. It has been previously noted that aliphatic fluorine compounds containing one or two hydrogen atoms have longer retention times on polar V.P.C. columns than the boiling points would lead us to expect.[135]

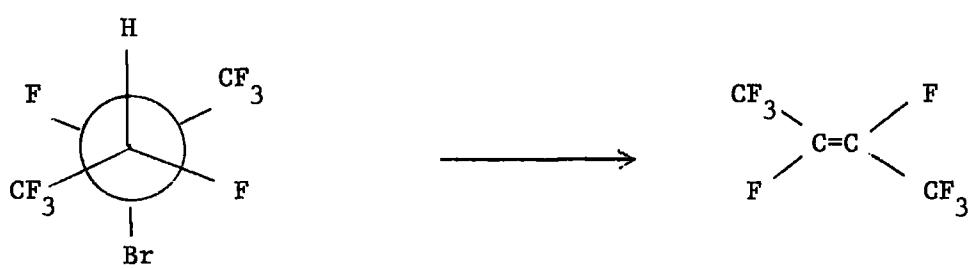
The ultraviolet catalysed addition of hydrogen bromide to octafluorobut-2-ene has been previously reported by Hazeldine and Osborne[27]. In addition to the normal adduct, some 2,3-dibromoöctafluorobutane is also formed by the addition of free bromine from the photolysis of the hydrogen bromide.

$$CF_3CF{=}CFCF_3 + HBr \xrightarrow[\text{u.v. 51 hrs}]{\text{Silica tube}} \underset{60\%}{CF_3CFHCFBrCF_3} + \underset{40\%}{CF_3CFBrCFBrCF_3}$$

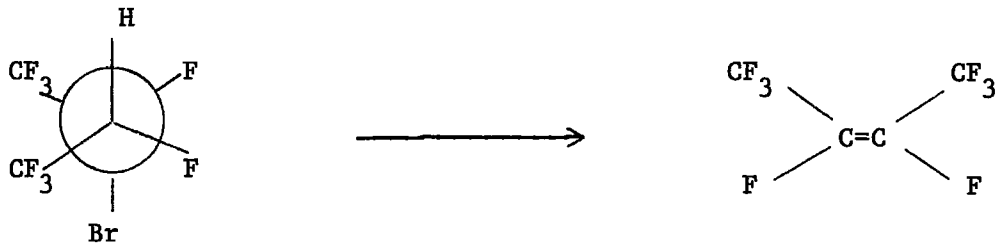
A similar result was obtained in this investigation. In a typical experiment irradiation of a 1:1.14 molar mixture of olefin:hydrogen bromide for 44.1/2 hours resulted in conversion of 65% of the olefin to product (56% $CF_3CFHCFBrCF_3$, 44% $CF_3CFBrCFBrCF_3$).

Since the two diastereomers of 2H-3-bromoöctafluorobutane are liquids boiling in the range 53-54°C separation using preparative scale V.P.C. (di-n-decyl phthalate stationary phase) presented no difficulties. By contrast the 2,3-dibromoöctafluorobutane present showed as an almost symmetrical peak of higher retention time. The presence of the two diastereomeric forms was shown by the ^{19}F N.M.R. spectrum which consisted of four different chemically shifted peaks.

Dehydrobromination of the first diastereomer of 2H-3-bromoöctafluorobutane yielded trans-octafluorobut-2-ene while the second diastereomer gave the cis isomer. (In the following discussion 'first' and 'second' refer to the order of appearance from a di-n-decyl phthalate V.P.C. column).



Diastereomer 1. Trans



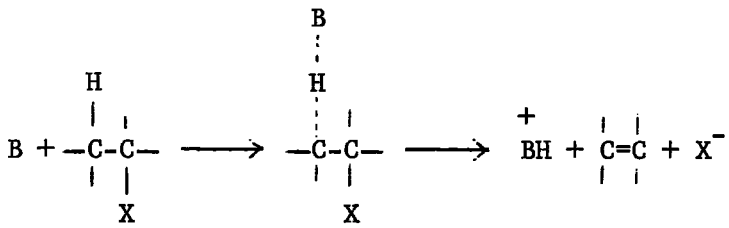
Diastereomer 2. Cis

The two geometrical isomers of the olefin were identified by infrared spectroscopy. In the trans isomer the C=C stretching vibration is infrared inactive owing to the symmetrical nature of the olefin while the cis isomer shows a C=C stretching absorption at 5.77 μ. The ^{19}F N.M.R. spectrum of each isomer consisted of two peaks indicating that each sample must have been at least 95% pure.

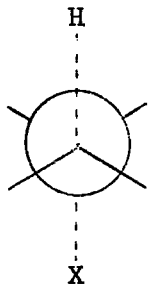
The dehydrobrominations were carried out at room temperature by stirring with 50% aqueous potassium hydroxide solution and yields were generally in the region of 65-75%. Some reactions were also carried out using a saturated solution of methanolic potassium hydroxide but these were found to be less satisfactory, owing to the possibility of ether formation by attack by methoxide ion on the olefin, and the tendency for some methanol vapour to be swept into the cold trap in which the olefin was collected. Other reagents which have been used to prepare fluoroolefins by dehydrohalogenation reactions include alkali metal alkoxides, organic bases such as quinoline and triethylamine,[136]

and alkaline ion exchange resins[137], but potassium hydroxide has found the most extensive application. In general the ease of displacement of halogen decreases in the following order I > Br > Cl > F,[138] hence there was no possibility of hydrogen fluoride being eliminated.

It is generally accepted that these reactions proceed by an E2 mechanism in which the carbon-hydrogen and carbon-halogen bonds are ruptured in the same single step.



The stereoelectronic preference for trans elimination involving a transition state which is anti-coplanar (the C-H, C-C and C-X bonds all in one plane as shown below), is well established.[139] Cis elimination only takes place from rigid substrates in which the attainment of an anti-coplanar configuration is impossible.



Trans elimination

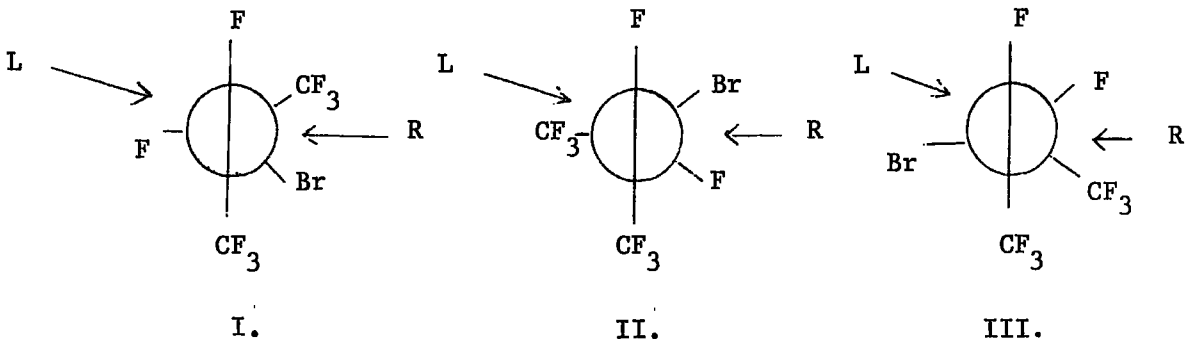
However this well-known fact does not appear to have been used previously for the preparation of pure geometrical isomers of fluoro-olefins.

The addition reaction of hydrogen bromide did not result in the production of equal amounts of the two diastereomers of 2H-3-bromo-octafluorobutane, and this aspect was investigated in more detail. Two small scale reactions were performed in which hydrogen bromide was added to pure cis- and trans-octafluorobut-2-ene, and the results are summarized below.

Olefin mole		HBr mole	Time hrs.	$CF_3CFHCFBrCF_3$ 1:2	% $CF_3CFBrCFBrCF_3$ in prod.
Trans	0.003	0.0068	11	68:32	3
Cis	0.0015	0.0068	11	62:32	11

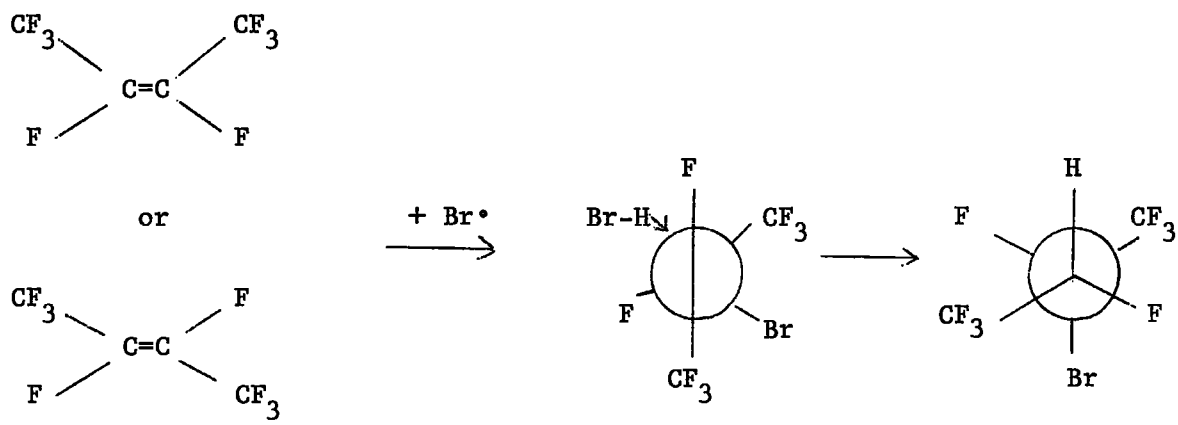
In both cases the first diastereomer of 2H-3-bromooctafluorobutane was the preferred product, indicating that inversion of the intermediate radical $CF_3\dot{C}FCFBrCF_3$ by rotation about the C2-C3 bond occurs before the transfer step. (This is the case using hydrocarbon but-2-enes at 25°C, and Hazeldine and Osborne have shown that fluoroolefins are less reactive than hydrocarbon olefins towards hydrogen bromide[27]). No check was made for olefin isomerization, so this could also have been taking place. The radical centre should be planar or very nearly so, and in the transfer step the hydrogen bromide should approach perpendicular to this plane. The intermediate radical may have three possible

conformations.



I. II. III.

L-attack on any of the rotamers gives the first diastereomer of 2H-3-bromooctafluorobutane. However structure (I) would be expected to be the preferred conformation and if the intermediate radical mainly reacts in this form, then L-attack is clearly favoured. Thus it is postulated that the hydrogen bromide reacted preferentially with a conformation of the intermediate radical in which the bromine is on the opposite side and interaction between the trifluoromethyl groups is at a minimum (i.e. structure I).



The amount of the dibromo compound formed in this reaction appears to vary with both the time of irradiation and the molar ratio of reactants, but this aspect was not investigated further.

3. Preparation of Trans-2H-Heptafluorobut-2-ene.

The preparation of 2H-heptafluorobut-2-ene by treating hexachlorobutadiene with anhydrous potassium fluoride in N-methyl-2-pyrrolidone solvent at approximately 200°C was first reported by Maynard in 1963[140]. The reaction may be done in ordinary glass apparatus, the product being collected in a trap at -78°C and hence this forms a very convenient preparation. Yields of up to 65% may be obtained and the product is almost pure (95% approx.). Complete purification is effected by distillation using vacuum jacketed fractionating column (B.P. product 8.5-15°C [140]). Other polar solvents may be used but in general these are not so effective[140]. The results of three preparations are summarized in Table 7.

Although a detailed mechanism was not given Maynard proposed that the reaction involves the 1,2 addition of 1 mole of hydrogen fluoride derived from initial attack of the solvent and potassium fluoride on the chloro compound, followed by a series of SN2' displacements of chlorine by fluorine. Once initiated this series of reactions tends to go to completion and intermediate compounds are not formed in any significant amounts.

TABLE 7. The Preparation of Trans-2H-Heptafluorobut-2-ene.

Wt. Hexachlorobutadiene g. (mole)		Wt. KF g.(mole)	Vol. Solvent ml.	Temp. °C	Time hrs.	$CF_3CH{=}CFCF_3$ Wt.g.	
133.5	(0.512)	270 (4.65)	750	200	6	55	(59%)
237	(0.909)	885 (15.2)	1500	200	6	102.2	(62%)
262	(1.005)	830 (14.3)	1500	200	7	114.5	(63%)

$$Cl^- + H^+ \longrightarrow HCl$$

$$HCl \xrightarrow{KF} HF$$

$$HF + CCl_2{=}CCl{-}CCl{=}CCl_2 \longrightarrow CCl_2F{-}CHCl{-}CCl{=}CCl_2$$

$$CCl_2F{-}CHCl{-}CCl{=}CCl_2 \xrightarrow[SN2']{KF} CF_3CH{=}CFCF_3$$

Analytical V.P.C. of the purified product gave one major peak, with a second very small one of higher retention time ($<$ 5%). A trace of low boiling material was also present. The ^{19}F N.M.R. spectrum consisted of only three different chemically shifted peaks, and examination of the fine structure showed that these were due to the trans isomer. This result was completely unexpected since Maynard had reported the reaction to yield a mixture of cis and trans isomers with the latter in excess. The ^{19}F N.M.R. spectrum was reported as consisting of three peaks, "doubling of the CF_3 resonances being attributed to cis-trans isomerism" [140].

In order to obtain further information on this point a mixture of cis- and trans-2H-heptafluorobut-2-ene was prepared by addition of chlorine to the trans form, followed by dechlorination of the resulting 2H-2,3-dichloroheptafluorobutane. Since neither of the steps is stereospecific, (see pages 91, 100) this resulted in partial isomerization of the olefin.

$$CF_3CH{=}CFCF_3 \xrightarrow[U.V.]{Cl_2} CF_3CHClCFClCF_3 \xrightarrow{Zn/EtOH} CF_3CH{=}CFCF_3$$

Trans — Cis and Trans

The ^{19}F N.M.R. spectrum of the product consisted of six peaks, and the three new ones were assigned to the cis isomer. This data together with the shifts reported by Maynard are given below (The latter were reported in c.p.s. using a 40-Mc instrument with trifluoroacetic acid as the reference, and have hence been recalculated as shifts in p.p.m from monofluorotrichloromethane as reference).

Chemical Shifts of Cis- and Trans-2H-Heptafluorobut-2-ene in p.p.m. relative to $CFCl_3$ Internal Reference.

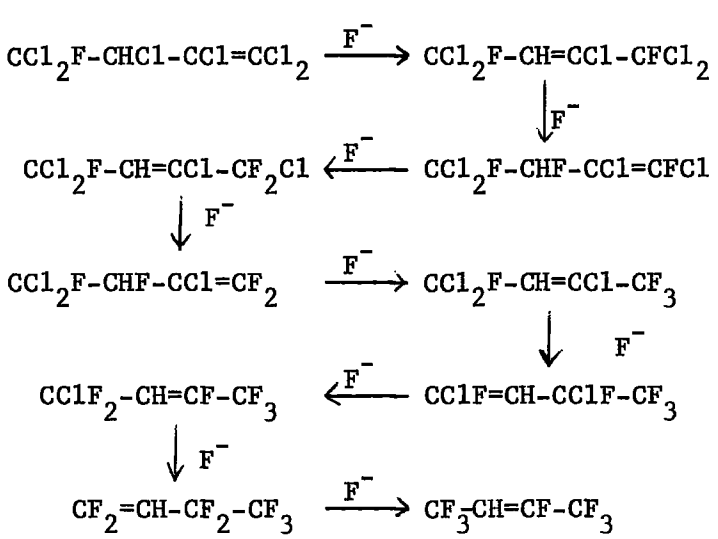
	1-CF_3	4-CF_3	3-F
Trans-$CF_3CH{=}CFCF_3$	+60.4(+63.1)	+74.6(+77.6)	+117.2(+120.6)
Cis-$CF_3CH{=}CFCF_3$	+56.8	+69.6	+113.2

Neat liquids were used. The results reported by Maynard are shown in brackets.

As can be seen the shifts for the trans isomer differ from those reported by a constant value of about 3 p.p.m. This can probably be accounted for by solvent effects or the method of referencing, about which no details were given. Some of the coupling constants for the two

olefins are listed on page 177. It may therefore be concluded that the preparation of 2H-heptafluorobut-2-ene from hexachlorobutadiene gives at least 95% of the trans isomer (limit of detection by N.M.R.). The second small peak of higher retention time in the V.P.C. trace is probably due to the cis isomer, (Maynard reported a similar result). The reported infrared spectrum, and that of the product obtained in these laboratories are identical, while the spectrum of the mixture of geometrical isomers showed additional bands.

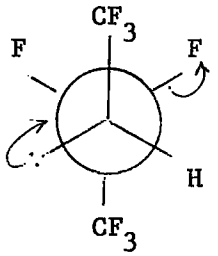
The formation of the trans isomer in this reaction could be due to a conformational preference of the carbanion involved in the final stage of the series of SN2' displacements. This series of reactions probably goes via the following course:

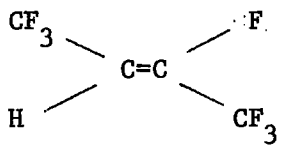


In the final stage the carbanion $CF_3\bar{C}HCF_2CF_3$ could exist in the following conformation in which the trifluoromethyl groups are opposite. Attack by

the electron pair and ejection of a fluoride ion would then take place on opposite sides of the molecule yielding the trans olefin. (Work related to this is discussed in Section 6 of this chapter).

$$CF_2{=}CH{-}CF_2{-}CF_3 \xrightarrow{F^-} CF_3{-}\bar{C}H{-}CF_2{-}CF_3 \quad \text{i.e.}$$





Preferred conformation.

This anion could also be formed by attack by fluoride ion on the 2H-heptafluorobut-2-ene.

$$CF_3CH{=}CFCF_3 \xrightarrow[F^-]{} CF_3\bar{C}HCF_2CF_3$$

If this is the case then it should be possible to convert the cis to the trans form by the same reaction conditions as used in the preparation, but this was not attempted.

Possible methods for obtaining pure cis 2H-heptafluorobut-2-ene are the addition and elimination of hydrogen bromide as used with octafluorobut-2-ene or straight V.P.C. of a mixture of geometrical isomers, (the two forms should be very much more easily separable than those of octafluorobut-2-ene). Neither of these two courses was investigated however.

4. Preparation of 2-Chloroheptafluorobut-2-ene

The ultraviolet initiated addition of chlorine to 2H-heptafluorobut-2-ene followed by dehydrochlorination of the adduct by 50% aqueous potassium hydroxide solution was found to be a very convenient method of obtaining 2-chloroheptafluorobut-2-ene

$$\underset{\text{Trans}}{CF_3CH{=}CFCF_3} \xrightarrow[\text{silica tube}]{Cl_2,\ u.v.} \underset{90\%}{CF_3CHClCFClCF_3} \xrightarrow[50\%\ \text{aq. KOH}]{} \underset{70\%}{CF_3CCl{=}CFCF_3}$$

Several other preparations of this olefin by different routes have been reported. Henne and Newby first reported the preparation of 2-chloroheptafluorobut-2-ene by the fluorination of a mixture of $CCl_2FCF_2CCl{=}CF_2$ and $CCl_3CF_2CCl{=}CF_2$ followed by dehalogenation of the product.[133]

$$CCl_2FCF_2CCl{=}CF_2/CCl_3CF_2CCl{=}CF_2 \xrightarrow[\text{autoclave } 200^oC]{SbCl_2F_3} CF_3CFClCCl_2CF_3 \quad 53\%$$

$$\downarrow \text{Zn/EtOH}$$

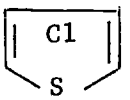
$$CF_3CF{=}CClCF_3$$

Cis and Trans
Quantitative.

Treatment of hexachlorobutadiene with antimony pentachloride in the presence of chlorine and hydrogen fluoride has also given 2-chloroheptafluorobut-2-ene together with 2,3-dichlorohexafluorobut-2-ene.[141]

$$CCl_2{=}CCl{-}CCl{-}{=}CCl_2 \xrightarrow[SbCl_5/HF/Cl_2]{40\text{-}60^{\circ}C:\ 20\ hrs.} CF_3CCl{=}CFCF_3 + CF_3CCl{=}CClCF_3$$

Christe and Pavlath have reported the same products from the reaction of tetrachlorothiophen and antimony pentafluoride[142].



$$\xrightarrow{SbF_5} \underset{19.5\%}{CF_3CF{=}CClCF_3} + \underset{66\%}{CF_3CCl{=}CClCF_3}$$

Two preparations from 2,3-dichlorohexafluorobut-2-ene have been reported[143,144], while Maynard found that 2-chloroheptafluorobut-2-ane was a minor product from the treatment of $CF_3CFClCCl_2CF_3$ and $CF_3CCl_2CCl_2CF_3$ with potassium fluoride in N-methyl-2-pyrrolidone.[140]

A 90% yield (based on chlorine) of 2H-2,3-dichloroheptafluorobut-and was obtained from the ultraviolet irradiation of an almost equimolar mixture of chlorine and trans-2H-heptafluorobut-2-ene in a silica tube for 17.25 hours.

$$\underset{\text{Trans}}{CF_3CH{=}CFCF_3} + Cl_2 \xrightarrow{u.v.} CF_3CHClCFClCF_3 \qquad 90\%$$

Analytical V.P.C. di-isodecyl phthalate column) showed a trace of lower boiling material, in addition to the two diastereomeric forms of the product (separate peaks). No replacement of the hydrogen in the molecule occurred under the conditions of this reaction. However V.P.C. analysis of the products of some later experiments showed a small

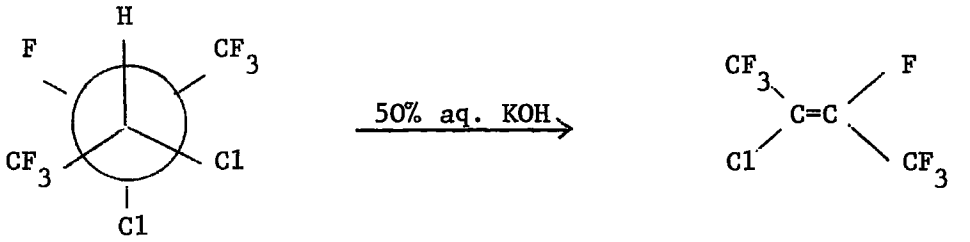
peak of higher retention time which could have been due to $CF_3CCl_2CFClCF_3$ but this aspect was not investigated further. In general liquid phase chlorination of fluorine-containing olefins occurs without substitution of hydrogen[145], but in the vapour phase some substitution of the addition product also takes place. For example, Hauptschein and Bigelow reported the gas phase addition of chlorine to 1,2-dichloro-3,3-difluoropropene to give both the addition product and $CCl_3CCl_2CHF_2$.[146]

$$CHCl{=}CClCHF_2 \xrightarrow{Cl_2} CHCl_2CCl_2CHF_2 + CCl_3CCl_2CHF_2$$

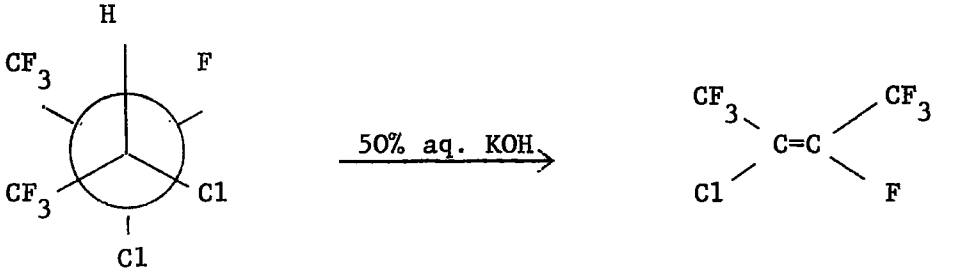
Tedder and co-workers have recently studied the gas phase chlorination and bromination of 1,1,1-trifluoropentane and shown that the trifluoromethyl group exerts a very powerful deactivating effect on halogenation at adjacant sites[147]. Earlier work by Henne and Whaley showed that in the sunlight-catalysed chlorination of $CH_3CH_2CF_3$ the final product is $CCl_3CH_2CF_3$, but that $CH_3CHClCF_3$ yields $CH_3CCl_2CF_3$ indicating that the tendency to accumulate chlorine on the same carbon atom is stronger than the repressive effect of the adjacent trifluoromethyl group[148]. Fredricks and Tedder have discussed the high reactivity of hydrogen atoms attached to the same carbon atom as a halogen, towards halogenation, in more detail[149,150].

Separation of the two diastereomers of 2H-2,3-dichloroheptafluorobutane was easily accomplished by preparative scale V.P.C. (di-n-decyl phthalate stationary phase), the difference in boiling point between

the two forms being of the order of 1-2°C. Dehydrochlorination using 50% aqueous potassium hydroxide at room temperature proceeded smoothly, yields of 2-chloroheptafluorobut-2-ene being in the order of 70%. As in the dehydrobromination of 2H-3-bromooctafluorobutane, the first diastereomer gave the trans olefin while the second gave the cis. The same mechanistic considerations apply as in the previous case.



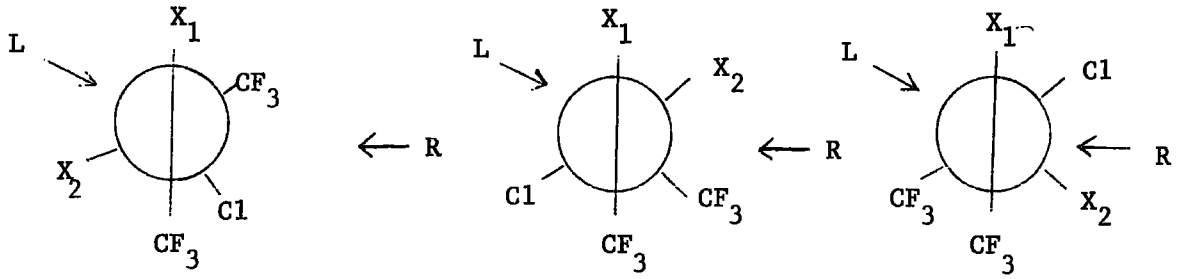
Diastereomer 1.



Diastereomer 2.

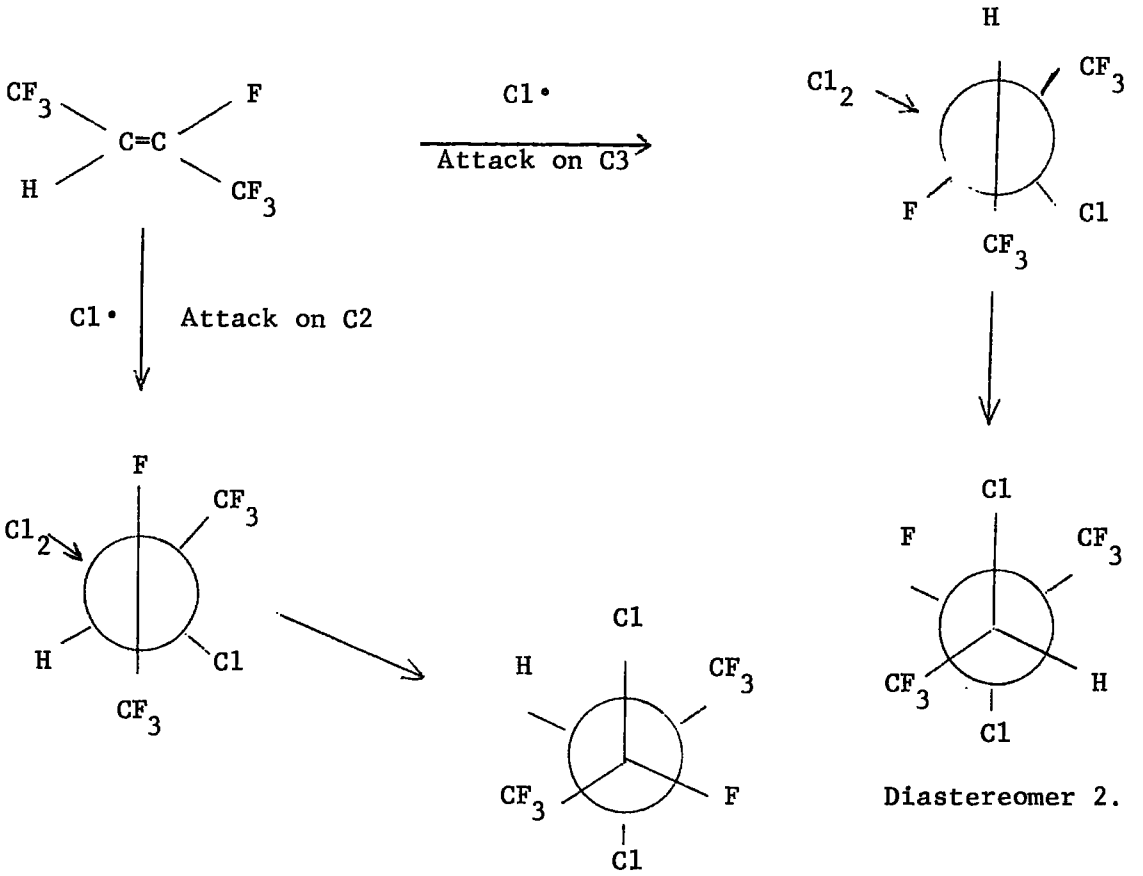
The two isomers of the olefin were indentified by ^{19}F N.M.R. spectroscopy, and these spectra have been fully analysed previously[151]. The infrared spectrum of the cis isomer also showed a very much stronger C=C stretching absorption than the trans form.

V.P.C. analysis of the 2H-2,3-dichloroheptafluorobutane showed that the two diastereomers were produced in a ratio of 41:59 (first: second). Although it was not shown that inversion of the intermediate radical was occurring during the addition of chlorine, this must be the case. Addition of bromine to a mixture of cis and trans 2H-heptafluorobut-2-ene gave the same ratio of diastereomers of $CF_3CHBrCFBrCF_3$ as when the pure trans isomer was used, and bromine is known to be a better transfer agent than chlorine. By the same considerations as apply in the addition of hydrogen bromide to octafluorobut-2-ene, it can be postulated that in the transfer step the chlorine molecule approaches the preferred conformation of the intermediate radical (trifluoromethyl groups opposite), from the least hindered side and this leads to preferential formation of the second diastereomer of $CF_3CHClCFClCF_3$, (trans addition). Comparison of the results reported for the addition of hydrogen bromide to trifluoroethylene (see page 99) indicates that it is likely that initial attack by the chlorine atom can take place at either C2 or C3. Thus two different intermediate radicals, $CF_3\dot{C}HCFClCF_3$ and $CF_3CHCl\dot{C}FCF_3$ should be involved and there are three possible rotamers of each (IV, V, VI). Structure (IV should be preferred and L-attack on this would be favoured giving the second diastereomer (Naturally L-attack on any of the rotamers would give this product).



IV. V. VI.

(X_1 = F, X_2 = H or X_1 = H, X_2 = F)



Diastereomer 2.

Diastereomer 2.

5. Preparation of 2-Bromoheptafluorobut-2-ene

The new fluoroölefin 2-bromoheptafluorobut-2-ene was prepared in an exactly analogous manner to 2-chloroheptafluorobut-2-ene

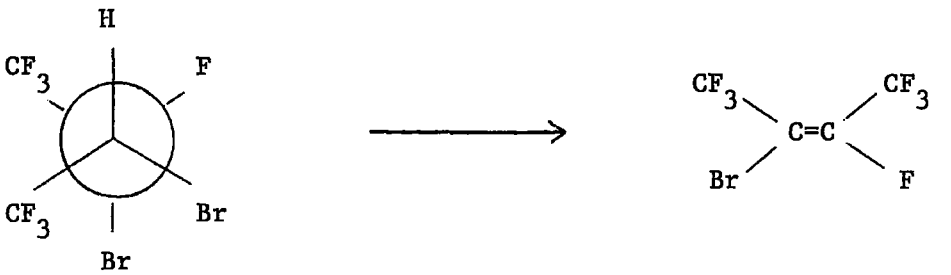
$$CF_3CH{=}CFCF_3 \xrightarrow{Br_2} \underset{\substack{\text{Separable diastereomers} \\ 86\%}}{CF_3CHBrCFBrCF_3} \xrightarrow{50\%\ \text{aq. KOH}} \underset{70\%}{CF_3CBr{=}CFCF_3}$$

The ultraviolet initiated addition of bromine to trans-2H-heptafluorobut-2-ene took place smoothly in a pyrex tube using an approximately equimolar ratio of reactants. No replacement of hydrogen was detected in any of the experiments. Bromination of fluorine containing olefins has been reported to take place without substitution in either the liquid or vapour phase, and bromination of partially fluorinated alkanes usually requires high temperatures.[152]

The two diastereomers of 2H-2,3-dibromoheptafluorobutane were produced in a ratio 34:66 (first:second), the difference in boiling points between the two forms being approximately 2-3°C. They were easily separated using preparative scale V.P.C. with a di-n-decyl phthalate column, as the presence of the single hydrogen atom causes a large difference in polarity as has been seen in other cases.

Dehydrobromination of 2H-2,3-dibromoheptafluorobutane was effected with 50% aqueous potassium hydroxide solution at room temperature,

giving a 70% yield of 2-bromoheptafluorobut-2-ene (identification by ^{19}F N.M.R. spectroscopy). Dehydrobromination of the second diastereomer gave the cis olefin, but the reaction was not performed on a pure sample of the first isomer which would presumably have yielded the pure trans form.



Diastereomer 2.

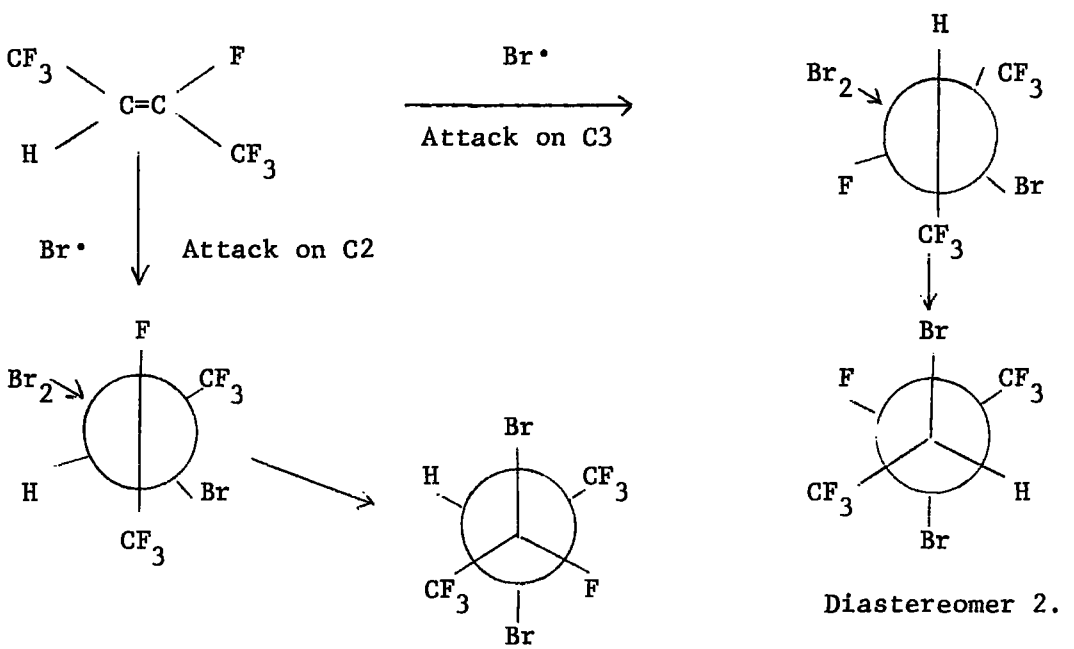
The preferential formation of the second diastereomer of 2H-2,3-dibromoheptafluorobutane may be explained in the same manner as in the addition of chlorine. Exactly analogous structures may be written for the intermediate radical, and in the transfer step the bromine atom tends to approach the least hindered side of a preferred conformation of this. (Inversion of the intermediate radical must take place before the transfer step since addition of bromine to a 2:3 cis: trans mixture of the olefin gives the same product ratio, and no isomerization of the olefin was detected in this reaction). This result is in contrast to the reported stereospecific trans addition of bromine to cis- and trans-but-2-ene-1,4-diol at $0^{o}C$. [128] Hazeldine and Osborne however have shown that the free radical addition

of chlorine and bromine to fluoroölefins takes place less readily than in the hydrocarbon case.[27] The formation of a greater excess of the preferred seond diastereomer with bromine as compared with the addition of chlorine is an indication of the more rigid stereochemical requirements of the larger bromine atom.

The results reported for the addition of hydrogen bromide to trifluoroethylene show that addition of a bromine atom can take place at either end of the molecule.[46]

$$CF_2{=}CFH + HBr \longrightarrow \underset{43\%}{BrCF_2CFH_2} + \underset{57\%}{BrCHFCHF_2}$$

It is thus likely that initial attack by both the chlorine and bromine atoms on 2H-heptafluorobut-2-ene can take place on either C2 or C3, but either intermediate radical leads to the same preferred mode of addition.



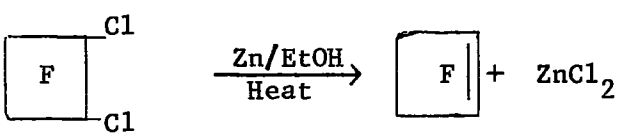
6. Dechlorination of 2H-2,3-Dichloroheptafluorobutane

The dechlorination of 2H-2,3-dichloroheptafluorobutane was investigated in order to enable examination of the ^{19}F N.M.R. spectrum of cis-2H-heptafluorobut-2-ene, and also to investigate the possibility of preparing a pure sample of this isomer by a stereo-specific elimination form a pure diastereomer.

$$CF_3CHClCFClCF_3 \xrightarrow{Zn/EtOH} CF_3CH{=}CFCF_3$$

Mixture of diastereomers — Cis and Trans

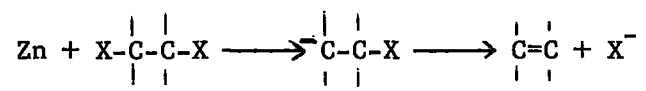
The dehalogenation of the appropriate 1,2-dihalides with zinc dust and a polar solvent such as ethanol is a widely used method for preparing fluoroölefins. Zinc will effect the elimination of chlorine, bromine and iodine but not fluorine. Yields are often quantitative as for example in the last stage of the preparation of perfluoro-cyclobutene[153].



100%

In addition, compound halogens such as ICl, BrCl, and also IF and CCF, may be eliminated by this procedure. The role of the solvent is that of a Lewis base which ties up the zinc halide formed and removes it from the surface of the metal in the form of a complex. Other polar solvents have been used in place of alcohols and magnesium has sometimes been substituted for zinc.[154]

The stereochemistry of the elimination in the reactions has been studied in the hydrocarbon case. Winstein, Pressman and Young proposed that a carbanion intermediate is involved in these reactions when the elimination is effected by iodide ion, and also by zinc[155].



The intermediate carbanion must have only a transient existence since no product of interaction with the solvent has ever been isolated and it is likely that the ion is bonded in some way to the metal surface[156].

Studies on diastereomeric acyclic dibromides have been made, and some of the results of Schubert and co-workers are summarized below[157].

Dibromide	% Trans olefin in product Mg in tetrahydrofuran	Zn in H_2O
95% meso-5% dl-CHDBrCHDBr	96.0, 93.0	96.0, 94.0
meso-$CH_3CHBrCHBrCH_3$	95.3, 94.8	95.2, 96.4
dl-$CH_3CHBrCHBrCH_3$	7.5, 4.6	3.5, 5.0, 3.0
meso-$C_6H_5CHBrCHBrC_6H_5$	98,100	97,100*
dl-$C_6H_5CHBrCHBrC_6H_5$	93, 88, 90	88,89

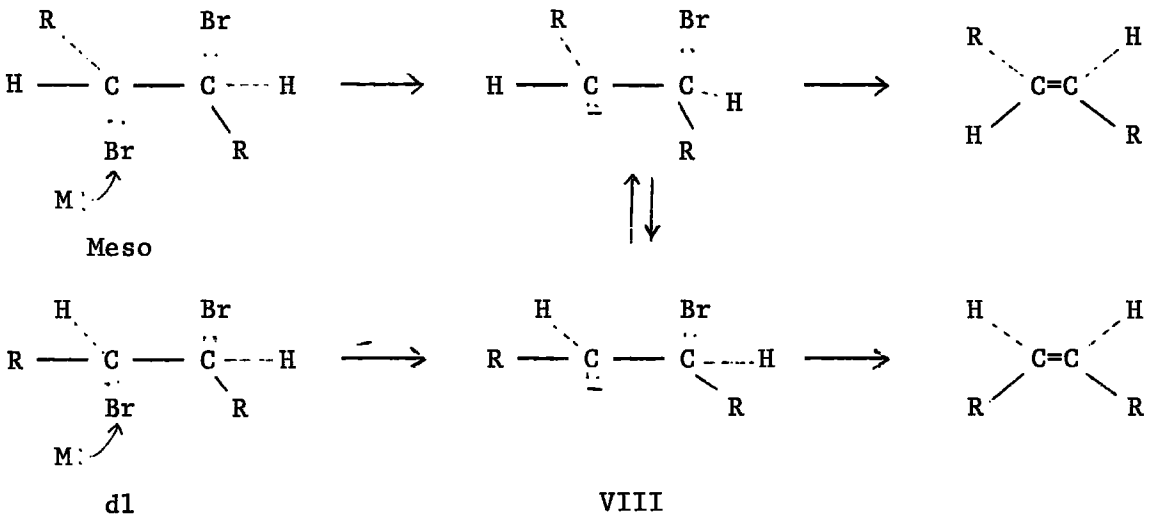
* Ethanol used as solvent.

Meso- and dl-2,3-dibromobutane give almost exclusively the trans and cis olefins respectively, indicating a stereospecific trans elimination process[157,158]. Nucleophilic attack by the metal with its electron pair (or rather electrophilic attack by the bromo compound on the metal

21 SEP 1967 GEORGIA LIBRARY

surface) yields the intermediate carbanion, this being followed by backside attack by the electron pair and ejection of a bromide ion yielding the olefins.

VII.

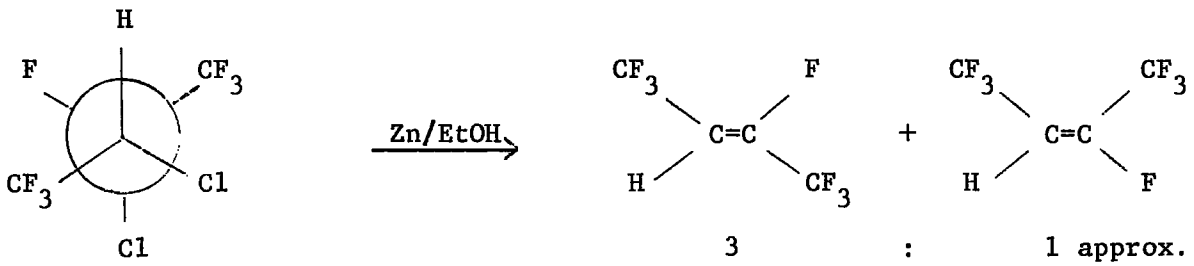


By contrast both the meso and dl forms of 1,2-diphenyl-1,2-dibromoethane give the trans olefin predominantly. In this case the carbanion is stabilized and there is thus time for inversion between (VII) and (VIII) by rotation about the C2-C3 bond. Thus the trans olefin is the predominant product owing to phenyl-phenyl repulsion. A similar result is obtained when the phenyl groups are substituted by carboxyl groups[157].

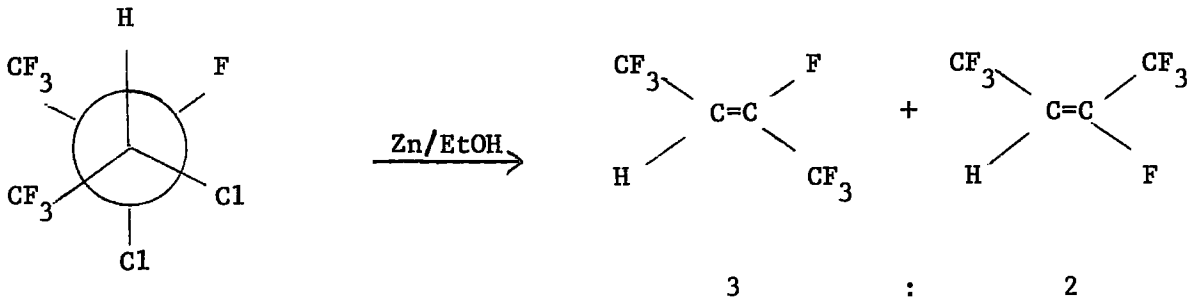
An alternative view of these reactions is that an organometallic compound e.g. BrZnCRHCRHBr is formed[158] through the mediation of a carbanion, and this then breaks down. However it has been pointed out that some reaction with the solvent at either the carbanion or final

organometallic stages would be expected[159]. There is no evidence for radical processes in these reactions.[158]

Treatment of the two diastereomers of 2H-2,3-dichloroheptafluorobutane with zinc in ethanol at 50-60°C yielded both cis- and trans-2H-heptafluorobut-2-ene in each case indicating that the elimination is non-stereospecific (identification by ^{19}F N.M.R. spectroscopy).



Diastereomer 1. Overall yield 72% 3 : 1 approx.

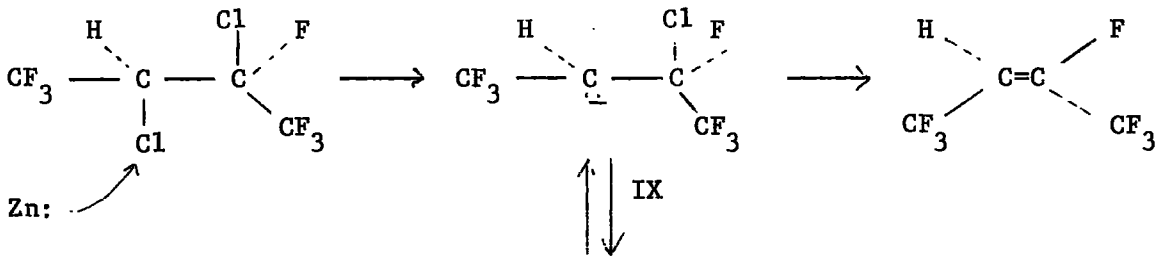


Diastereomer 2. Overall yield 60% 3 : 2

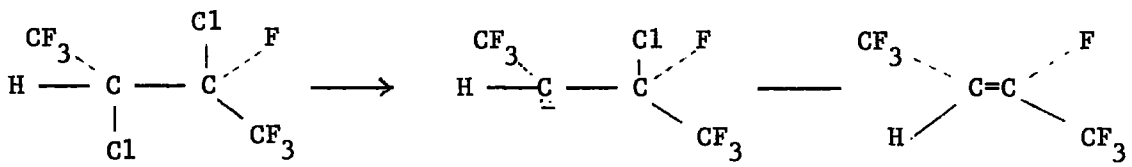
It cannot be stated which chlorine atom is removed by the zinc initially, probably attack would take place at both. Of the two possible intermediate carbanions, $CF_3\bar{C}HCFClCF_3$ would be expected to be more stable than $CF_3\bar{C}FCHClCF_3$ since an α-fluorine stabilizes a carbanion less than a

β-fluorine,[160] and measurements of the acidities of substituted nitromethanes have shown that an α-fluorine is less stabilizing than an α-hydrogen.[161]

The intermediate carbanion would be expected to be very much more stable in the case of the fluorine-substituted butane than in the hydrocarbon case, and hence it is of sufficient lifetime to enable rotation about the C2-C3 bond to take place. Repulsion between the two trifluoromethyl groups results in preferential formation of intermediate (X) leading to the trans olefin. The projections below have been drawn showing abstraction of chlorine at the 2-position. There is no evidence for this, but the steric requirements are similar whichever chlorine is abstracted initially.



Diastereomer 1.



Zn: Distereomer 2.

X

It is difficult to speculate on reasons for the difference in the relative ratios of the geometrical isomers of the olefin produced from the two diastereomers without further data. However the ratios could only be deduced approximately and the difference is probably not of great significance.

CHAPTER 4.

DISCUSSION OF EXPERIMENTAL WORK

PART 2.

STEREOCHEMICAL ASPECTS OF THE FREE RADICAL ADDITION OF SOME ORGANIC MOLECULES TO POLYFLUOROBUT-2-ENES.

1. Introduction

Although free radical additions to fluoroölefins resulting in the formation of both carbon-carbon and carbon-heteroatom bonds have been widely studied particularly for synthetic purposes, very little attention has been directed towards the stereochemical aspects of these reactions. The work described here was principally concerned with the factors affecting the stereochemistry of the addition of aldehydes and alcohols, but the addition of methanethiol and ethyl acetate were also investigated.

No report of an investigation into the stereochemistry of the addition of aldehydes and alcohols to cyclic or acyclic hydrocarbon olefins has appeared in the literature, and almost all the reported additions of these addenda are to terminal olefins. Kisby observed in these laboratories that the addition of acetaldehyde to decafluorocyclohexene gave one predominant product resulting from stereospecific addition and that both cis and trans addition took place with octafluorocyclohexa-1,4-diene, while alcohols added to both these olefins to give both cis and trans products.[45] The present work was therefore undertaken in order to obtain a greater understanding of the factors affecting the stereochemistry of the addition of these addenda by extending the reactions to acyclic fluoroölefins. While this work was in progress Muramatsu and co-workers reported the results of the addition of various alcohols[52], aldehydes[50], and ethers[55] to some cyclic

fluoroölefins and noted the formation of cis and trans isomers of the adducts in various proportions. Nearly all free radical additions to acyclic fluoroölefins involving the formation of new carbon-carbon bonds so far reported have been to terminal olefins. Some additions of polyhaloalkanes to fluorine-containing but-2-enes[27,162] (and also to fluoroacetylenes[163,164]) have been reported but no investigation was made into the stereochemistry involved. Similarly LaZerte and Koshar added methanol to octafluorobut-2-ene but did not investigate the stereochemical aspects.[44]

As has been seen earlier excellent yields of the 1:1 adducts are obtained from the addition of alcohols and aldehydes to perfluoroölefins and hence the fluorine-containing but-2-enes, the preparations of which have been described in chapter 3, were very suitable for this study. Indeed the low reactivity of these addenda with non-terminal acyclic hydrocarbon olefins is presumably the reason why no comparable work has been done in the hydrocarbon case. (The addition of acetaldehyde to cis- and trans-but-2-ene has been reported[165] but since the products are not diastereomeric owing to the presence of two hydrogen atoms on C3 no stereochemical deductions could be made). In every case in the present work the two diastereomeric forms of the adduct $CF_3CHXCFRCF_3$, resulting from the addition of the addend RH, were produced in the same proportions from either the cis or the trans isomer of the olefin.

$$CF_3CX{=}CFCF_3 + RH \longrightarrow CF_3CHXCFRCF_3$$

$$(X = F, Cl)\ (R = RCHOH, RCO, CH_3S).$$

The reactions were initially carried out on a large scale using mixtures of geometrical isomers of the olefins (except in the case of 2H-heptafluorobut-2-ene where large quantities of the trans form were available) to enable characterisation of the adducts. The stereochemical aspects of these reactions were then determined by small scale reactions on pure cis and trans isomers, the ratios of the diastereomeric forms of the products being determined by analytical V.P.C. All of the additions were carried out in sealed evacuated pyrex tubes and in general γ-radiation was used for initiation, but benzoyl peroxide was also found to be a satisfactory initiator for some large scale reactions. In the case of small-scale reactions on pure geometrical isomers of the olefins γ-radiation was the only practicable method of initiation.

2. Reaction Conditions and Yields

a. Alcohol Additions

The addition of methanol to octafluorobut-2-ene, and 2H,- 2-chloro-, and 2-bromoheptafluorobut-2-ene has been studied, the products being the expected fluorine containing primary alcohols. Also, ethanol and n-propanol have been added to octafluorobut-2-ene to give secondary alcohols. With 2-chloroheptafluorobut-2-ene (and presumably also in the

in the 2-bromo case) attack took place exclusively at the carbon bearing the fluorine atom but in the case of 2H-heptafluorobut-2-ene both possible orientations of addition occurred. (Identifications by ^{19}F N.M.R. spectroscopy).

$$CF_3CX{=}CFCF_3 + RCH_2OH \longrightarrow CF_3CHXCF(CF_3)CHOHR$$

Two diastereomers (R = H)

(X = F, Cl, Br. R = H, CH_3, C_2H_5)

$$CF_3CH{=}CFCF_3 + CH_3OH \longrightarrow CF_3CHFCH(CF_3)CH_2OH$$

Two diastereomers

$$+ CF_3CH_2CF(CF_3)CH_2OH$$

The results of the γ-ray initiated additions are given in table 7. The addition of methanol and n-propanol to octafluorobut-2-ene were also investigated using benzoyl peroxide for initiation but yields were not so high. In all cases the two diastereomeric forms of the adducts were separable using V.P.C. with a di-n-decyl phthalate column. The products resulting from the addition of ethanol and n-propanol to octafluorobut-2-ene have three asymmetric centres and exist as four diastereomers.

$$\overset{1}{CF_3}\overset{2}{\underset{*}{C}}H\overset{3}{\underset{*}{C}}F(CF_3)\overset{4}{\underset{*}{C}}HOHR \qquad (R = CH_3,\ C_2H_5)$$

I

* Asymmetric centres in ethanol and n-propanol adducts.

TABLE 7. γ-Ray Initiated Addition of Alcohols to Polyfluorobut-2-enes (Cis-Trans Mixtures).

Olefin	gm (mole)	Addend	gm (mole)	Molar Ratio Addend/Olefin	Irradiation Time (hrs)	Irradiation Total Dose Rads x 10^6	Product(s)	Yield(%)
C_4F_8	26.5(0.133)	CH_3OH	11.7(0.367)	2.76[a]	112.5	22.2	$CF_3CHFCF(CF_3)CH_2OH$	>95[c]
C_4F_8	18.0(0.0900)	C_2H_5OH	14.9(0.323)	3.59[a]	159	31.4	$CF_3CHFCF(CF_3)CHOHCH_3$	>95[c]
C_4F_8	15.5(0.0775)	n-C_3H_7OH	23.7(0.394)	5.02[a]	312	61.5	$CF_3CHFCF(CF_3)CHOHC_2H_5$	>95[c]
C_4F_7Cl	8.5(0.0395)	CH_3OH	6.2(0.194)	4.91	481.5	94.6	$CF_3CHClCF(CF_3)CH_2OH$	94
C_4F_7Br	8.2(0.0314)	CH_3OH	5.2(0.163)	5.17	434	85.5	$CF_3CHBrCF(CF_3)CH_2OH$	14
C_4F_7H[d]	16.7(0.0917)	CH_3OH	10.5(0.328)	3.58	600[b]	54.6	$CF_3CHFCH(CF_3)CH_2OH$ $CF_3CH_2CF(CF_3)CH_2OH$	74

All the reactions were carried out at room temperature (20-25°C) and all the reaction tubes were touching the tube in which the ^{60}Co source was contained.

a. Reactants only partially miscible.

b. Reaction tube 2 cm. from source.

c. Based on olefin recovered

d. Trans isomer.

The V.P.C. trace of these compounds (di-n-decyl phthlate column) showed three peaks, the one of highest retention time being asymmetrical and larger than the other two. Kisby reported that compounds of the type CF_3CHFCF_2CHOHR gave two overlapping peaks on V.P.C. using a di-isodecyl phthalate column[45]. In the latter cases the asymmetric centres are at the 2 and 4 positions and this results in overlapping peaks on V.P.C. The compound resulting from the addition of methanol to octafluorobut-2-ene $CF_3CHFCF(CF_3)CH_2OH$ has asymmetric centres at the 2 and 3 positions and gives two separate peaks on V.P.C. By comparing these results it is thus likely that in compounds of type (I) the first two small peaks on the V.P.C. traces result from diastereomers having the same configurations about the 2 and 3 positions but a different configuration at the 4 position. The third large peak in each case would be expected to result from two diastereomeric forms again having different configurations about the 4 position but having the same configuration about the 2 and 3 positions (which would of course be different from that in the other two diastereomers). This has not been proved however.

Except in the case of 2-bromoheptafluorobut-2-ene high yields of the adducts were obtained. The reaction mixtures were colourless liquids and very little by-product formation took place in any of the reactions. Generally a 3 to 5 molar excess of the alcohol was used, but the molar ratio of reactants did not appear to be particularly

critical. (Muramatsu and co-workers used an approximately 3:1 excess of alcohol/olefin for γ-ray initiated additions to hexafluorocyclobutene). In the case of the additions to octafluorobut-2-ene the olefin formed a separate lower layer inside the tubes, but despite this almost quantitative yields were obtained in these cases. Thus the two reactants must have been at least partially miscible and presumably reaction can take place in either of the layers until the conversion of the olefin is complete giving a homogeneous mixture of the alcohol and adduct.

Total radiation dosages were in the order of 20 to 100 x 10^6 rads but with additions to octafluorobut-2-ene and 2-chloroheptafluorobut-2-ene substantially shorter periods of irradiation would probably have been sufficient. Although the only really valid method of comparing olefin reactivities is by competition reactions it may be noted here that on a purely qualitative basis 2H-heptafluorobut-2-ene appeared to be somewhat less reactive towards methanol than either octafluorobut-2-ene or 2-chloroheptafluorobut-2-ene. This may be explained by greater inductive withdrawal of the π electrons in the latter two olefins making them more susceptible to the strongly nucleophilic α-hydroxyalkyl radicals.

2-bromoheptafluorobut-2-ene and methanol gave only a small yield of the 1:1 adduct after prolonged irradiation. The reaction mixture was slightly yellow in colour but very little product formation had taken

place and starting materials were mostly recovered. This lack of reactivity could possibly be accounted for by increased steric hindrance in this case, although with all these olefins attack takes place on a carbon atom bearing a fluorine and a trifluoromethyl group. Muramatsu has noted a decrease in reactivity in the addition of propan-2-ol to 1-fluoro-1,2,2-trichloroethylene compared with ethanol attributing this to steric hindrance by the chlorine atoms[51]. Possibly the greater stability of the intermediate radical could account for the low reactivity of 2-bromoheptafluorobut-2-ene.

In his studies of alcohol additions to chlorofluoroolefins Muramatsu found the following order of alcohol reactivity $CH_3OH < C_2H_5OH \sim n\text{-}C_3H_7OH < i\text{-}C_3H_7OH$ which is consistent with the amount of hyperconjugative resonance stabilization of the α-hydroxyalkyl radicals formed.[51]

e.g. $$R_2CH\dot{C}ROH \longleftrightarrow R_2C{=}CROH$$
$$\bullet H$$

Any differences in the reactivity of methanol, ethanol, or n-propanol were not detected in these experiments however since the periods of irradiation used were of sufficient length to effect virtually complete conversion of the olefin regardless of the reactivity of the alcohols.

Heating a 2.04:1 molar mixture of methanol and octafluorobut-2-ene at 125°-130°C for 18 hours using benzoyl peroxide (1% by weight) as initiator gave a 50% yield of adduct while a 3.54:1 molar mixture of

n-propanol and octafluorobut-2-ene gave a 33% yield of adduct under similar conditions. In both cases the reactants were miscible at the higher temperature. LaZerte and Koshar have reported the peroxide initiated addition of methanol to this olefin in 70% yield (95% conversion of olefin)[44]. Peroxide initiation was less satisfactory in general due to lower conversions and greater by-product formation and was not used in other cases.

b. Aldehyde Additions

The results of the γ-ray initiated free radical addition of acetaldehyde to the four fluorine containing but-2-enes and also the addition of propionaldehyde to octafluorobut-2-ene are given in table 8. The products were the expected fluoroketones, and the orientation of addition was exactly the same as for the addition of methanol, as would be expected. The structures of the products were again determined by ^{19}F N.M.R. spectroscopy.

$$CF_3CX{=}CFCF_3 + RCHO \longrightarrow CF_3CHXCF(CF_3)COR$$

Two diastereomers

$(X = F, Cl, Br, R = CH_3, C_2H_5)$

$$CF_3CH{=}CFCF_3 + CH_3CHO \longrightarrow CF_3CHFCH(CF_3)COCH_3 + CF_3CH_2CF(CF_3)COCH_3$$

Two diastereomers

Benzoyl peroxide was found to be a satisfactory initiator for the

addition of acetaldehyde to octafluorobut-2-ene a 94% yield of the adduct being obtained, but this was the only case in which this method of initiation was tried. The diastereomeric forms of the adducts $CF_3CHXCF(CF_3)COR$ (X = F, Cl, Br) were separable using preparative scale V.P.C. (di-n-decyl phthalate column) but the two diastereomers of $CF_3CHFCH(CF_3)COCH_3$ gave a single asymmetrical peak. As with the alcohol adducts the infrared and ^{19}F NM.R. spectra of the two forms showed distinct differences and the boiling points differed by several degrees in some cases.

γ-Radiation proved to be a very satisfactory method of initiating these reactions. An excess of the aldehyde was used and in all cases the reactants were miscible at room temperature. Muramatsu and co-workers used approximately 2-3 molar excesses of aldehydes for γ-ray initiated additions to perfluorocyclobutene but in the present work the molar ratio of reactants did not appear to be particularly critical and good yields of the 1:1 adducts were obtained with all the olefins except 2-bromoheptafluorobut-2-ene. Total radiation dosages were in the order of 30-120 x 10^6 rads, but with octafluorobut-2-ene and 2-chloroheptafluorobut-2-ene shorter periods of irradiation would probably have been sufficient as was the case with the addition of methanol.

The reaction mixtures were light brown in colour with a little tarry material present indicating that some by- products were also produced but separation of the adducts from these and the aldehydes was easily

TABLE 8. γ-Ray Initiated Addition of Aldehydes to Polyfluorobut-2-enes (Cis-Trans Mixtures).

	Olefin gm (mole)	Addend gm (mole)	Molar Ratio Addend/Olefin	Irradiation Time (hrs)	Irradiation Total Dose Rads. x 10^6	Product(s)	Yield(%)
C_4F_8	73.1(0.366)	CH_3CHO 22.0(0.499)	1.37	166	32.7	$CF_3CHFCF(CF_3)COCH_3$	89
C_4F_8	19.0(0.0950)	C_2H_5CHO 15.7(0.283)	2.98	159	31.4	$CF_3CHFCF(CF_3)COC_2H_5$	82
C_4F_7Cl	7.65(0.0355)	CH_3CHO 7.9(0.180)	5.06	481.5	94.8	$CF_3CHClCF(CF_3)COCH_3$	85
C_4F_7Br	13.3(0.0509)	CH_3CHO 6.6(0.150)	2.97	434	85.5	$CF_3CHBrCF(CF_3)COCH_3$	6
C_4F_7H*	17.9(0.0984)	CH_3CHO 20.0(0.454)	4.62	595	117.2	$CF_3CHFCH(CF_3)COCH_3$ $CF_3CH_2CF(CF_3)COCH_3$	76

All the reactions were carried out at room temperature (20-25°C) with the reaction tubes touching the tube containing the ^{60}Co source.

* Trans isomer.

effected by fractional distillation. Some paraldehyde may also have been formed in some of the acetaldehyde additions.

2-Bromoheptafluorobut-2-ene and acetaldehyde gave only a very small yield of the 1:1 adduct but large quantities of an unsublimable solid were obtained, this being presumably polymeric material. This might have resulted from cleavage of the carbon-bromine bond of the adduct followed by further reaction of the radicals formed but this reaction was not investigated further. A similar order of olefin reactivity to that in the methanol additions was observed, 2H-heptafluorobut-2-ene appearing to be somewhat less reactive than either octafluorobut-2-ene or 2-chloroheptafluorobut-2-ene. Again this may be explained in terms of greater inductive withdrawal of the π electrons in the latter two cases.

Propionaldehyde added to octafluorobut-2-ene in good yield but it is difficult to make any comparison of the reactivity of this and acetaldehyde from the present results. Muramatsu and co-workers found that acetaldehyde added to perfluorocyclobutene to give a 25% yield of the 1:1 adduct whereas propionaldehyde and butyraldehyde gave 62% and 77% yields respectively[50]. However acetaldehyde and propionaldehyde appear to show about the same reactivity towards 1,2-dichloro-1,2-difluoroethylene and 1,1-dichloro-2,2-difluoroethylene.[60]

The peroxide initiated addition of acetaldehyde to octafluorobut-2-ene took place in 94% yield when a 1.36:1 molar ratio of addend

to olefin was used. LaZerte and Koshar found that 1:1 molar mixtures of various aldehydes and perfluoroölefins gave excellent yields using peroxide initiation.[44] In the present case however rather more by-products were formed than from the γ-ray initiated addition, and this was the only reaction in which peroxide initiation was used.

c. Thiol Additions.

Methanethiol has been added to octafluorobut-2-ene and 2H-hepta-fluorobut-2-ene using γ-ray initiation

$$CF_3CF{=}CFCF_3 + CH_3SH \longrightarrow CF_3CHFCF(CF_3)SCH_3 \qquad 52\%$$

Separable diastereomers

(Molar ratio thiol:olefin = 2.09:1 Total dose = 31.7×10^6 rads)

$$CF_3CH{=}CFCF_3 + CH_3SH \longrightarrow CF_3CHFCH(CF_3)SCH_3 \qquad 26\%$$

Trans Separable diastereomers

(Molar ratio thiol:olefin = 1.89:1 Total dose = 26.7×10^6 rads)

The reaction mixtures were pale yellow liquids but very little by-product formation occurred in the addition to octafluorobut-2-ene. In the case of 2H-heptafluorobut-2-ene only the diastereomeric products resulting from radical attack at the carbon bearing the hydrogen atom were isolated. V.P.C. analysis of the reaction product indicated the presence of another component the proportions of which varied with the experimental conditions, but ^{19}F N.M.R. spectroscopy showed that this was

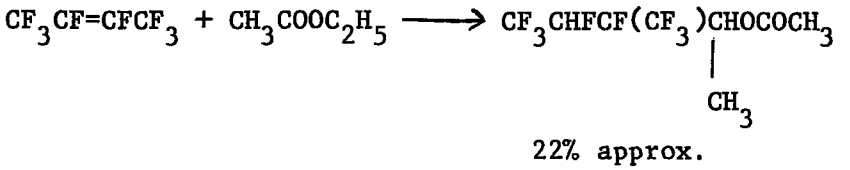
not the product resulting from attack at the other end of the double bond, and it was not characterised. The possibility of the product resulting from the opposite orientation of addition being formed in small amounts and escaping detection remains however.

The electrophilic nature of thiyl radicals has been previously noted and hence lower yields would be expected for thiol additions to these olefins compared with those obtained for alcohols and aldehyde additions, as is observed. Harris and Stacey report that little or no adduct could be obtained from the ultraviolet initiated addition of the extremely electrophilic $CF_3S\bullet$ radical to octafluorobut-2-ene although it added to hexafluoropropene and other terminal fluoroolefins[41]. This demonstrates the low reactivity of thiols towards addition to internal fluoroolefins.

X-rays and ultraviolet light have been used to initiate the addition of thiols to fluoroolefins[41] and Kisby reported the γ-ray initiated addition of methanethiol to hexafluoropropene in 88% yield.[45] No other method of initiation was investigated in the present work however.

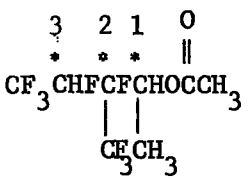
d. Addition of Ethyl Acetate to Octafluorobut-2-ene.

Esters have generally been found to be rather unreactive addenda and only low yields were obtained in the addition of ethyl acetate to octafluorobut-2-ene



22% approx.

(Molar ratio ester:olefin = 3.18:1 Total dose = 80.4 x 10^6 rads). The major product resulted from cleavage of an α-carbon-hydrogen bond in the ethyl group of the ester. It is separable into two forms by preparative scale V.P.C. (di-n-decyl phthalate column), these presumably being due to the asymmetric centres at C2 and C3, (by comparison with additions which yielded only two diastereomers). Each of these forms shows as two overlapping peaks and this is presumably due to asymmetry at C1. There are thus four diastereomers of this compound.



* Asymmetric centres.

2,3,4,4,4-Pentafluoro(2-trifluoromethyl)(1-methyl)butyl acetate

V.P.C. analysis of the reaction mixture indicated that some minor products were also present (20% of the total product) and these may possibly have been the adducts resulting from cleavage of a carbon-hydrogen bond in the acetate group of the addend, but no positive identification was made.

Cadogan and co-workers have shown that high addend/olefin ratios are necessary for ester additions to hydrocarbon olefins[69,70] and fluoro-olefins do not seem to show any marked increase in reactivity. Only low

yields have been reported for the addition of ethyl acetate and diethyl malonate to various fluoroölefins[45]. Kisby has postulated that the initial formation of the radical from the ester rather than the ease of attack on the olefin is the limiting factor in these reactions.[45]

3. Orientation of Addition.

The addition of acetaldehyde and methanol to 2-chloroheptafluoro-but-2-ene gave only the products resulting from radical attack at the carbon bearing the fluorine atom. (Identification by ^{19}F N.M.R. spectroscopy). This would be predicted since these are favoured on both radical stability (chlorine more stabilizing than fluorine) and polar grounds

e.g. $CF_3CF(R)\dot{C}ClCF_3$ more stable than $CF_3CCl(R)\dot{C}FCF_3$

$$\overset{\delta+}{CF_3CF}=\overset{\delta-}{CClCF_3}$$

The polarization of the double bond would be expected to be as shown above owing to the greater positive π-inductive effect of fluorine compared with chlorine,[166,167] and hence attack by the nucleophilic acyl and α-hydroxyalkyl radicals would be expected to take place in the observed direction. (Nucleophilic attack on chlorotrifluoroethylene occurs exclusively on the CF_2 group[168]). The relative stabilities of the two possible intermediate radicals must be the predominant effect

however since attack by the extremely electrophilic $CF_3S\cdot$ radical on chlorotrifluoroethylene also takes place at the more positive CF_2 group.[41]

The same considerations apply in the addition of methanol and acetaldehyde to 2-bromoheptafluorobut-2-ene, only the two diastereomeric forms of the structures $CF_3CHBrCFRCF_3$ (R = CH_2OH, CH_3CO) being obtained in each case. The orientation of addition with this olefin was not proved however. Additions of aldehydes to bromotrifluoroethylene have been reported to yield only products of the structure $RCOCF_2CHBrF$ (R = alkyl group)[63].

Addition of acetaldehyde and methanol to 2H-heptafluorobut-2-ene yielded both possible products, but in the addition of methanethiol only the product resulting from attack on the carbon bearing the fluorine atom was detected.

$$CF_3CH{=}CFCF_3 + CH_3CHO \longrightarrow \underset{76\%}{CF_3CHFCH(CF_3)COCH_3} + \underset{24\%}{CF_3CH_2CF(CF_3)COCH_3}$$

$$CF_3CH{=}CFCF_3 + CH_3OH \longrightarrow \underset{72\%}{CF_3CHFCH(CF_3)CH_2OH} + \underset{28\%}{CF_3CH_2CF(CF_3)CH_2OH}$$

$$CF_3CH{=}CFCF_3 + CH_3SH \longrightarrow CF_3CHFCH(CF_3)SCH_3$$

In the addition of acetaldehyde the minor product had the lower retention time on V.P.C. (di-n-decyl phthalate column) while in the case of methanol the gas chromatogram of the product showed three peaks,

the middle one being due to the minor adduct and the other two arising from the two diastereomeric forms of $CF_3CFHCH(CF_3)CH_2OH$. 2H-heptafluorobut-2-ene may be compared with trifluoroethylene and several additions to the latter olefin have been reported to take place at both ends of the molecule, the results being listed in table 9.

As postulated by Hazeldine and Steele[46], there is little difference in the stabilities of the two possible intermediate radicals, $RCHF\dot{C}F_2$ being somewhat more stable than $RCF_2\dot{C}HF$. The polarization of the double bond is as follows $\overset{\delta+}{C}F_2=\overset{\delta-}{C}HF$, due to the positive π inductive effect of the fluorine atoms and the relative amounts of attack on the CHF group can be correlated with the electrophilicities of the radicals. Thus the $CF_3S\bullet$ radical shows more tendency to attack the negative CHF group than the less electrophilic $CH_3S\bullet$ radical.

Similarly the direction of polarization of the double bond in 2H-heptafluorobut-2-ene would be expected to be $CF_3\overset{\delta-}{C}H=\overset{\delta+}{C}FCF_3$ and this factor should be important since the two possible intermediate radicals would not be expected to differ greatly in stability. Thus attack by the nucleophilic acyl and α-hydroxyalkyl radicals is favoured at C3 on polar grounds, while the relative stabilities of the two intermediate radicals favour attack at C2 ($CF_3CHR\dot{C}FCF_3$ would be expected to be rather more stable than $CF_3\dot{C}HCFRCF_3$). It is surprising that the relative amounts of attack by the $CH_3\dot{C}O$ and $\bullet CH_2OH$ radicals on the relatively positive C3 atom in 2H-heptafluorobut-2-ene are only

TABLE 9. Orientation of Some Free Radical Additions to Trifluoroethylene.

Radical	%Attack on Starred Carbon Atom		Reference
	$CF_2{=}\overset{*}{C}HF$	$\overset{*}{C}F_2{=}CHF$	
$CF_3S\bullet$	98	2	41
$CH_3S\bullet$	75	25	41
$Br\bullet$	57	43	46
$HS\bullet$	85	15	74
$CF_3\bullet$	80	20	46
$CF_2Br\bullet$	80	20	169

about the same as the proportion of attack by the electrophilic $CH_3S\bullet$ radical on the CF_2 group in trifluoroethylene. However, this observation that attack on C3 in 2H-heptafluorobut-2-ene is relatively less favoured compared with attack on the CF_2 group in trifluoroethylene is in line with the fact that in the addition of methanethiol to the former olefin no product resulting from attack by the $CH_3S\bullet$ radical at C3 was definitely established (Attack by the $CH_3S\bullet$ radical at this position is less favoured on both radical stability and polar grounds).

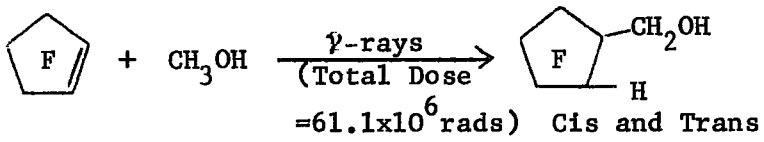
It is difficult to give any precise explanation for these results. As has been noted in section 2c, internal fluoroölefins seem to be very unreactive towards thiyl radicals. It could be that the greater degree of steric interaction (producing the decrease in reactivity) in the case of 2H-heptafluorobut-2-ene compared with trifluoroethylene could be sufficient to eliminate attack by the $CH_3S\bullet$ radical at the unfavoured C3 position altogether. However the difference in the amounts of steric hindrance involved in attack at either end of the double bond in 2H-heptafluorobut-2-ene would not be expected to be great.

As has been seen in table 4 attack by the $CF_3S\bullet$ and $CH_3S\bullet$ radicals on hexafluoropropene takes place at the more hindered 2-position in proportions of 55% and 9% respectively. (Attack at this position is favoured only on polar grounds, $CF_3\overset{\delta-}{C}F=\overset{\delta+}{C}F_2$). Harris and Stacey have

suggested that in this case the transition state involved in attack by thiyl radicals on C2 could be stabilized by interaction of the thiyl radical with the negative screen of the fluorine atoms in the trifluoromethyl group and the relatively negative carbon atom[41] (page 38). If this is the case then this factor would also favour attack by the $CH_3S\cdot$ radical at the relatively negative C2 carbon atom in 2H-heptafluorobut-2-ene. In the absence of more data however it is impossible to speculate further on this topic.

4. Addition of Methanol to Octafluorocyclopentene.

No free radical additions of organic molecules to octafluorocyclopentene have been previously reported and only the addition of methanol was investigated in this work. Irradiation of a 5.05:1 molar mixture of methanol and octafluorocyclopentene gave an approximately 60% yield of 2H-octafluorocyclopentylmethanol



The reactants were only partially miscible at room temperature, the olefin forming a separate lower layer in the tube. The olefin was very unreactive and a long period of irradiation was necessary in order to obtain a satisfactory yield of the adduct. Muramatsu and co-workers have found that the addition of alcohols to 1,2-dichlorohexafluoro-

cyclopentene results in the almost exclusive formation of the dehydrochlorinated adducts[52] (page 35). Since the radical dechlorination competes with the transfer step this indicates the low reactivity of this system also.

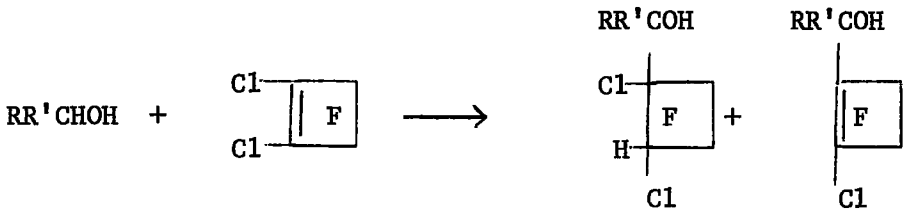
No significant yield of adducts could be obtained using benzoyl peroxide as initiator illustrating the superiority of γ-ray initiation in cases where the olefin is unreactive. The cis and trans isomers of the product gave separate peaks on a di-n-decyl phthalate V.P.C. column and were produced in a ratio of approximately 60:40. The structures were not assigned however and hence it is not known whether cis or trans addition is preferred.

5. Stereochemistry of Addition.

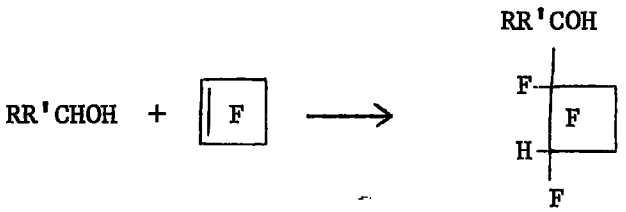
The stereochemical aspects of the reactions which have been described in the previous sections were studied by means of small scale reactions on pure geometrical isomers of the olefins. The ratios in which the diastereomeric products were produced were determined using analytical V.P.C. except in the addition of acetaldehyde to 2H-heptafluorobut-2-ene where ^{19}F N.M.R. spectroscopy was used. The results for alcohols and aldehydes are summarized in tables 10 and 11 and full details of the reaction conditions are given in the experimental section. In view of the low reactivity of 2-bromoheptafluorobut-2-ene no additions to pure geometrical isomers of this olefin were carried out.

a. Alcohol Additions

Muramatsu and co-workers have reported the addition of various alcohols to 1,2-dichlorotetrafluorocyclobutene and hexafluorocyclobutene and the results have been summarized on pages 33 and 34.



Cis and trans.



Cis and trans.

(R,R' = H or alkyl)

The results for 1,2-dichlorotetrafluorocyclobutene were attributed to steric effects (page 34). The proportions of cis and trans forms of the adducts produced in the addition of alcohols to hexafluorocyclobutene however show no definite trend when related to the size of the alkyl group in the alcohol. Kisby found that the addition of various alcohols to decafluorocyclohexene and octafluorocyclohexa-1,4-diene gave both cis and trans forms of the adducts[45]. ^{19}F N.M.R. spectroscopy has shown

TABLE 10. γ-Ray Initiated Additions of Alcohols to Cis- and Trans-Polyfluorobut-2-enes.

Addend	Olefin	Molar Ratio Addend/Olefin	Product	Ratio of Diastereomers (1st:2nd)
CH_3OH	Cis-C_4F_8[a]	3.13	$CF_3CHFCF(CF_3)CH_2OH$[d]	47:53
CH_3OH	Trans-C_4F_8[a]	4.20	$CF_3CHFCF(CF_3)CH_2OH$[d]	44:56
CH_3OH	Trans-C_4F_8[a c]	0.24	$CF_3CHFCF(CF_3)CH_2OH$[d]	42:58
CH_3OH	Cis-C_4F_7Cl	3.92	$CF_3CHClCF(CF_3)CH_2OH$[d]	35:65
CH_3OH	Trans-C_4F_7Cl	2.21	$CF_3CHClCF(CF_3)CH_2OH$[d]	38:62
CH_3OH	Cis-C_4F_7Cl[b]	8.38	$CF_3CHClCF(CF_3)CH_2OH$[d]	23:77
CH_3OH	Trans-C_4F_7Cl[b]	3.36	$CF_3CHClCF(CF_3)CH_2OH$[d]	26:74
C_2H_5OH	Trans-C_4F_8[a]	1.65	$CF_3CHFCF(CF_3)CHOHCH_3$	22:28:50[e]
n-C_3H_7OH	Trans-C_4F_8[a]	2.80	$CF_3CHFCF(CF_3)CHOHC_2H_5$	17:31:52[e]
CH_3OH	Trans-C_4F_7H	5.38	$CF_3CHFCH(CF_3)CH_2OH$[f]	58:42

a. Reactants only partially miscible.

b. Reaction carried out at -78° to -60°C.

c. No isomerization of recovered olefin.

d. No interconversion to the other form was detected when a pure diastereomer was irradiated in the presence of methanol.

e. The last figure is for a mixture of diastereomers resulting from asymmetry about C4 (see page 109).

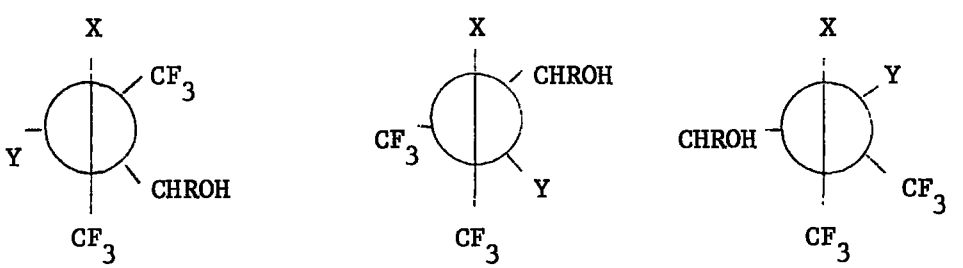
f. $CF_3CH_2CF(CF_3)CH_2OH$ also produced.

that in the addition of methanol, ethanol, n-propanol and n-butanol cis addition is preferred, the major products having the hydroxyalkyl group equatorial and the hydrogen atom axial, while the minor product has both groups equatorial.[170] (No interconversion between the two chair conformations of the cyclohexane ring takes place in any of the adducts). Thus in these cases the bulky hydroxyalkyl group goes into the least crowded equatorial position and again the stereochemistry of the reactions appears to be controlled by steric effects.

The results of the free radical addition of various alcohols to pure geometrical isomers of the polyfluorobut-2-enes are given in Table 10. Where both geometrical isomers of an olefin were used it may be seen that the diastereomers of the products were produced in the same ratio in each case indicating that the two possible forms of the intermediate radicals equilibrate before the transfer step. No olefin isomerization was detected when methanol was irradiated with an excess of trans-octafluorobut-2-ene.

Stereoselectivity of addition was most marked in the addition of methanol to 2-chloroheptafluorobut-2-ene, and additions to octafluorobut-2-ene and 2H-heptafluorobut-2-ene also showed a slight stereoselectivity. (The two diastereomers of $CF_3CHBrCF(CF_3)CH_2OH$ were produced in a ratio of approximately 40:60 when a mixture of geometrical isomers of 2-bromoheptafluorobut-2-ene was used and inversion of the intermediate radical must take place in this case also.) At the

present time the structures of the diastereomers of the products have not been assigned however and hence it is difficult to account for the preferential formation of one form. The intermediate radicals may have three possible conformations as shown below and the variation in preference for attack on either side of the radical centre presumably depends on the relative magnitudes of the steric repulsions (or possibly polar effects) in each case. These appear to show little variation and the results for the addition of ethanol and n-propanol to trans-octafluorobut-2-ene show that increasing the size of the alkyl group on the alcohol has little or no effect.



(R = H, CH_3, C_2H_5, X = F, Cl, Br, Y = F, H).

Additions of methanol to pure geometrical isomers of octafluorobut-2-ene and 2-chloroheptafluorobut-2-ene in a temperature range of -78°C to -60°C were also carried out. No adducts were obtained with the former olefin however, this being probably due to the immiscibility of the reactants. With 2-chloroheptafluorobut-2-ene however it may be seen that the preference for the major diastereomer of $CF_3CHClCF(CF_3)CH_2OH$

was slightly increased. This is presumably due to the fact that the formation of the minor diastereomeric form is somewhat less favourable energetically.

A possible method for assigning the structures of the diastereomers is by dehydrofluorination reactions and determination of the structures of the olefinic products, but this was not attempted. (The secondary fluorine atom would certainly be eliminated preferentially).

e.g. $CF_3CHXCF(CF_3)CH_2OH \longrightarrow CF_3CX{=}C(CF_3)CH_2OH$

(X = F, Cl)

$CF_3CHFCH(CF_3)CH_2OH \longrightarrow CF_3CH{=}C(CF_3)CH_2OH$

Kisby has reported the dehydrofluorination of $CF_3CFHCF_2CHOHC_2H_5$ using 2.5N aqueous potassium hydroxide solution at 100°C yielding $CF_3CF{=}CFCHOHC_2H_5$.[45]

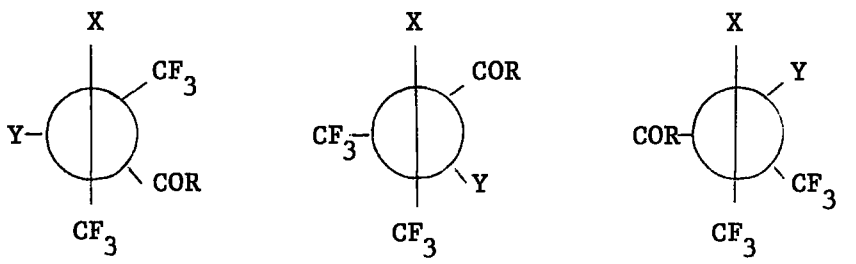
b. Aldehyde Additions.

The results reported by Muramatsu and co-workers for the addition of aldehydes to hexafluorocyclobutene (see page 29) show a consistent preference for trans addition with little variation with the size of the alkyl group.[50] Kisby showed that acetaldehyde adds to decafluorocyclohexene virtually stereospecifically,[45] and the ^{19}F N.M.R. spectrum of the product has shown that the acyl group occupies an equatorial position, with the hydrogen atom axial.[170] (Chair-chair interconversion of the cyclohexane ring of the adduct does not take place). Thus cis

addition is preferred in this case. With octafluorocyclohexa-1,4-diene both cis and trans addition of acetaldehyde occurs.[45]

The results for aldehyde additions to pure geometrical isomers of the polyfluorobut-2-enes are listed in table 11. As with the alcohol additions interconversion of the two possible forms of the intermediate radical took place before the displacement step since the diastereomeric products were produced in the same ratios from either the cis or trans forms of the olefins. Olefin isomerization was also found to take place however, in the addition of acetaldehyde to trans-octafluorobut-2-ene about 20% of the recovered olefin from this reaction having been converted to the cis form.

In all the additions the formation of one diastereomer was preferred. (The addition of acetaldehyde to a mixture of cis- and trans-2-bromoheptafluorobut-2-ene gave the two diastereomers of $CF_3CHBrCF(CF_3)COCH_3$ in a ratio of approximately 66:34). As has been shown in previous cases the intermediate radical may have three possible conformations. Little can be said about the relative stability of these.



(R = CH_3, C_2H_5, X = F, Cl, Br, Y = F, H).

TABLE 11. γ-Ray Initiated Additions of Aldehydes to Cis- and Trans-Polyfluorobut-2-enes.

Addend	Olefin	Molar Ratio Addend/Olefin	Product	Ratio of Diastereomers (1st:2nd)
CH_3CHO	Cis-C_4F_8	1.48	$CF_3CHFCF(CF_3)COCH_3$ [d]	78:22
CH_3CHO	Trans-C_4F_8	2.20	$CF_3CHFCF(CF_3)COCH_3$ [d]	76:24
CH_3CHO	Trans-C_4F_8 [b]	0.18	$CF_3CHFCF(CF_3)COCH_3$ [d]	83:17
C_2H_5CHO	Cis-C_4F_8	1.13	$CF_3CHFCF(CF_3)COC_2H_5$ [e]	72:28
C_2H_5CHO	Trans-C_4F_8	1.30	$CF_3CHFCF(CF_3)COC_2H_5$ [e]	76:24
CH_3CHO	Cis-C_4F_7Cl	2.42	$CF_3CHClCF(CF_3)COCH_3$ [d]	61:39
CH_3CHO	Trans-C_4F_7Cl	3.66	$CF_3CHClCF(CF_3)COCH_3$ [d]	62:38
CH_3CHO	Cis-C_4F_7Cl [a]	2.71	$CF_3CHClCF(CF_3)COCH_3$ [d]	68:32
CH_3CHO	Trans-C_4F_7Cl [a]	8.14	$CF_3CHClCF(CF_3)COCH_3$ [d]	70:30
CH_3CHO	Trans-C_4F_7H	4.28	$CF_3CHFCH(CF_3)COCH_3$	64:36 [c]

All reactions were carried out at room temperature except where otherwise indicated.

a. Reaction in the temperature range -78° to $-60^{o}C$.

b. Approximately 20% of the recovered olefin was isomerized to the cis form.

c. From ^{19}F N.M.R. spectroscopy.

d. No interconversion to the other form was detected when a pure diastereomer was irradiated in the presence of acetaldehyde.

e. No interconversion when a pure diastereomer was irradiated alone.

It cannot be definitely stated why one mode of addition is preferred. Propionaldehyde shows almost exactly the same stereoselectivity as acetaldehyde in these results and in those for addition to hexafluorocyclobutene,[50] and hence the size of the alkyl group does not appear to be an important factor. The addition of acetaldehyde to 2-chloroheptafluorobut-2-ene (and also to the 2-bromo olefin) is less stereospecific than with octafluorobut-2-ene despite the fact that displacement takes place on a radical centre to which the larger chlorine atom is attached on the latter case. It may be that polar interaction of the carbonyl group ($\overset{\delta+}{C}=\overset{\delta-}{O}$) with the intermediate radical is an important factor in these additions but this is only speculative. An attempt to assign the structure of the major diastereomer produced in the addition of acetaldehyde to octafluorobut-2-ene was unsuccessful (section 6 of this chapter).

c. Addition of Methanethiol.

No work on the stereochemistry of thiol additions to fluoroolefins has been reported despite the fact that this subject has received wide attention in the hydrocarbon case. The results of the addition of methanethiol to cis- and trans-octafluorobut-2-ene and trans-2H-heptafluorobut-2-ene are given below

Olefin	Ratio of Methanethiol/ Olefin	Product	Ratio of Diastereomers (1st:2nd)
Cis-C_4F_8	1.86 *	$CF_3CHFCF(CF_3)SCH_3$	45:55
Trans-C_4F_8	1.70 *	$CF_3CHFCF(CF_3)SCH_3$	46:54
Trans-C_4F_7H	1.89	$CF_3CHFCH(CF_3)SCH_3$	59:41

All reactions carried out at room temperature.

* Reactants only partially miscible.

Additions of thiols to hydrocarbon but-2-enes at 25°C are non-stereospecific and as fluoroolefins are less reactive it would be expected that inversion of the intermediate radical would take place before the transfer step in these cases as is observed. The same considerations apply as in the additions of aldehydes and alcohols, and it is surprising that very little stereoselectivity of addition is observed in view of the large size of the sulphur atom upon which displacement takes place. It is not known whether any olefin isomerization occurs in these reactions but no conversion to the other form took place when a pure diastereomer of either adduct was irradiated in the presence of methanethiol.

Neureiter and Bordwell found that the addition of thiolacetic acid to 2-chlorobut-2-ene was stereoselective and accounted for this in terms of polar and steric effects in the transfer step[104] (page 62). Similar effects do not seem to be very important in the present cases however, although in the case of 2H-heptafluorobut-2-ene the addition is rather more selective. The structures of the adducts could possibly have been assigned by dehydrofluorination reactions similar to those proposed for the alcohol adducts but these were not investigated.

d. Addition of Ethyl Acetate to Trans-Octafluorobut-2-ene.

The addition of ethyl acetate to trans-octafluorobut-2-ene gave the two pairs of diastereomeric forms of the product. Each pair probably arises from asymmetry about the two carbon atoms of the former double while the two forms making up each pair would result from the asymmetric centre at C4 (section 2d). In view of the very low reactivity of ethyl acetate inversion of the intermediate radical would be expected to take place before the transfer step, and hence the proportions of the products must depend on steric and/or polar factors, but little definite can be deduced. No check was made for olefin isomerization, but interconversion of the diastereomeric forms did not take place under irradiation.

$$CH_3COOC_2H_5 + C_4F_8(\text{trans}) \longrightarrow CF_3CHFCF(CF_3)CH(CH_3)OCOCH_3$$

Molar ratio 1.1:1 Ratio of pairs of diastereomers = 58:42.

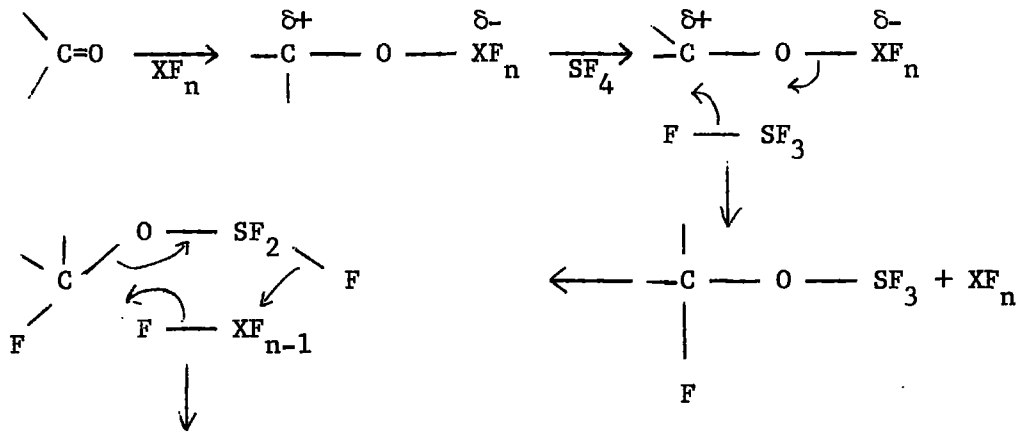
6. Attempted Determination of the structures of the Diastereomers of The Adduct of Acetaldehyde and Octafluorobut-2-ene.

The attempted assignation of the structures of the two diastereomers of $CF_3CHFCF(CF_3)COCH_3$ by means of a dehydrofluorination reaction was unsuccessful. Since treatment of fluoroketones with base results in haloform cleavage[171,172] it was necessary to convert the carbonyl function to an inert group before dehydrofluorination. This was accomplished by

treating the adduct with sulphur tetrafluoride.

$$CF_3CHFCF(CF_3)COCH_3 \xrightarrow[\text{Anhyd. HF present}]{SF_4} CF_3CHFCF(CF_3)CF_2CH_3 \quad 41\%$$

Smith and co-workers found that sulphur tetrafluoride replaces the oxygen of a carbonyl compound giving the equivalent difluoride[173,174]. It was also found that the reaction is catalyzed by hydrogen fluoride and other fluorides which are Lewis acids, such as BF_3, AsF_3, PF_5 and TiF_4, and the following mechanism was proposed.



(XF_n may be one of the catalysts or SF_4 itself).

The initial step is thought to be coordination of the fluoride XF_n with the carbonyl compound to bring about a polarization of the carbonyl group. The complex may then react with sulphur tetrafluoride as shown above. The ability of a substance to act as a catalyst can be

correlated with its strength as a Lewis acid with respect to a carbonyl group. Additional evidence that the reaction may be initiated by co-ordination with a Lewis acid is provided by the fact that compounds having strongly electron attracting groups attached to the carbonyl group are significantly less reactive. In these the Lewis base character of the carbonyl group is decreased.[174]

When a 4:1 molar mixture of sulphur tetrafluoride and $CF_3CHFCF(CF_3)COCH_3$ (mixture of diastereomers) was heated in an autoclave at 110° to 115°C for 72 hours in the presence of anhydrous hydrogen fluoride a 41% yield of $CF_3CHFCF(CF_3)CF_2CH_3$ was obtained. A mixture of products was obtained when the reaction was carried out under similar conditions in the absence of hydrogen fluoride. About 30% of this consisted of an olefin of molecular weight 246 (from mass spectrometry) corresponding to a formula $C_6F_9H_3$ but this was not fully characterised.

The dehydrofluorination of a mixture of diastereomers of $CF_3CHFCF(CF_3)CF_2CH_3$ was attempted using both aqueous and molten potassium hydroxide. When the fluoroalkane was heated with 2N aqueous potassium hydroxide solution at 100-105°C for sixteen hours a 10% conversion to two products of lower retention time on analytical V.P.C. was obtained. Increasing the reaction time to six days resulted in an approximately 20% conversion to the same products. The compound of lower retention time was not identified, but the other product from this

reaction showed as two overlapping peaks on a V.P.C. trace (di-isodecyl phthalate column) and this was tentatively identified as a mixture of the cis and trans isomers of $CF_3CF{=}C(CF_3)CF_2CH_3$. The infrared spectrum showed a band at 5.85 μ indicating an olefinic bond[175], while the mass spectrum had a parent peak at 246 corresponding to the above formula and a fragmentation pattern consistent with the structure.

The conversion in the reaction was increased to approximately 60% by passing the fluoroalkane through molten potassium hydroxide at approximately 160°C. (A little potassium fluoride and water were added to lower the melting point). Insufficient material could be obtained for an N.M.R. spectrum or analysis of the olefin however as the high volatility of the products hampered their separation using preparative scale V.P.C. Since it was only practicable to carry out the sulphur tetrafluoride reaction on fairly large quantities of material (at least 10g.) the reaction was not attempted starting from a pure diastereomer of the adduct.

When $CF_3CHFCF(CF_3)COCH_3$ was treated with powdered potassium hydroxide in di-n-butyl ether at 100° a 32% yield of 2H-heptafluorobut-2-ene was obtained. This compound is formed by haloform cleavage and dehydrofluorination of the fluoroketone and both cis and trans isomers were present (infrared spectroscopy).

$$CF_3CHFCF(CF_3)COCH_3 \xrightarrow[\text{KOH}]{} CF_3CHFCHFCF_3 + CH_3COOK$$

$$CF_3CHFCHFCF_3 \xrightarrow{-HF} CF_3CH{=}CFCF_3$$

CHAPTER 5.

EXPERIMENTAL WORK.

All the free radical addition reactions were carried out in sealed evacuated Carius or Silica tubes, and gases were handled by means of a conventional vacuum system. Analytical V.P.C. was carried out using a Perkin Elmer Model 451 Fractomer, and an Aerograph A 700 'Autoprep' was used for preparative scale gas chromatography.

Infrared spectra were recorded using either Griffin and George type Spectromaster or G.S.2A instruments. Analyses were carried out under the supervision of Mr. T.F. Holmes, either the biphenyl sodium method,[176] or fusion with potassium being used in the case of halogens. Molecular weights were determined by Regnault's method (i.e. vapour density) and an A.E.I. M.S.9 machine was used for mass spectrometric measurements. Boiling points were determined by Siwoloboff's method and are uncorrected. In all the large scale additions to octafluorobut-2-ene the trans and cis forms were present in a ratio of approximately 70:30 respectively. In general the organic addends used were analar grade and were not purified further. Where several diastereomeric forms of a compound were produced these are listed in order of appearance from a di-n-decyl phthalate V.P.C. column.

Part 1. Preparation of Polyfluorobut-2-enes.

Addition of Hydrogen Bromide to Octafluorobut-2-ene (Cis-Trans Mixture.

A typical reaction was carried out as follows. Octafluorobut-2-ene (2.2 g., 0.0111 mole) and hydrogen bromide (1.02 g., 0.0126 mole) were

introduced into a silica tube and irradiated with a 500w. Hanovia ultraviolet lamp at a distance of 25 cm. for 44.5 hours. The reactants were miscible at room temperature. After reaction free bromine was present and unreacted starting materials were allowed to boil off after the tube was opened. The liquid remaining was then shaken with sodium metabisulphite solution and the lower organic layer was separated giving a colourless liquid (2.8 g.) Analytical V.P.C. (di-iso-decyl phthalate at 20°) showed that three major components were present together with a small amount of material of lower retention time. The major components were separated using preparative scale V.P.C. (di-n-decyl phthalate at 50°) giving (in order of retention times):- (i) The first diastereomer of 2H-3-bromoöctafluorobutane (20%). Infrared spectrum No.1. (ii) The second diastereomer of 2H-3-bromoöctafluorobutane (16%). Infrared spectrum No.2. (iii) 2,3-Dibromoöctafluorobutane (28%). N.B. This reaction has been previously reported by Haszeldine and Osborne[27] but the 2H-3-bromooctafluorobutane was characterised as a mixture of diastereomers.

Preparation of Trans-2H-Heptafluorobut-2-ene.

The method reported by Maynard[140] was used. The potassium fluoride used was dried by heating for two days with a Bunsen burner and stored in a desicator. The N-methyl-2-pyrrolidone was redistilled (vacuum), the first and last fractions being rejected, and stored under dry nitrogen. The apparatus consisted of a 3 litre three-necked flask fitted

with a thermometer well, mercury seal stirrer, and a three piece adaptor with reflux condenser, dropping funnel and nitrogen inlet. A trap at -183° was fitted above the reflux condenser and dry nitrogen was passed through the apparatus.

In a typical experiment (reaction 1, table 7) the flask was charged with N-methyl-2-pyrrolidone (750 ml.) and potassium fluoride (270 g., 4.64 mole) and stirring was commenced. The temperature was raised to 200° over a period of one hour. Hexachlorobutadiene (133.5 g., 0.512 mole) was run in over a period of three hours and the reaction mixture was maintained at approximately 200° for a further three hours. During the time of the reaction the solution in the flask became brown-black in colour and the product (56.7 g.) was collected in the trap at -183°. Analytical V.P.C. (acetonyl acetone at -5°) showed that this consisted of almost entirely one component with some impurities of lower retention time. Distillation of the product using a vacuum-jacketed fractionating column gave trans-2H-heptafluorobut-2-ene (55 g., 59%) (identification by ^{19}F N.M.R. and infrared spectroscopy) containing some material of higher retention time which was probably the cis isomer (less than 5% of the total). Infrared spectrum No.3.

Addition of Chlorine to Trans-2H-Heptafluorobut-2-ene.

A typical experiment was carried out as follows. 2H-Heptafluorobut-2-ene (17.7 g., 0.0973 mole) and chlorine (6.7 g., 0.0945 mole) were first condensed into a silica tube. The two reactants were miscible

at room temperature and were irradiated with a 500w. Hanovia ultraviolet lamp at a distance of 25 cm. for 17.25 hours. After reaction the liquid in the tube was yellow in colour, and the tube was then opened and any low boiling material allowed to evaporate off. The product was then distilled giving a colourless liquid (21.5 g.). Analytical V.P.C. (di-isodecyl phthalate at 50°) showed two separable major components and a trace of material of lower retention time. Separation of the major components using preparative scale V.P.C. (di-n-decyl phthalate at 60°) gave:- (i) The first diastereomer of 2H-2,3-dichloroheptafluorobutane (Found: C,18.9; H,0.4; F,51.9; Cl,28.4. $C_4HF_7Cl_2$ requires C,19.0; H,0.4; F,52.6; Cl,28.0%). B.p. 73°/763 mm. Infrared spectrum No.5. (ii) The second diastereomer of 2H-2,3-dichloroheptafluorobutane (Found: C,18.9; H,0.4; F,52.8; Cl,27.1%). B.p. 74-75°/763 mm. Infrared Spectrum No.6. (Overall yield of the mixture of diastereomers based on chlorine, 90%, ratio of first:second diastereomer 41:59).

Addition of Bromine to Trans-2H-Heptafluorobut-2-ene.

In a typical experiment, trans-2H-heptafluorobut-2-ene (5.0 g., 0.027 mole) and bromine (5.4 g., 0.034 mole) were sealed in pyrex tube and irradiated with a 500w. Hanovia ultraviolet lamp at a distance of 25 cm. for 37.25 hours. After reaction the liquid in the tube was homogeneous with bromine present. This was then shaken with sodium metabisulphite solution and the colourless lower organic layer separated

(8.55 g.). Analytical V.P.C. (di-isodecyl phthalate at 72°) showed the presence of two major components. These were separated by preparative scale V.P.C. (di-n-decyl phthalate at 95°) giving:- (i) The first diastereomer of 2H-2,3-dibromoheptafluorobutane (Found: C,14.2; H,0.2; F,38.7; Br,46.3. $C_4HF_7Br_2$ requires C,14.05; H,0.3; F,38.9; Br, 46.7%). B.p. 108°/765 mm. Infrared spectrum No.7. (ii) The second diastereomer of 2H-2,3-dibromoheptafluorobutane (Found: C,13.9; H,0.4; F,38.4; Br, 46.7%). B.p. 110-111°/765 mm. Infrared Spectrum No.8. (Overall yield of the mixture of diastereomers 86%, ratio of first to second diastereomer 34:66).

Irradiation of 2H-heptafluorobut-2-ene (4.3 g., 0.024 mole) (cis: trans ratio 2:3 approx.) and bromine (4.5 g., 0.028 mole) under similar conditions for 15.50 hours gave 2H-2,3-dibromoheptafluorobutane (6.8 g., 84%) (ratio of first:second diastereomer 34:66).

Irradiation of trans-2H-heptafluorobut-2-ene (4.0 g., 0.022 mole) and bromine (0.5 g., 0.0031 mole) under the same conditions gave 2H-2,3-dibromoheptafluorobutane (0.6 g.). No isomerization of the recovered olefin was detected by comparison of its infrared spectrum with that of the pure trans form.

Dehydrohalogenation Reactions.

All the dehydrohalogenation reactions were carried out in a 250 ml. three-necked flask fitted with a reflux condenser, dropping funnel, nitrogen inlet, and magnetic stirrer. A trap at -183° was placed above the reflux condenser. Nitrogen was passed through the apparatus to

carry the product into the trap.

Dehydrobromination of the First Diastereomer of 2H-3-Bromooctafluorobutane

A typical experiment was carried out as follows. Potassium hydroxide (20.0 g., 0.357 mole) in water (20 ml.) was first run into the flask and stirring was commenced. The first diastereomer of 2H-3-bromooctafluorobutane (7.2 g., 0.0256 mole) was then added over a period of 30 minutes and stirring was continued. A gas condensed in the trap. After a further 30 minutes the flask was warmed on a water bath to ensure that reaction was complete. The material in the trap was identified from its ^{19}F N.M.R. and infrared spectra as trans-octafluorobut-2-ene (3.7 g., 72%). Infrared spectrum No.9.

Dehydrobromination of the Second Diastereomer of 2H-3-Bromooctafluorobutane.

By exactly the same procedure the second diastereomer of 2H-3-bromooctafluorobutane (6.2 g., 0.0221 mole) and potassium hydroxide (20.2 g., 0.360 mole) in water (20 ml.) gave cis-octafluorobut-2-ene (3.5 g., 79%). (Identification by infrared and ^{19}F N.M.R. spectroscopy). Infrared spectrum No.10.

When a saturated solution of potassium hydroxide in methanol was used in these reactions yields were in the order of 60%.

Dehydrochlorination of a Mixture of Diastereomers of 2H-2,3-Dichloroheptafluorobutane.

In a typical experiment potassium hydroxide (20.0 g., 0.357 mole) in water (20 ml.) was placed in the flask and stirring was commenced. 2H-2,3-Dichloroheptafluorobutane (10.0 g., 0.0395 mole) was then run into the flask over a period of about 20 minutes and the solution was gently warmed to about 60°C on a water bath. The lower organic layer disappeared and after about one hour the solution was again warmed. The gas collected in the trap gave two overlapping peaks on analytical V.P.C. (di-isodecyl phthalate at 20°) and was identified by ^{19}F N.M.R. spectroscopy as a cis-trans mixture of 2-chloroheptafluorobut-2-ene (5.91 g., 70%) (Found: M.W. 215; $\frac{m}{e}$ = 216(P), 218 (P + 2). Calc. for C_4F_7Cl:M.W. 216.5; $\frac{m}{e}$ = 216(P), 218 (P + 2)).

Pure geometrical isomers of 2-chloroheptafluorobut-2-ene were prepared by the same procedure starting from pure diastereomers of 2H-2,3-dichloroheptafluorobutane.

Dehydrochlorination of the First Diastereomer of 2H-2,3-Dichloroheptafluorobutane

The first diastereomer 2H-2,3-dichloroheptafluorobutane (2.45 g., 9.69 m.mole) when treated with potassium hydroxide (17.5 g., 0.312 mole) in water (20 ml.) gave trans-2-chloroheptafluorobut-2-ene (1.6 g., 75%), identified by its ^{19}F N.M.R. and infrared spectra. Infrared spectrum No.11.

Dehydrochlorination of the Second Diastereomer of 2H-2,3-Dichloroheptafluorobutane.

Similarly the second diastereomer of 2H-2,3-dichloroheptafluorobutane (3.75 g., 0.0148 mole) and potassium hydroxide (19.8 g., 0.353 mole) in water (20 ml.) gave cis-2-chloroheptafluorobut-2-ene (1.95 g., 61%) again identified by ^{19}F N.M.R. and infrared spectroscopy. Infrared spectrum No.12.

Dehydrobromination of a Mixture of Diastereomers of 2H-2,3-Dibromoheptafluorobutane.

2H-2,3-Dibromoheptafluorobutane (51.6 g., 0.204 mole) was run into a stirred solution of potassium hydroxide (35.5 g., 0.633 mole) in water (55 ml.) over a period of thirty minutes. The mixture became warm and stirring was continued. A little material was collected in the trap (at -78°) above the reflux condenser. After about one hour the flask was warmed on a water bath to approximately 50° to ensure that reaction was complete. The lower organic layer in the flask (19.0 g.) and the material collected in the cold trap (8.8 g.) gave two overlapping peaks on analytical V.P.C. (di-isodecyl phthalate at 53°) and was shown by ^{19}F N.M.R. spectroscopy to be cis- and trans-2-bromoheptafluorobut-2-ene (71%) (Found: Br,31.0; M.W.258; $\frac{m}{e}$ = 260(P), 262 (P + 2). C_4F_7Br requires Br,30.6%; M.W.261; $\frac{m}{e}$ = 260(P), 262 (P + 2)). B.p. 50-51°/760 mm. (micro distillation). Infrared spectrum No.13.

Dehydrobromination of the Second Diastereomer of 2H-2,3-Dibromoheptafluorobutane.

By the same method as above the second diastereomer of 2H-2,3-

dibromoheptafluorobutane (3.1 g., 9.07 mmole) and potassium hydroxide (12.5 g., 0.223 mole) in water (20 ml.) gave cis-2-bromoheptafluorobut-2-ene (1.5 g., 68%) identified by its ^{19}F N.M.R. spectrum.

Dechlorination of 2H-2,3-Dichloroheptafluorobutane.

These reactions were carried out using the same apparatus as the dehydrohalogenation reactions described above.

Dechlorination of the First Diastereomer of 2H-2,3-Dichloroheptafluorobutane.

The flask was first charged with zinc dust (5.5 g., 0.0841 mole) and methylated spirits (50 ml.) followed by a few drops of glacial acetic acid to activate the zinc. The first diastereomer of 2H-2,3-dichloroheptafluorobutane (1.25 g., 4.94 m.moles) was then run in and the solution was refluxed on a water bath with stirring for one hour. A gas was condensed in the trap at -183° above the reflux condenser and this was identified by ^{19}F N.M.R. spectroscopy as a mixture of cis- and trans-2H-heptafluorobut-2-ene (0.65 g., 72%) in the ratio of approximately 1:3 respectively, with a trace of impurity present.

Dechlorination of the Second Diastereomer of 2H-2,3-Dichloroheptafluorobutane.

By the same procedure, zinc dust (6.0 g., 0.0918 mole) in methylated spirits (50 ml.) and the second diastereomer of 2H-2,3-dichloroheptafluorobutane (1.85 g., 7.31 m.mole) gave a mixture of cis- and

trans-heptafluorobut-2-ene (0.8 g., 60%) in a ratio of approximately 2:3 respectively. (Identification by ^{19}F N.M.R. spectroscopy). Infrared spectrum No.4.

Part 2. Free Radical Addition of Organic Molecules to Fluoroolefins

All large scale γ-ray initiated additions were carried out at room temperature using a ^{60}Co source. The reaction tubes were touching the tube containing the source unless otherwise stated.

Alcohol Additions.

Peroxide Initiated Addition of Methanol to Octafluorobut-2-ene (Cis-Trans Mixture).

Methanol (9.8 g., 0.306 mole) and octafluorobut-2-ene (30.1 g., 0.151 mole) were heated in a Carius tube with benzoyl peroxide (0.15 g.) at 125-130° for 18 hours. After reaction a small lower layer of liquid was seen in the tube this being unreacted olefin, and when the tube was opened unreacted octafluorobut-2-ene (15.1 g.) was vented off. The material remaining in the tube was then transferred to a distillation apparatus and methanol (0.9 g.) was distilled off. The remainder of the liquid was then distilled at reduced pressure (b.p. 60°/20 cm.) giving a colourless liquid (13.5 g.,) a little residue being left in the flask. Analytical V.P.C. (di-isodecyl phthalate at 110°) showed that the distillate consisted of methanol and two components of higher retention time. These were separated using preparative scale V.P.C.

(di-n-decyl phthalate 140°) into:- (i) The first diastereomer of 2,3,4,4,4-pentafluoro-(2-trifluoromethyl)-butan-1-ol (Found: C,25.9; H,1.8; F,64.9. Calc. for $C_5H_4F_8O$: C,25.9; H,1.7; F,65.5%). B.p. 118-119°/761 mm. Infrared spectrum No.14. (ii) The second diastereomer of 2,3,4,4,4-pentafluoro-(2-trifluoromethyl)-butan-1-ol (Found: C,26.1; H,1.8; F,65.2%) B.p. 119°/744 mm. Infrared spectrum No.15. Total yield of the two diastereomers (based on olefin recovered) 50%. B.p. lit.[44] for a mixture of diastereomers 118°. This reaction has been previously reported, the adduct being characterised as a mixture of diastereomers[44].

γ-Ray Initiated Addition of Methanol to Octafluorobut-2-ene(Cis-Trans Mixture).

Irradiation of methanol (11.65 g., 0.367 mole) and octafluorobut-2-ene (26.5 g., 0.133 mole) (reactants only partially miscible)in a Carius tube for 112.5 hours (total dose 22.2 x 10^6 rads) gave the two diastereomeric forms of the adduct in $>$95% yield. (Based on olefin recovered).

γ-Ray Initiated Addition of Ethanol to Octafluorobut-2-ene (Cis-Trans Mixture).

Ethanol (14.9 g., 0.323 mole) and octafluorobut-2-ene (18.0 g., 0.0745 mole) were irradiated in a Carius tube for 159 hours (total dose 31.4 x 10^6 rads). The reactants were only partially miscible at

room temperature but after reaction a colourless homogeneous liquid was present in the tube. On opening the tube a negligible amount of olefin was recovered and the liquid in the tube was then distilled through a vigreux column and some of the excess ethanol (5.9 g.) was distilled off. The remaining liquid was then distilled under reduced pressure (b.p. 60°-80°/5 cm.). Analytical V.P.C. (di-iso - decyl phthalate at 120°) of the vacumm distillate (26.5 g.) indicated the presence of three components of higher retention time in addition to ethanol which was also present. Separation of these using preparative scale V.P.C. (di-n-decyl phthalate at 140°) gave:- (i) The first diastereomer of 1,1,1,2,3-pentafluoro-(3-trifluoromethyl)-pentan-4-ol (Found: C,29.5; H,2.5; F,61.5. $C_6H_6F_8O$ requires C,29.3; H,2.5; F, 61.8%). B.p. 124°/728 mm. Infrared spectrum No.16. (ii) The second diastereomer of 1,1,1,2,3-pentafluoro-(3-trifluoromethyl)-pentan-4-ol (Found: C,29.4; H,2.5; F,61.4%). B.p. 126°/728 mm. Infrared spectrum No.17. (iii) A mixture of two diastereomers of 1,1,1,2,3-pentafluoro-(3-trifluoromethyl)-pentan-4-ol (Found: C,29.1; H,2.45; F,61.8%). B.p. 127°/728 mm. Infrared spectrum No.18 . Total yield of the four diastereomers of the adduct (based on olefin recovered) $>$ 95%.

γ-Ray Initiated Addition of n-Propanol to Octafluorobut-2-ene (Cis-Trans Mixture).

n-Propanol (23.7 g., 0.394 mole) and octafluorobut-2-ene (15.5 g.,

0.0775 mole) were irradiated in a Carius tube for 312 hours. (Total dose 61.5×10^6 rads). The reactants were only partially miscible at room temperature but after reaction a colourless homogeneous liquid was present in the tube. On opening the tube a negligible amount of olefin was recovered. The material in the tube was then transferred to a distillation apparatus and n-propanol and a little of the adduct (13.2 g.) were distilled off. The remainder of the liquid was then distilled at reduced pressure (b.p. 50°/5-3 cm.) giving a colourless liquid (23.6 g.), a little residue being left in the flask. Analytical V.P.C. (di-isodecyl phthalate at 120°) showed that the distillate consisted of n-propanol and three components of higher retention time. These were then separated using preparative scale V.P.C. (di-n-decyl phthalate at 140°) giving:(i) The first diastereomer of <u>1,1,1,2,3-pentafluoro-(3-trifluoromethyl)-hexan-4-ol</u> (Found: C,32.4; H,3.0; F, 57.5. $C_7H_8F_8O$ requires C,32.3; H,3.1; F,58.4%). B.p. 136°/753 mm. Infrared spectrum No.19. (ii) The second diastereomer of <u>1,1,1,2,3-pentafluoro-(3-trifluoromethyl)-hexan-4-ol</u> (Found: C,32.1; H,2.9; F, 57.7%). B.p. 138°/753 mm. Infrared spectrum No.20. (iii) A mixture of two diastereomers of <u>1,1,1,2,3-pentafluoro-(3-trifluoromethyl)-hexan-4-ol</u> (Found: C,32.5; H,3.0; F,58.2%). B.p. 141°/753 mm. Infrared spectrum No.21. Total yield of the four diastereomers of the adduct (based on olefin recovered) $>$ 95%.

Peroxide Initiated Addition of n-Propanol to Octafluorobut-2-ene

A 33% yield (based on olefin recovered) of the four diastereomers of the adduct was obtained when n-propanol (20.2 g., 0.336 mole) and octafluorobut-2-ene (19.0 g., 0.0950 mole) were heated with benzoyl peroxide (0.2 g.) in a Carius tube at 125-130° for 13 hours.

γ-Ray Initiated Addition of Methanol to Trans-2H-Heptafluorobut-2-ene

Methanol (10.5 g., 0.328 mole) and trans-2H-heptafluorobut-2-ene (16.7 g., 0.0917 mole) were irradiated in a Carius tube for 600 hours the reactants being miscible at room temperature (Tube 2 cm. from tube containing source, total dose 54.6 x 10^{6} rads). After reaction the tube was opened and a little unreacted olefin was vented off. The colourless liquid remaining in the tube was then transferred to a distillation apparatus and methanol plus a little adduct (8.1 g.) distilled off (b.p. 60-70°). The remaining liquid was then distilled at reduced pressure (b.p. 50-70°/-20 cm) giving a colourless liquid (14.6 g.). Analytical V.P.C. (di-isodecyl phthalate at 120°) showed that the distillate consisted of a little methanol plus three components of higher retention time. These were separated using preparative scale V.P.C. (di-n-decyl phthalate at 140°) giving:- (i) The first diastereomer of 3,4,4,4-tetrafluoro-(2-trifluoromethyl)-butan-1-ol (31%) (Found: C, 27.8; H,2.3; F,61.7. $C_5H_5F_7O$ requires C,28.05; H,2.35; F,62.1%). B.p. 120°/759 mm. Infrared spectrum No.22. (ii) 2,4,4,4-tetrafluoro-(2-trifluoromethyl)-butan-1-ol (21%) (Found: C, 28.2; H,2.3; F,61.9%).

B.p. 123°/761 mm. Infrared spectrum No.23. (iii) The second diastereomer of 3,4,4,4-tetrafluoro-(2-trifluoromethyl)-butan-1-ol (22%) (Found: C,28.2; H,2.25; F,61.6%). B.p. 131°/761 mm. Infrared spectrum No.24.

γ-Ray Initiated Addition of Methanol to 2-Chloroheptafluorobut-2-ene (Cis-Trans Mixture).

Methanol (6.2 g., 0.194 mole) and 2-chloroheptafluorobut-2-ene (8.5 g., 0.0395 mole) were irradiated in a Carius tube for 481.5 hours (total dose 94.8 x 10^6 rads.) The reactants were miscible at room temperature. A clear liquid was present in the tube after reaction and this was then transferred to a distillation apparatus and unreacted methanol (4.1 g.) was distilled off. The remaining liquid was then distilled at reduced pressure (b.p. 50°-70°/1-30 cm.). Analytical V.P.C. (di-isodecyl phthalate at 120°) showed that the distillate consisted of methanol and a trace of material of low retention time, plus two major products of higher retention time. These were separated using preparative scale V.P.C. (di-n-decyl phthalate at 130°) giving:- (i) The first diastereomer of 3-chloro-2,4,4,4-tetrafluoro-(2-trifluoromethyl)-butan-1-ol (Found: C,23.8; H,1.6; F,52.4; Cl,14.7. $C_5H_4F_7ClO$ requires C,24.2; H,1.6; F,53.5; Cl,14.3%). B.p. 142°/770 mm. Infrared spectrum No.25. (ii) The second diastereomer of 3-chloro-2,4,4,4-tetrafluoro-(2-trifluoromethyl)-butan-1-ol (Found: C,24.1; H,1.3; F,52.7; Cl,13.5%). B.p. 144-145°/770 mm. Infrared spectrum No.26. Total yield of the two

diastereomers of the adduct 94%.

γ-Ray Initiated Addition of Methanol to 2-Bromoheptafluorobut-2-ene (Cis-Trans Mixture).

Methanol (5.2 g., 0.163 mole) and 2-bromoheptafluorobut-2-ene (8.2 g., 0.0314 mole) were irradiated in a Carius tube for 434 hours (total dose 85.5 x 10^6 rads) the reactants being miscible at room temperature. After reaction the liquid in the tube was yellow in colour and this was distilled mainly methanol and unreacted olefin being recovered (B.p. 40-68°). The remainder of the liquid was then distilled at reduced pressure (b.p. 40-60°/1-20 cm.) giving a colourless liquid. Analytical V.P.C. (di-isodecyl phthalate at 120°) showed that the distillate consisted of methanol and two major products of higher retention time. Shaking this with water followed by redistillation of the organic layer gave a pure sample of the two major components and these were identified as the two diastereomers of 3-bromo-2,4,4,4-tetrafluoro-(2-trifluoromethyl)-butan-1-ol (14% (Found: C,20.8; H, 1.65; F,44.8; Br,27.0. $C_5H_4F_7BrO$ requires C,20.5; H,1.4; F,45.4; Br, 27.3%). B.p. 154-157°/746 mm. Infrared spectrum No.27. (Ratio of first:second diastereomer of the adduct 40:60).

γ-Ray Initiated Addition of Methanol to Octafluorocyclopentene*

Methanol (9.2 g., 0.286 mole) and octafluorocyclopentene were irradiated in a Carius tube for 310 hours. (total dose 61.1 x 10^6 rads). The reactants were only partially miscible at room temperature but after

*Octafluorocyclopentene was prepared by the method reported by Maynard, ref.140.

reaction a colourless homogeneous liquid was present. The tube was then opened and unreacted methanol and octafluorocyclopentene (4.45 g.) were vented into an evacuated trap at -183°. The material remaining in the tube was then transferred to a distillation apparatus and unreacted methanol (3.85 g.) distilled off. The remainder of the liquid was then distilled at reduced pressure (b.p. 50-60°/5-20 cm.) giving a colourless liquid. Analytical V.P.C. (di-isodecyl phthalate at 120°) showed that this consisted of methanol and two components of higher retention time. These were separated using preparative scale V.P.C. (silicone elastomer at 95°) giving:- (i) The first isomer of 2H-octafluorocyclopentylmethanol (36%). (Found: C,29.4; H,1.7; F,61.7. $C_6H_4F_8O$ requires C,29.5; H,1.65; F,62.3%). B.p. 150°/758 mm. Infrared spectrum No.28. (ii) The second isomer of 2H-octafluorocyclopentylmethanol (24%) (Found: C,29.4; H,1.4; F,60.8%). B.p. 154°/758 mm. Infrared spectrum No.29. The structures of the isomers were not assigned.

Aldehyde Additions

In all cases the reactants were miscible at room temperature.

Peroxide Initiated Addition of Acetaldehyde to Octafluorobut-2-ene (Cis-Trans Mixture).

Acetaldehyde (6.6 g., 0.150 mole), octafluorobut-2-ene (22.0 g., 0.110 mole) and benzoyl peroxide (0.2 g.) were heated in a Carius tube at 120° for 16 hours. After reaction a yellow liquid was present in the tube and on opening a little unreacted olefin (0.8 g. was recovered.

The liquid in the tube was then distilled through a vigreux column giving acetalehyde (3.0 g.) and a higher boiling fraction (25.25 g.), a little residue being left in the flask. Analytical V.P.C. (di-isodecyl phthalate at 50°) showed the higher boiling material to consist of two components. These were separated by preparative scale V.P.C. (di-n-decyl phthalate at 60°) giving:- (i) The first diastereomer of 1,1,1,2,3-pentafluoro-(3-trifluoromethyl)-pentan-4-one (Found: C,29.6; H,1.7; F,61.8. $C_6H_4F_8O$ requires C,29.5; H,1.65; F,62.3%). B.p. 82-83°/751 mm. Infrared spectrum No.30. (ii) The second diastereomer of 1,1,1,2,3-pentafluoro-(3-trifluoromethyl)-pentan-4-one (Found: C,29.8; H,1.7; F,61.9%). B.p. 87°/767 mm. Infrared spectrum No.31. The total yield of the two diastereomers was 94%.

γ-Ray Initiated Addition of Acetaldehyde to Octafluorobut-2-ene (Cis-Trans Mixture).

Irradiation of acetaldehyde (22.1 g., 0.502 mole) and octafluorobut-2-ene (73.1 g., 0.366 mole) in a Carius tube for 166 hours (total dose 32.7 x 10^6 rads) also gave the two diastereomeric forms of the adduct (79.6 g., 89%).

γ-Ray Initiated Addition of Propionaldehyde to Octafluorobut-2-ene(Cis-Trans)

Propionaldehyde (15.7 g., 0.283 mole) and octafluorobut-2-ene (19.0 g.,0.0950 mole) were irradiated in a Carius tube for 159 hours (total dose 31.4 x 10^6 rads). After reaction the liquid in the tube was

a pale yellow colour with a little solid present. The liquid was then transferred to a distillation apparatus and unreacted propionaldehyde and a small amount of adduct (8.7 g.) were distilled off. The remaining liquid was then distilled at approximately 100° to give a clear liquid (20.65 g.) leaving a brown residue plus a little liquid in the flask. Analytical V.P.C. (di-isodecyl phthalate at 45°) showed that the distillate consisted of a little propionaldehyde plus two other components. These were separated using preparative scale V.P.C. (di-n-decyl phthalate at 90°) giving:- (i) The first diastereomer of 1,1,1,2,3-pentafluoro-(3-trifluoromethyl)-hexan-4-one (Found: C,32.9; H,2.3; F,58.7. $C_7H_6F_8O$ requires C,32.6; H,2.3; F,58.9%). B.p. 101-102°/765 mm. Infrared spectrum No.32 (ii) The second diastereomer of 1,1,1,2,3-pentafluoro-(3-trifluoromethyl)-hexan-4-one (Found: C,32.2; H,1.85; F,58.5%) B.p. 105-106°/765 mm. Infrared spectrum No.33. The total yield of the two adducts was 82%.

γ-Ray Initiated Addition of Acetaldehyde to Trans-2H-Heptafluorobut-2-ene

Acetaldehyde (20.0 g., 0.454 mole) and trans-2H-heptafluorobut-2-ene (17.9 g., 0.0984 mole) were irradiated in a Carius tube for 595 hours. (total dose 117.2 x 10^6 rads). After reaction a little of the olefin was vented from the tube. The liquid in the tube was light brown in colour and this was distilled at 40-50° giving unreacted acetaldehyde (11.4 g.). The remainder of the liquid was then distilled at reduced

pressure (b.p. 60°C approx./10-20 cm.) giving an almost colourless distillate (16.8 g.) with a little residue left in the flask. Analytical V.P.C. (di-isodecyl phthalate at 60°) showed that this consisted of a small amount of a acetaldehyde plus two components of higher retention time. Separation of these using preparative scale V.P.C. (di-n-decyl phthalate at 80°) gave:- (i) 1,1,1,3-tetrafluoro-(3-trifluoromethyl)-pentan-4-one (18%) (Found: C,31.6; H,2.2; F,58.6. $C_6H_5F_7O$ requires C,31.9; H,2.2; F,58.8%). B.p. 87°/754 mm. Infrared spectrum No.34. (ii) The two diastereomers of 1,1,1,2-tetrafluoro-(3-trifluoromethyl)-pentan-4-one (58%) (Found: C,31.9; H,2.4; F,58.4%). B.p. 106°/751 mm. Infrared spectrum No.35. (Identifications by ^{19}F N.M.R. spectroscopy).

γ-Ray Initiated Addition of Acetaldehyde to 2-Chloroheptafluorobut-2-ene (Cis-Trans Mixture).

Acetaldehyde (7.9 g., 0.180 mole) and 2-chloroheptafluorobut-2-ene were irradiated in a Carius tube for 481.5 hours (total dose 94.8×10^6 rads). A brown liquid was present in the tube after reaction with a little solid material present. The reaction mixture was then distilled, acetaldehyde (3.1 g.) being recovered. The remaining liquid was distilled at reduced pressure (b.p. 40-60°/5-20 cm), giving a pale yellow liquid (8.15 g.). Some brown residue was left in the flask. Analytical V.P.C. (di-isodecyl phthalate at 75°C) indicated that the

distillate consisted of two major components in addition to a little acetaldehyde. These were separated using preparative scale V.P.C. (di-n-decyl phthalate at 90°) giving:- (i) The first diastereomer of 2-chloro-1,1,1,3-tetrafluoro-(3-trifluoromethyl)-pentan-4-one (Found: C,27.9; H,1.5; Cl,13.3. $C_6H_4F_7ClO$ requires C,27.7; H,1.55; F, 51.1; Cl, 13.6%). B.p. 108°/754 mm. Infrared spectrum No.36. (ii) The second diastereomer of 2-chloro-1,1,1,3-tetrafluoro-(3-trifluoromethyl)-pentan-4-one (Found: C,27.9; H,1.6; F,50.5; Cl,14.0%). B.p. 113-114°/754 mm. Infrared spectrum No.37. The total yield of the two diastereomers was 85%.

γ-Ray Initiated Addition of Acetaldehyde to 2-Bromoheptafluorobut-2-ene (Cis-Trans Mixture).

Acetaldehyde (6.65 g., 0.151 mole) and 2-bromoheptafluorobut-2-ene (13.3 g., 0.0509 mole) were irradiated in a carius tube for 434 hours (total dose 85.5 x 10^6 rads). After irradiation a black solid and a little liquid were present in the tube. After opening the tube the black solid (5.9 g.) was collected and the dark liquid was distilled. Some low boiling liquid was collected (b.p. 40-50°) this being mainly unreacted starting materials with some by-products. The remaining liquid was then distilled at reduced pressure (b.p. 60-80°/3-20 cm.) giving a yellow liquid (0.9 g.), and leaving a brown tar (2.0 g.) in the flask. The distillate was then redistilled in a micro distillation apparatus again giving a yellow liquid. Analytical V.P.C. (di-isodecyl

phthalate at 100°C) showed that this consisted of two major components and a minor one (~5%) of lower retention time together with a little acetaldehyde. On shaking with water the yellow colour was removed giving an impure sample of what was tentatively identified as the two diastereomers of 2-bromo-1,1,1,3-tetrafluoro-(3-trifluoromethyl)-pentan-4-one (6%) (Found: C,24.4; H,1.2; $\frac{m}{e}$ = 304 (P), 306(P + 2). $C_6H_4F_7BrO$ requires C, 23.6; H,1.3%; $\frac{m}{e}$ = 304(P), 306(P + 2). Infrared spectrum No.38. Ratio of first:second diastereomer = 66:34 approx.

Thiol Additions.

γ-Ray Initiated Addition of Methanethiol to Octafluorobut-2-ene (Cis-Trans Mixture).

Methanethiol (9.0 g., 0.188 mole) and octafluorobut-2-ene (18.0 g., 0.0900 mole) were irradiated in a Carius tube for 161 hours (total dose 31.7 x 10^6 rads). The reactants were only partially miscible at room temperature. After reaction the tube was opened and vented to a trap at -183° and unreacted starting materials (14.9 g.) were recovered. Distillation of the remainder of the material in the tube (b.p. 98-100°) gave a clear liquid (12.1 g.). Analytical V.P.C. (di-isodecyl phthalate at 75°) showed that this consisted of two components plus a trace of material of lower retention time which was probably dissolved methanethiol. Separation of these using preparative scale V.P.C. (di-n-decyl phthalate at 85°) gave:- (i) The first diastereomer of 2H-(1-trifluoromethyl)-pentafluoropropyl methyl sulphide (Found: C,24.1; H,1.6; F, 61.4. $C_5H_4F_8S$ requires C, 24.2; H,1.6; F,61.25%). B.p. 98-99°/765 mm.

Infrared spectrum No.39. (ii) The second diastereomer of 2H-(1-trifluoromethyl)-pentafluoropropyl methyl sulphide (Found: C,24.5; H,1.5; F,61.5%). B.p. 103°/765 mm. Infrared spectrum No.40. Overall yield of the two diastereomers 52%.

γ-Ray Initiated Addition of Methanethiol to Trans-2H-Heptafluorobut-2-ene

Methanethiol (11.9 g., 0.247 mole) and trans-2H-heptafluorobut-2-ene (23.8 g., 0.131 mole) were irradiated in a Carius tube for 295 hours at a distance of 2 cm. from the tube containing the source (total dose 26.7 x 10^6 rads). The reactants were miscible at room temperature. After reaction the tube was opened and vented to a trap at -183° unreacted starting materials (26.0 g.) being recovered. The yellow liquid remaining in the tube was then distilled (b.p.100-110°) giving a colourless liquid (9.5 g.) a little residue being left in the flask. Analytical V.P.C. (di-isodecyl phthalate at 74°) showed that the distillate consisted of four components A, B, C, and D in proportions 0.3:4.4:3.1:1 (in order of retention time). These were separated using preparative scale V.P.C. (di-n-decyl phthalate at 90°) and B was identified as the first diastereomer of 1H,2H-(1-trifluoromethyl)-tetrafluoropropyl methyl sulphide (15%) (Found: C, 26.0; H,2.2; F,58.0. $C_5H_5F_7S$ requires C,26.1; H,2.2; F,57.8%). B.p. 102-103°/748 mm. Infrared spectrum No.41. C was identified as

the second diastereomer of 1H,2H-(1-trifluoromethyl)-tetrafluoropropyl methyl sulphide (11%) (Found: C,26.1; H,2.1; F,58.2%). B.p. 109-110°/748 mm. Infrared spectrum No.42. The other two components were not identified.

Ester Addition.

γ-Ray Initiated Addition of Ethyl Acetate to Octafluorobut-2-ene

Ethyl acetate (27.9 g., 0.317 mole) and octafluorobut-2-ene (20.0 g., 0.0997 mole) were irradiated in a Carius tube for 408 hours (total dose 80.4 x 10^6 rads), the reactants being miscible at room temperature. After reaction the tube was opened and unreacted olefin was allowed to boil off. A colourless liquid remained in the tube and this was distilled through a vigreux column yielding unreacted ethyl acetate (22.0g.). The remainder of the liquid was then distilled at reduced pressure (b.p. 80-100°/5-15 mm.) giving a colourless liquid (10.7 g.). Analytical V.P.C. (di-isodecyl phthalate at 110°) showed that this consisted of ethyl acetate plus two major products (both giving two overlapping peaks) and also three components of higher retention time. A yellow liquid (0.8 g.) was left in the flask. The vacuum distillate was separated using preparative scale V.P.C. (di-n-decyl phthalate at 130°) giving the two major components which consisted of (i) Two diastereomers of 2,3,4,4,4-pentafluoro-(1-methyl)-(2-trifluoromethyl)-butyl acetate (Found: C,33.5; H,2.25; F,52.9.

$C_8H_8F_8O_2$ requires C,33.35; H,2.8; F,52.7%). B.p. 145°/761 mm. Infrared spectrum No.43. (ii) Two diastereomers of 2,3,4,4,4-pentafluoro-(1-methyl)(2-trifluoromethyl)-butyl acetate (Found: C,33.7; H,2.5; F,53.2%). B.p. 151°/761 mm. Infrared spectrum No.44. The total yield of the four diastereomers was approximately 22%. The three components of higher retention time were not identified.

Part 3. γ-Ray Initiated Additions of Organic Molecules to Pure Geometrical Isomers of the Polyfluorobut-2-enes.

All the reactions were carried out in small sealed evacuated pyrex tubes. The ratios of the diastereomers of products were determinded by analytical V.P.C. using a Perkin Elmer Model 451 Fractomer, with either hot wire or thermistor detectors. Since diastereomers have almost equal thermal conductivities and specific heats no correction for possible unequal responses of the detectors was necessary. When a 50:50 mixture of the two diastereomers of $CF_3CHFCF(CF_3)COCH_3$ was injected two peaks of exactly the same area were obtained. All the reactions were carried out at room temperature (20-25°) unless otherwise stated.

Addend (g., mmole)			Olefin(g.,mmole)			Irradiation Constants Distance (cm.)	Time (hrs.)	Total Dose (rads x 10^6)	Product (Diastereomeric)	Ratio of 1st:2nd Diastereomer
Aldehydes										
CH_3CHO	0.15	(3.4)	Cis-C_4F_8	0.45	(2.3)	3	92.5	6.6	$CF_3CHFCF(CF_3)COCH_3$[f]	78:22
CH_3CHO	0.2	(4.4)	Trans-C_4F_8	0.4	(2.0)	3	92.5	6.6	"	76:24
CH_3CHO	0.05	(1.1)	Trans-C_4F_8	1.2	(6.0)[c]	2	314	28.6	"	83:17
C_2H_5CHO	0.1	(1.7)	Cis-C_4F_8	0.3	(1.5)	2	141	12.8	$CF_3CHFCF(CF_3)COC_2H_5$[f]	72:28
C_2H_5CHO	0.15	(2.6)	Trans-C_4F_8	0.4	(2.0)	2	141	12.8	"	76:24
CH_3CHO	0.15	(3.4)	Cis-C_4F_7Cl	0.3	(1.4)	2	170.5	15.5	$CF_3CHClCF(CF_3)COCH_3$[f]	61:39
CH_3CHO	0.15	(3.4)	Trans-C_4F_7Cl	0.2	(0.93)	2	170.5	15.5	"	62:38
CH_3CHO	0.25	(5.7)	Cis-C_4F_7Cl	0.45	(2.1)	4	189	10.6	"	68:32[b]
CH_3CHO	0.25	(5.7)	Trans-C_4F_7Cl	0.15	(0.70)	4	189	10.6	"	70:30[b]
CH_3CHO	10.9	(248)	Trans-C_4F_7H	9.25	(58)	0	236.5	46.4	$CF_3CHFCH(CF_3)COCH_3$	64:36[e]
Alcohols										
CH_3OH	0.15	(4.7)	Cis-C_4F_8	0.3	(1.5)[a]	3	243.5	17.3	$CF_3CHFCF(CF_3)CH_2OH$[f]	47:53
CH_3OH	0.2	(6.3)	Trans-C_4F_8	0.3	(1.5)[a]	0	142	28.0	"	44:56
CH_3OH	0.05	(1.6)	Trans-C_4F_8	1.3	(6.5)[ad]	2	314	28.6	"	42:58

Addend (g.,mmole)			Olefin(g.,mmole)			Irradiation Constants Distance (cm.)	Time (hrs.)	Total Dose ($rads \times 10^6$)	Product (Diastereomeric)	Ratio of 1st:2nd Diastereomer
Alcohols										
CH_3OH	0.15	(4.7)	Cis-C_4F_7Cl	0.25	(1.2)	2	170.5	15.5	$CF_3CHClCF(CF_3)CH_2OH$[f]	35:65
CH_3OH	0.1	(3.1)	Trans-C_4F_7Cl	0.3	(1.4)	2	170.5	15.5	"	38:62
CH_3OH	0.25	(7.8)	Cis-C_4F_7Cl	0.2	(0.93)	4	189	10.6	"	23:77[b]
CH_3OH	0.3	(9.4)	Trans-C_4F_7Cl	0.6	(2.8)	4	189	10.6	"	26:74[b]
C_2H_5OH	0.15	(3.3)	Trans-C_4F_8	0.4	(2.0)[a]	2	141	12.8	$CF_3CHFCF(CF_3)CHOHCH_3$	22:28:50[g]
n-C_3H_7OH	0.25	(4.2)	Trans-C_4F_8	0.3	(1.5)[a]	2	141	12.8	$CF_3CHFCF(CF_3)CHOHC_2H_5$	17:31:52[g]
CH_3OH	7.6	(237)	Trans-C_4F_7H	8.05	(44)	0	236.5	46.4	$CF_3CHFCH(CF_3)CH_2OH$	58:42
Methanethiol										
CH_3SH	0.3	(5.2)	Cis-C_4F_8	0.55	(2.8)[a]	2	90	8.2	$CF_3CHFCF(CF_3)SCH_3$[f]	45:55
CH_3SH	0.2	(3.4)	Trans-C_4F_8	0.4	(2.0[a]	2	141	12.8	"	46:54
CH_3SH	11.9	(247)	Trans-C_4F_7H	23.8	(131)	2	295	26.7	$CF_3CHFCH(CF_3)SCH_3$[f]	59:41
Ethyl Acetate										
$CH_3COOC_2H_5$	0.1	(1.1)	Trans-C_4F_8	0.2	(1.0)	2	141	12.8	$CF_3CHFCF(CF_3)CH(CH_3)OCOCH_3$	58:42[g]

a. Reactants only partially miscible.

b. Reaction at -78 to -60°.

c. Approximately 20% of recovered olefin isomerized.

d. No isomerization of recovered olefin.

e. Approximate figures from ^{19}F N.M.R. spectroscopy.

f. No interconversion to the other form was detected when a pure diastereomer was irradiated in the presence of the addend.

g. Four diastereomers.

Addition of Hydrogen Bromide to Octafluorobut-2-ene (U.V. Initiation)

Olefin (g.mmole)		HBr (g.mmole)	$CF_3CFHCFBrCF_3$ 1:2	$\%CF_3CFBrCFBrCF_3$ in prod.
Trans	0.6 (3.0)	0.55 (6.8)	68:32	3
Cis	0.3 (1.5)	0.55 (6.8)	62:38	11

In both reactions the silica tubes were irradiated with a 500w. Hanovia ultraviolet lamp at a distance of 15 cm. for 11 hours.

Part 4. Reactions on the Adducts.

Reaction of 1,1,1,2,3-Pentafluoro-(3-trifluoromethyl)-pentan-4-one $CF_3CHFCF(CF_3)COCH_3$ with Sulphur Tetrafluoride.

(i) An autoclave was first charged with $CF_3CHFCF(CF_3)COCH_3$ (34 g., 0.139 mole) (mixture of diastereomers), sulphur tetrafluoride (63 g., 0.583 mole) and anhydrous hydrogen fluoride (15 ml.). After the materials had been introduced the autoclave was cooled to -183° and evacuated, and then heated at 110-115° for 73.5 hours. After reaction the autoclave was again cooled to -183°C and the valve opened. It was then allowed to warm up and unreacted sulphur tetrafluoride, together with thionyl fluoride and hydrogen fluoride were vented off. After this the autoclave was cooled -78° and opened. Water (150 ml.) was then added followed by 30% aqueous potassium hydroxide solution (200 ml.). The material was then transferred to a separating funnel and the lower organic layer run off (25.1 g.). (Both layers were brown in colour). This was then distilled giving a colourless liquid (15.1 g.), an unidentifiable brown oil being left in the flask. Analytical V.P.C. (silicone elastomer at 55°) showed that the distillate was a single compound and this was identified as 1,1,1,2,3,4,4-heptafluoro-(3-trifluoromethyl)-pentane (41%) (Mixture of diastereomers). (Found: C,27.3; H, 1.7; F,70.7. $C_6H_4F_{10}$ requirés C, 27.05, H,1.5; F,71.4%). B.p. 75-76°/743 mm. Infrared spectrum No.45.

Reaction in the Absence of Hydrogen Fluoride

When sulphur tetrafluoride (11.0 g., 0.112 mole) and $CF_3CHFCF(CF_3)COCH_3$ (13.0 g., 0.0533 mole) were heated in an autoclave at 105-110° for 65 hours, followed by a similar work up to that described above the organic material isolated was shown by analytical V.P.C. (silicone elastomer at 20°) to contain three major components, which were not identified. These were separated using preparative scale V.P.C. (di-n-decyl phthalate at 50°). The infrared spectrum of the substance of lowest retention indicated the presence of a carbon-carbon double bond, while the mass spectrum had a parent peak of 246 corresponding to a formula $C_6H_3F_9$.

Attempted Dehydrofluorination of 1,1,1,2,3,4,4-heptafluoro-(3-trifluoromethyl)-pentane, $CF_3CHFCF(CF_3)CF_2CH_3$.

(i) Using Aqueous Potassium Hydroxide.

$CF_3CFHCF(CF_3)CF_2CH_3$ (1.5 g., 6.15 mmoles), potassium hydroxide (1.05 g., 18.7 mmoles) and water (5 ml.) were introduced into a Carius tube (both the liquids by vacuum transfer) and this was sealed under vacuum. The tube was then rotated in an oil bath at 100° for 212 hours. After reaction the tube was opened and the lower organic layer separated. Analytical V.P.C. (di-isodecyl phthalate at 30°) showed that an approximately 20% conversion to two components of lower retention time had occurred. These were separated using preparative scale V.P.C. (di-n-decyl phthalate at 50°) but only a trace of each

product could be obtained and the one with the lower retention time was not identified. The second product which showed as two overlapping peaks on analytical V.P.C. was tentatively identified as $CF_3CF{=}C(CF_3)CF_2CH_3$ from its infrared spectrum (band at 5.9 μ) and by mass spectrometry ($\frac{m}{e}$ = 246(P). $C_6H_6F_9$ requires $\frac{m}{e}$ = 246(P)).

(ii) Using Molten Potassium Hydroxide.

The apparatus used was similar to that described by Vince[177], the fluoro-alkane being passed through molten potassium hydroxide containing potassium fluoride (5%) and water (2.5%) at approximately 160° and then into a trap at -78°C.

$CF_3CHFCF(CF_3)CF_2CH_3$ (2.0 g., 7.5 mmole) was slowly distilled into a stream of nitrogen and passed through the molten KOH mixture at 160°. A clear liquid (0.9 g.) was collected in the trap and analytical V.P.C. (di-isodecyl phthalate at 20°) showed that the same products as were obtained using aqueous potassium hydroxide had been produced in approximately 60% yield.

Reaction of 1,1,1,2,3-Pentafluoro-(3-trifluoromethyl)-pentan-4-one with Potassium Hydroxide in Di-n-butyl Ether.

The apparatus consisted of a three-necked flask fitted with stirrer, dropping funnel and reflux condenser. A trap at -23° was fitted above the reflux condenser.

Di-n-butyl ether (50 ml.) and powdered potassium hydroxide (41 g.,

0.731 mole) were first placed in the flask and $CF_3CHFCF(CF_3)COCH_3$ (27.3 g., 0.112 mole) was then run in slowly with stirring. The reaction mixture became hot and turned brown in colour and a clear liquid was collected in the trap. After about 40 minutes the flask was warmed on an oil bath to 130° causing further liquid to condense in the trap. The trap was then renoved and the contents sealed in a tube (7.1 g.). Analytical V.P.C. (silicone elastomer at 20°) showed that the product consisted of one major component plus a small amount of lower boiling impurity. The major product was purified by fractionation and was identified as cis-trans-2H-heptafluorobut-2-ene (6.5 g., 32%) from its infrared spectrum and by the addition of bromine which yielded a known product. (M.W. found 179. Calc. for C_4HF_7 M.W. 182).

Part 5. Source Dosimetry. *

The ^{60}Co γ-ray source was calibrated by the method of Weiss.[178] This uses the ferrous/ferric oxidation system the overall reaction being

$$2H_2O + O_2 + 4Fe^{++} \longrightarrow 4Fe^{+++} + 4OH^-$$

The G value for this reaction (i.e. the number of molecules which have changed for 100 ev. of energy absorbed) is 15.5. A standard dosimeter solution of ferrous ammonium sulphate was made up and this was

*These results were obtained in collaboration with G.D. Dixon.

irradiated under various standard conditions. The amount of reaction which had taken place was then determined by measuring the optical densities of the solutions and radiation dosages (in rads) were calculated from the formula below.

$$\text{Dose} = \frac{\text{Optical density}}{\text{Extinction coefficient}} \times \frac{10^3 \times 0.97}{15.5}$$

(One rad corresponds to the absorption of 100 ergs/g. This is an energy density and is independent of the absorbing material and the type of radiation).

The extinction coefficient was determined from the slope of a graph of optical density against concentration of ferric ion, this being obtained by using standard solutions of ferric alum.

Experimental

The disometer solution was made up to 1 litre with ferrous ammonium sulphate (0.378 g.) and potassium chloride (0.060 g.) in 0.8N H_2SO_4 in deionised water. (The potassium chloride is added so that conductivity water need not be used. For some unknown reason the salt nullifies the effect of any impurities in the deionised water).

Samples of this solution were then placed in stoppered glass tubes and these were irradiated at various distances from the source tube at a level corresponding to the centre of the source. The time intervals were chosen so that the optical densities of the solution would be in approximately the same range as those of the standard

ferric alum solutions used to calibrate the spectrophotometer. One measurement was made in which the source was lowered and then immediately raised, with a sample of the solution touching the source tube. This was subtracted from the readings obtained with solutions touching the source tube in order to correct for reaction which occurred while the source was being raised and lowered. All the measurements were made on a Unicam S.P. 500 instrument at 305 mμ. using a slit width of 1.715 mm. These results together with those for the standard ferric alum solutions used to calculate the extination coefficient are given below.

Ferric Alum

Wt.(mg).	Micromoles/litre	Optical Density
10.1	104.7	0.377
22.1	229.2	0.762
31.3	324.5	0.995
47.2	489.3	1.31

From a plot of these results the extinction coefficient was found to be 0.3043.

Distance from Source Tube (cm.)	Irradiation Time (mins.)	Optical Density	Dose Rate rads/hr. x 10^4
Touching	6	1.030	19.95 [a]
Touching	5	0.846	19.44 [a]
5	30	1.038	4.268
10	30	0.336	1.382
20	30	0.101	0.415
Touching	Source raised and lowered	0.060	

a. Corrected for lowering and raising of the source.

A graph of dose rate against distance was drawn and the following dose rates at various distances from the source were then read off.

Distance from Source Tube (cm.)	Dose Rate rads/hr. x 10^4
Touching	19.7
2	9.1
3	7.1
4	5.6

APPENDIX 1.

N.M.R. DATA

N.M.R. Data

^{19}F N.M.R. spectra were recorded using either A.E.I. R.S.2 or Perkin Elmer R.10 instruments, while all the ^{1}H spectra were run on the latter instrument.

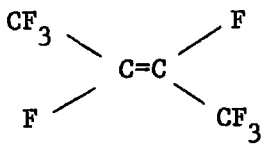
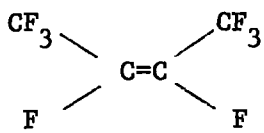
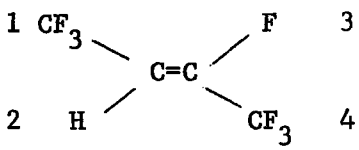
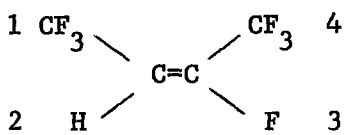
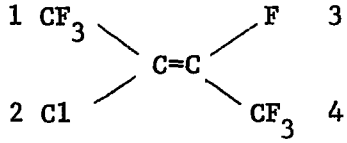
The geometrical isomers of 2H-, 2-chloro- and 2-bromoheptafluorobut-2-ene were distinguished by the coupling constants of the 1-CF_3 groups with the 3-F atom. It has been shown in halogenated propenes that JCF_3-F is fairly constant at about 23 c.p.s. when these groups are cis to each other, while JCF_3-F is about 9.5 c.p.s. when the groups are trans[179]. The cis and trans isomers of octafluorobut-2-ene are complex systems and these spectra were not analysed.

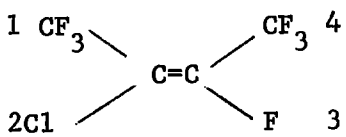
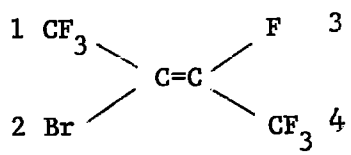
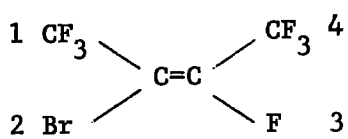
The structures of the addition products were established by examination of the chemical shifts and fine structures of the resonances of the former vinylic fluorine atoms of the olefins. F-H geminal coupling has a characteristic value of approximately 50 c.p.s.[180] and the presence or absence of this, together with the chemical shift of these resonances was sufficient to establish the orientation of addition to the unsymmetrical olefins. (The chemical shift of a fluorine atom attached to a carbon bearing a hydrogen atom occurs between about 35 and 85 p.p.m. up field from C_6F_6 [181]).

The structures of the adducts resulting from the addition of ethyl acetate to octafluorobut-2-ene and acetaldehyde to 2H-heptafluorobut-2-ene were further elucidated by ^{1}H N.M.R. spectroscopy.

^{19}F N.M.R. Spectra of Polyfluorobut-2-enes

The chemical shifts were measured from $CFCl_3$ as internal reference. Positive shifts are to high field, and the spectra were recorded using neat liquids.

Olefin	Chemical Shift p.p.m.	Structure and Coupling Constants c.p.s.	Assignation
	69.9	Complex	CF_3
	160.9	Complex	F
	67.2	Complex	CF_3
	143.7	Complex	F
	60.4	J13=17.7, J12=6.9 J14 1-2	1-CF_3
	74.6	J43=8.9	4-CF_3
	117.2	Complex	3-F
	56.8	Complex	1-CF_3
	69.6	J41=10.2, J43=7.8	4-CF_3
	113.2	Complex	3-F
	64.8	J13=24.7 J14=1.3	1-CF_3
(Ref.151)	68.4	J41=1.3 J43=5.5	4-CF_3

Olefin	Chemical Shift p.p.m.	Structure and Coupling Constants c.p.s.	Assignation
	113.7	J31=24.8 J34=5.4	3-F
	62.2	J13=8.7 J14=11.3	1-CF_3
(Ref.151)	66.3	J41=11.4 J43=7.7	4-CF_3
	106.8	J31=8.1 J34=8.1	3-F
	62.6	J13=25.5 J14=1.3 approx.	1-CF_3
	68.1	J43=4.0 J41=1.3 approx.	4-CF_3
	102.4	Complex	3-F
	59.8	J13=9.0 J14=11.4	1-CF_3
	66.2	J41=11.0 J43=7.2 approx.	4-CF_3
	95.6	Complex	3-F

^{19}F N.M.R. Spectra of the Olefin Addition Products

The chemical shifts have been measured from hexafluorobenzene as internal reference. Positive shifts are to high field of this.

Compound	Chemical Shifts p.p.m.	Coupling Constants	Assignation
$CF_3CHFCFBrCF_3$ (1)	-91.0		CF_3
CCl_4 soln.	-84.0		CF_3
	-23.3		CFBr
	33.4		CFH
$CF_3CHFCFBrCF_3$ (2)	-91.6		CF_3
CCl_4 soln.	-85.8		CF_3
	-18.7		CFBr
	32.6		CFH
$CF_3CFBrCFBrCF_3$	-89.6		CF_3
2 diastereomers	-89.3		CF_3
CCl_4 soln.	-34.4		CFBr
	-33.1		CFBr
$CF_3CHClCFClCF_3$ (1)	-94.0		CF_3
CCl_4 soln.	-82.6		CF_3
	-38.0		CFCl
$CF_3CHClCFClCF_3$ (2)	-94.3		CF_3
CCl_4 soln.	-84.4		CF_3
	-38.3		CFCl

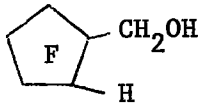
Compound	Chemical Shifts p.p.m.	Coupling Constants	Assignation
$CF_3CHBrCFBrCF_3$ (1)	-97.0		CF_3
Neat liquid	-84.9		CF_3
	-41.3		CFBr
$CF_3CHBrCFBrCF_3$ (2)	-97.5		CF_3
Neat liquid	-87.2		CF_3
	-45.4		CFBr
$CF_3CHFCF(CF_3)CH_2OH$ (1)	-87.9		CF_3
Neat liquid	-85.5		CF_3
	26.0		CF
	51.8	JF-H gem.=43.5 c.p.s.	CHF
$CF_3CHFCF(CF_3)CH_2OH$ (2)	-87.7		CF_3
Neat liquid	-86.2		CF_3
	26.9		CF
	51.7	JF-H gem=43c.p.s.	CHF
$CF_3CHFCF(CF_3)CHOHCH_3$ (1)	-90.5 (two overlapping peaks)		CF_3 groups
Neat liquid	20.7		CF
	46.4	JF-H gem =46c.p.s.	CHF
$CF_3CHFCF(CF_3)CHOHCH_3$ (2)	-90.7 (Asymmetrical peak)		CF_3 groups
Neat liquid	24.1		CF
	48.4	JF-H gem=48c.p.s. (approx).	CHF

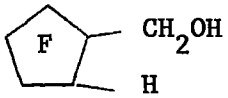
Compound	Chemical Shifts p.p.m.	Coupling Constants	Assignation
$CF_3CHFCF(CF_3)CHOHCH_3$ (3)	-90.7 (Four overlapping peaks)		CF_3 groups
2 Diastereomers	16.3		CF
Neat liquid	25.9		CF
	46.6 (Two overlapping peaks)		CHF
$CF_3CHFCF(CF_3)CHOHC_2H_5$ (1)	-89.0 (Two overlapping peaks)		CF_3 groups
CCl_4 soln.	21.7		CF
	48.3		CHF
$CF_3CHFCF(CF_3)CHOHC_2H_5$ (2)	-89.2 (Two overlapping peaks)		CF_3 groups
CCl_4 soln.	23.9		CF
	49.5		CHF
$CF_3CHFCF(CF_3)CHOHC_2H_5$ (3)	-91.2		CF_3
2 Diastereomers	-89.9 (Three overlapping peaks)		CF_3 groups
CCl_4 soln.	16.5		CF
	24.5		CF
	47.9 (Two overlapping peaks)		CHF

Compound	Chemical Shifts p.p.m.	Coupling Constants	Assignation
$CF_3CHFCH(CF_3)CH_2OH$ (1)	-94.4		CF_3
$CHCl_3$ soln.	-84.4		CF_3
	48.2		CHF
$CF_3CH_2CF(CF_3)CH_2OH$	-101.6		CF_3
$CHCl_3$ soln.	-82.0		CF_3
	-17.0		CF
$CF_3CHFCH(CF_3)CH_2OH$ (2)	-97.8		CF_3
$CHCl_3$ soln.	-85.4		CF_3
	47.8		CHF
$CF_3CHClCF(CF_3)CH_2OH$ (1)	-94.4		CF_3
CCl_4 soln.	-88.0		CF_3
	13.0		CF
$CF_3CHClCF(CF_3)CH_2OH$ (2)	-94.8		CF_3
CCl_4 soln.	-89.0		CF_3
	12.4		CF
$CF_3CHFCF(CF_3)COCH_3$ (1)	-88.1		CF_3
Neat liquid	-87.5		CF_3
	28.9		CF
	56.3	JF-H gem=45 c.p.s.	CHF
$CF_3CHFCF(CF_3)COCH_3$ (2)	-88.2		CF_3
Neat liquid	-87.3		CF_3
	28.2		CF
	51.2	JF-H gem=40 c.pps. approx.	CHF

Compound	Chemical Shifts p.p.m.	Coupling Constants	Assignation
$CF_3CHFCF(CF_3)COC_2H_5$ (1)	-90.8		CF_3
Neat liquid	-90.2		CF_3
	31.0		CF
	54.6		CHF
$CF_3CHFCF(CF_3)COC_2H_5$ (2)	-89.0		CF_3
Neat liquid	-88.0		CF_3
	31.4		CF
	50.8		CHF
$CF_3CH_2CF(CF_3)COCH_3$	-101.6		CF_3
CCl_4 soln.	-82.8		CF_3
	18.4		CF
$CF_3CHFCH(CF_3)COCH_3$	-100.4		CF_3
2 Diastereomers	-99.0		CF_3
Neat liquid	-85.8		CF_3
	-85.2		CF_3
	41.0	JF-Hgem=47 c.p.s. approx.	CHF
	46.2	JF-H gem=48 c.p.s. approx.	CHF
$CF_3CHClCF(CF_3)COCH_3$ (1)	-94.8		CF_3
CCl_4 soln.	-89.4		CF_3
	24.6		CF

Compound	Chemical Shifts p.p.m.	Coupling Constants	Assignation
$CF_3CHClCF(CF_3)COCH_3$ (2)	-93.0		CF_3
	-89.0		CF_3
	22.6		CF
$CF_3CHFCF(CF_3)SCH_3$ (1)	-91.0		CF_3
Neat liquid	-87.6		CF_3
	-1.8		CF
	38.8	JF-H gem=48 c.p.s. approx.	CHF
$CF_3CHFCF(CF_3)SCH_3$ (2)	-91.6		CF_3
Neat liquid	-89.6		CF_3
	3.0		CF
	38.2		CHF
$CF_3CHFCH(CF_3)SCH_3$ (1)	-92.6		CF_3
CCl_4 soln.	-85.2		CF_3
	38.3		CHF
$CF_3CHFCH(CF_3)SCH_3$ (2)	-96.2		CF_3
CCl_4 soln.	-86.6		CF_3
	33.4		CHF
$CF_3CHFCF(CF_3)CH(CH_3)OCOCH_3$	(1) -90.3 (Four overlapping peaks)		CF_3 groups
2 Diastereomers	20.1		CF
Neat liquid	22.6		CF
	46.6 (Two overlapping peaks)		CHF

Compound	Chemical Shifts p.p.m.	Coupling Constants	Assignation
$CF_3CHFCF(CF_3)CH(CH_3)OCOCH_3$ (2)	-91.3		CF_3
2 Diastereomers	-89.9 (Three overlapping peaks)		CF_3 groups
Neat liquid	17.7		CF
	23.3		CF
	48.6 (Two overlapping peaks)		CHF
$CF_3CHFCF(CF_3)CF_2CH_3$	-89.9		CF_3
2 Diastereomers	-88.1 (Three overlapping peaks)		CF_3 groups
Neat liquid	-64.3		CF_2
	-62.1 (Three overlapping peaks)		CF_2
	24.8		CFR
	51.0		CHF
 (1)	Group of peaks between -45 and -29 p.p.m.		CF_2 groups
Neat liquid	16.6		CFR
	49.6	JF-H gem=46 c.p.s.	CHF

Compound		Chemical Shifts p.p.m.	Coupling Constants	Assignation
	(2)	Group of peaks between -49 and -26 p.p.m.		CF_2 groups
Neat liquid		30.4		CFR
		60.6	JF-H gem = 47 c.p.s.	CHF

^{1}H N.M.R. Spectra of Olefin Addition Products

The chemical shifts were measured from $(CH_3)_4Si$ as internal reference.

Compound	δ p.p.m.	Structure and Coupling Constants	Assignation
$CF_3CH_2CF(CF_3)COCH_3$	1.4	Doublet J = 6 c.p.s.	CH_3
CCl_4 soln.	1.8	Complex	CH_2
$CF_3CHFCH(CF_3)COCH_3$	2.5	Singlet	CH_3
(2 Diastereomers)	4.1	Complex	$CH(CF_3)R$
Neat liquid	5.4	Doublet with further splitting JF-H gem = 44 c.p.s.	CHF
$CF_3CHFCF(CF_3)CH(CH_3)OCOCH_3$ (1)	~1.5	Doublet J = 6 c.p.s.	$\underline{CH_3}$-CH
Neat liquid	2.1	Singlet	$\underline{CH_3}O$
	4.5-6	Two complex broad peaks	CH's
$CF_3CHFCF(CF_3)CH(CH_3)OCOCH_3$ (2)	~1.55	Doublet J = 6 c.p.s.	$\underline{CH_3}$-CH
Neat liquid	2.2	Singlet	$\underline{CH_3}$-O
	4.5-6	Two complex broad peaks	CH's

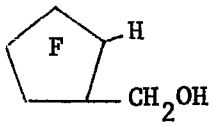
APPENDIX 2.

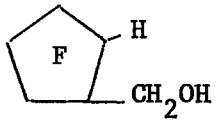
INFRARED SPECTRA

Infrared Spectra

All the spectra shown on the following pages are of previously unreported compounds apart from the exceptions listed. Where there are two or more diastereomeric forms of a compound the numbers in parentheses behind the formulae refer to the order of appearance from a di-n-decyl phthalate V.P.C. column.

$CF_3CHFCFBrCF_3$[27] (Nos. 1 and 2) and $CF_3CHFCF(CF_3)CH_2OH$[44] (Nos. 14 and 15) have been previously reported as mixtures of diastereomers. $CF_3CH{=}CFCF_3$[140] (Nos. 3 and 4), $CF_3CF{=}CFCF_3$[133] (Nos. 9 and 10) and $CF_3CCl{=}CFCF_3$ (Nos. 11 and 12) are also previously reported compounds but the spectra of the geometrical isomers of these are included for comparison purposes.

1. $CF_3CHFCFBrCF_3$ (1)
2. $CF_3CHFCFBrCF_3$ (2)
3. Trans-$CF_3CH{=}CFCF_3$
4. Cis-$CF_3CH{=}CFCF_3$ 40%
   Trans-$CF_3CH{=}CFCF_3$ 60%
5. $CF_3CHClCFClCF_3$ (1)
6. $CF_3CHClCFClCF_3$ (2)
7. $CF_3CHBrCFBrCF_3$ (1)
8. $CF_3CHBrCFBrCF_3$ (2)
9. Trans $CF_3CF{=}CFCF_3$
10. Cis-$CF_3CF{=}CFCF_3$
11. Trans-$CF_3CCl{=}CFCF_3$
12. Cis-$CF_3CCl{=}CFCF_3$
13. Cis-$CF_3CBr{=}CFCF_3$ ~35%
    Trans-$CF_3CBr{=}CFCF_3$~65%
14. $CF_3CHFCF(CF_3)CH_2OH$ (1)
15. $CF_3CHFCF(CF_3)CH_2OH$ (2)
16. $CF_3CHFCF(CF_3)CHOHCH_3$ (1)
17. $CF_3CHFCF(CF_3)CHOHCH_3$ (2)
18. $CF_3CHFCF(CF_3)CHOHCH_3$ (3)
    (Two diastereomers).
19. $CF_3CHFCF(CF_3)CHOHC_2H_5$ (1)
20. $CF_3CHFCF(CF_3)CHOHC_2H_5$ (2)
21. $CF_3CHFCF(CF_3)CHOHC_2H_5$ (3)
    (Two diastereomers).
22. $CF_3CHFCH(CF_3)CH_2OH$ (1)
23. $CF_3CH_2CF(CF_3)CH_2OH$
24. $CF_3CHFCH(CF_3)CH_2OH$ (2)
25. $CF_3CHClCF(CF_3)CH_2OH$ (1)
26. $CF_3CHClCF(CF_3)CH_2OH$ (2)
27. $CF_3CHBrCF(CF_3)CH_2OH$
    (Two diastereomers).
28. 

(1)
29. 

(2)
30. $CF_3CHFCF(CF_3)COCH_3$ (1)
31. $CF_3CHFCF(CF_3)COCH_3$ (2)
32. $CF_3CHFCF(CF_3)COC_2H_5$ (1)
33. $CF_3CHFCF(CF_3)COC_2H_5$ (2)
34. $CF_3CH_2CF(CF_3)COCH_3$
35. $CF_3CHFCH(CF_3)COCH_3$
    (Two diastereomers).
36. $CF_3CHClCF(CF_3)COCH_3$ (1)

37. $CF_3CHClCF(CF_3)COCH_3$ (2)

38. $CF_3CHBrCF(CF_3)COCH_3$

(Two diastereomers, slightly impure).

39. $CF_3CHFCF(CF_3)SCH_3$ (1)

40. $CF_3CHFCF(CF_3)SCH_3$ (2)

41. $CF_3CHFCH(CF_3)SCH_3$ (1)

42. $CF_3CHFCH(CF_3)SCH_3$ (2)

43. $CF_3CHFCF(CF_3)CH(CH_3)OCOCH_3$ (1)

(Two diastereomers).

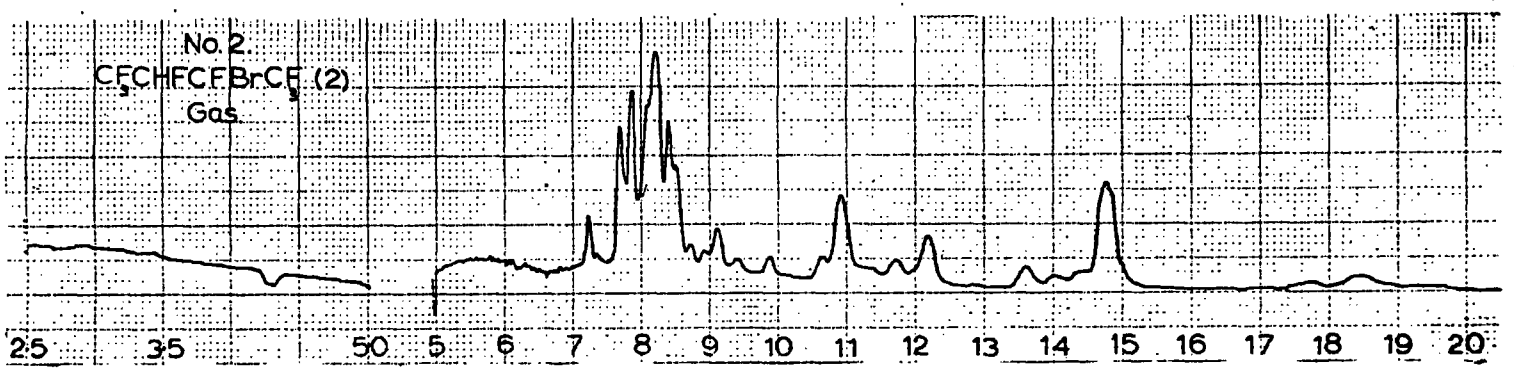
44. $CF_3CHFCF(CF_3)CH(CH_3)OCOCH_3$ (2)

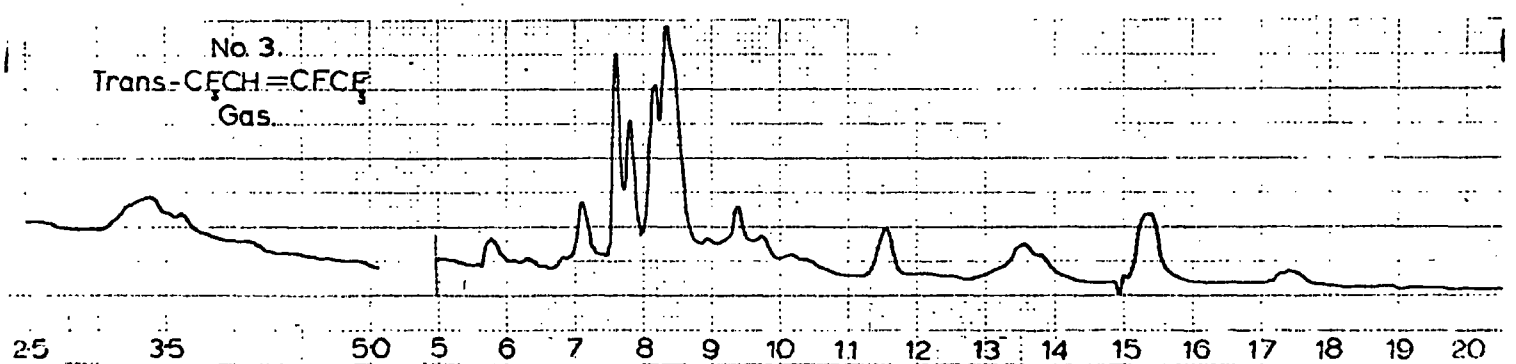
(Two diastereomers).

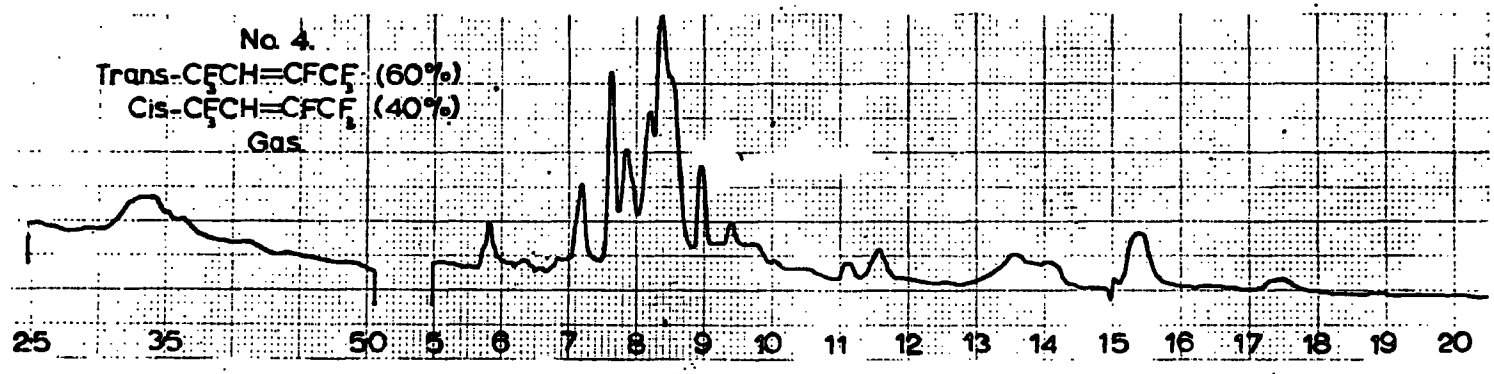
45. $CF_3CHFCF(CF_3)CF_2CH_3$

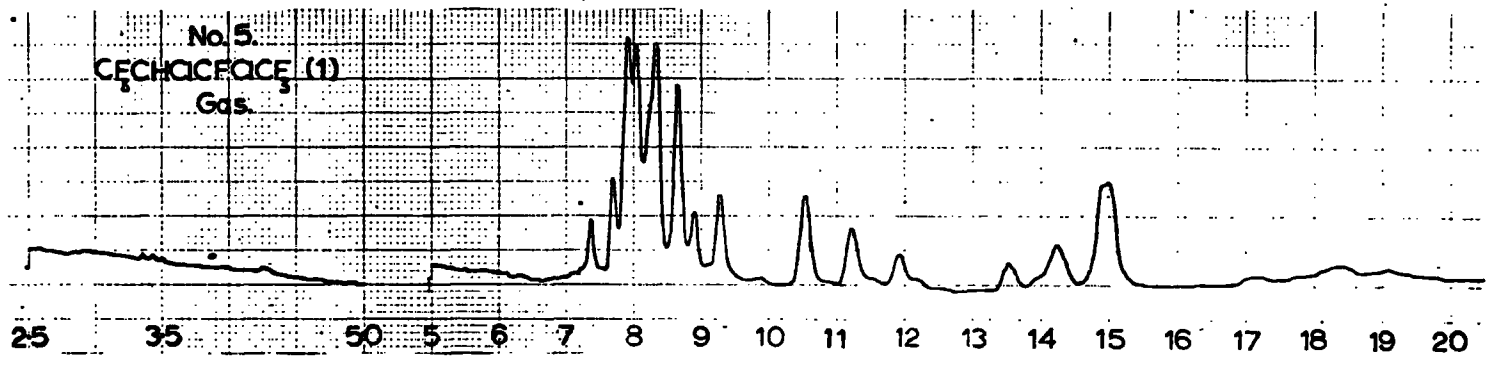
(Two diastereomers).

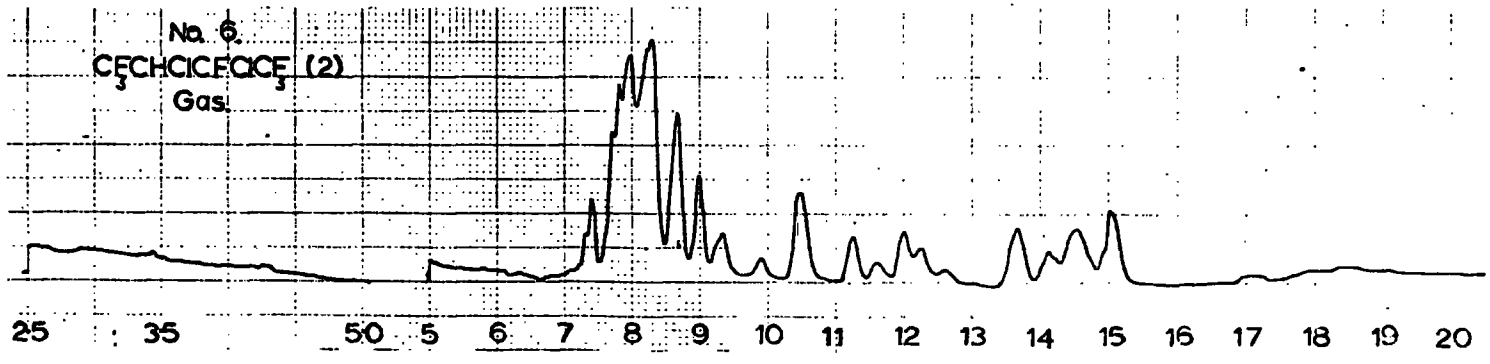
No. 1.
$CF_3CHFCFBrCF_3$ (1)
Gas.
2.5
3.5
5.0
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

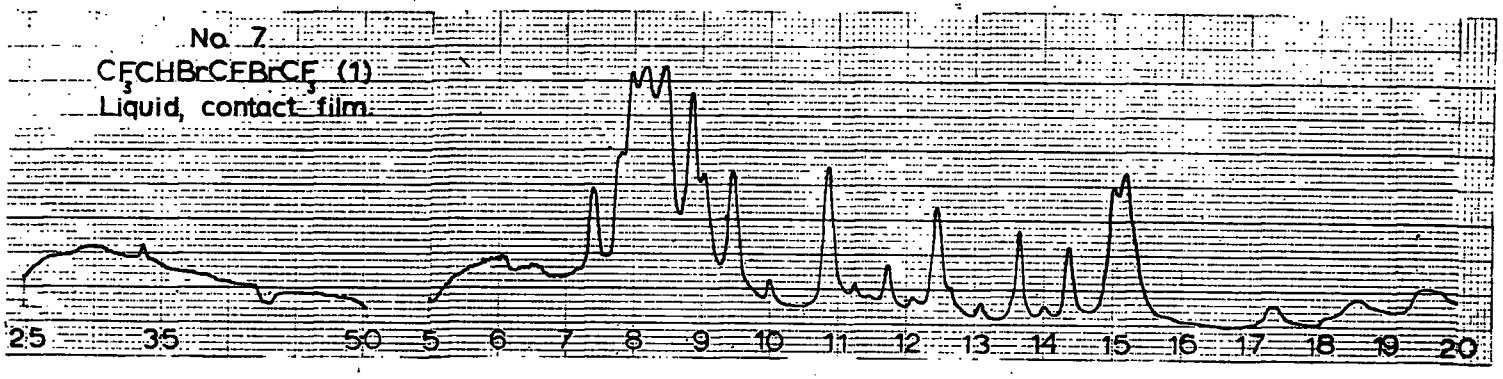

No. 2.
$CF_3CHFCFBrCF_3$ (2)
Gas.
2.5
3.5
5.0
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

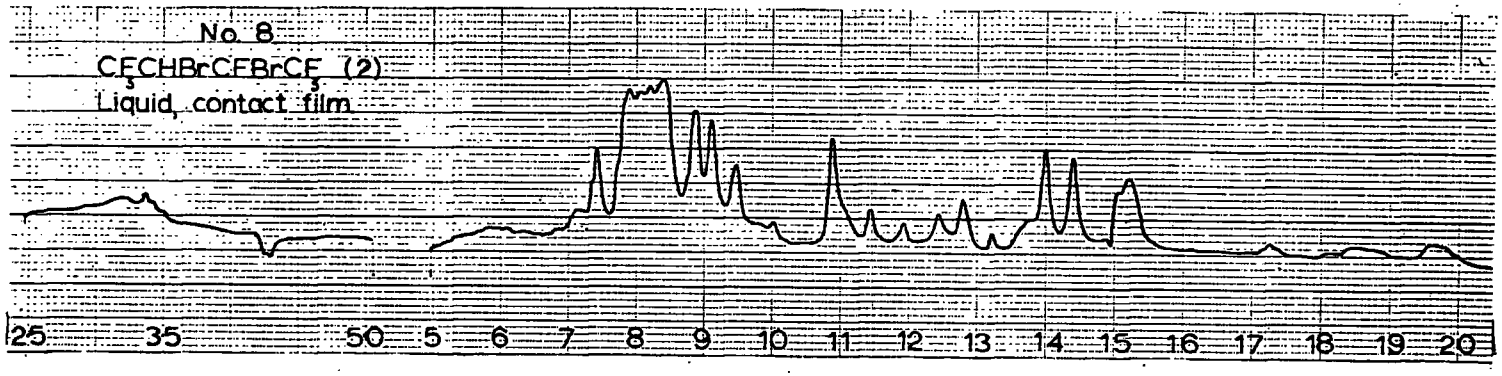

No. 3.
Trans-$CF_3CH{=}CFCF_3$
Gas.
2.5
3.5
5.0
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

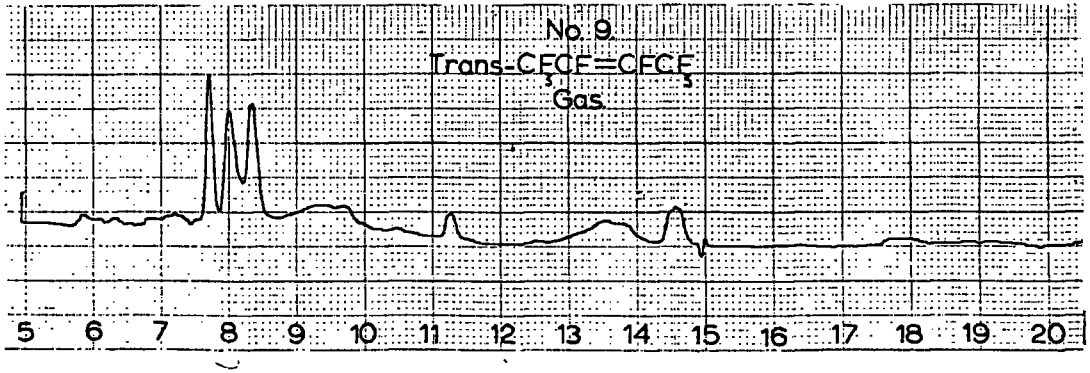

No. 4.
Trans-$C_2F_5CH{=}CFCF_3$ (60%)
Cis-$C_2F_5CH{=}CFCF_3$ (40%)
Gas.
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

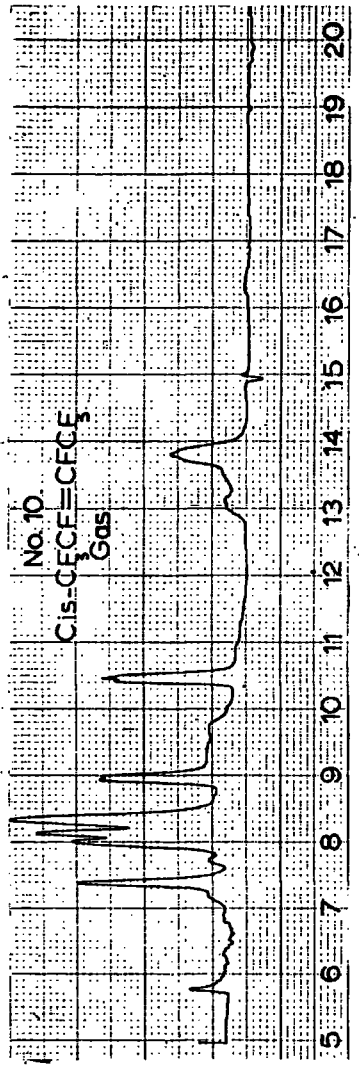

No. 5.
$C_2F_5CHClCFClCF_3$ (1)
Gas.
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

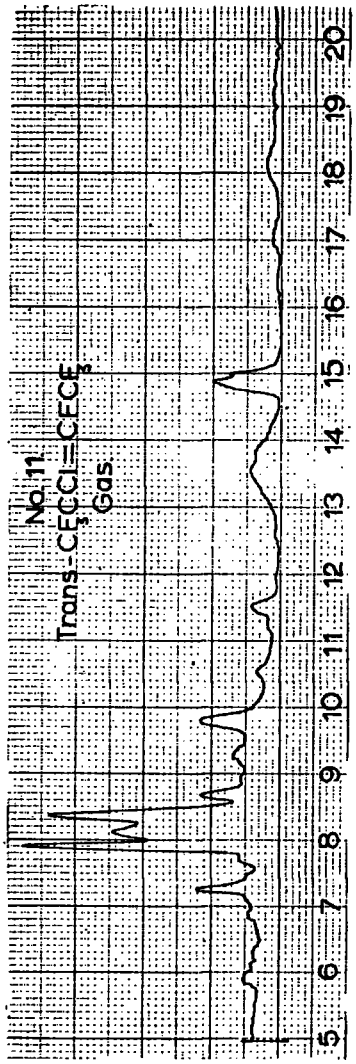

No. 6.
$C_2F_5CHClCFClCF_3$ (2)
Gas.
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

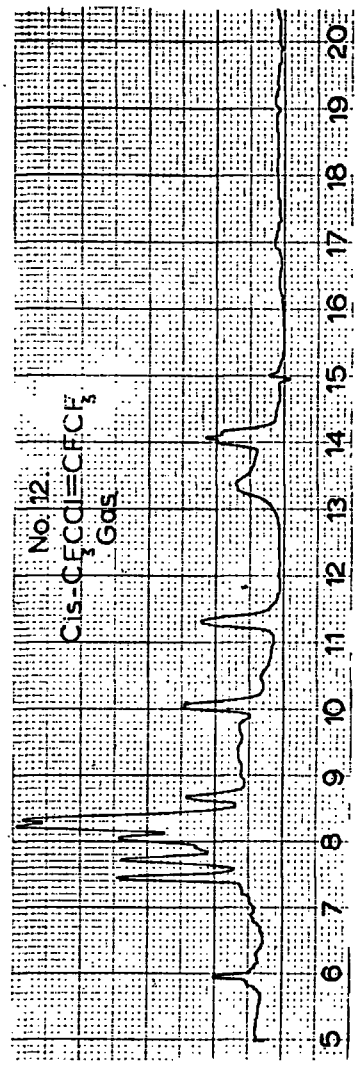

No. 7
$CF_3CHBrCFBrCF_3$ (1)
Liquid, contact film
25
35
50
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

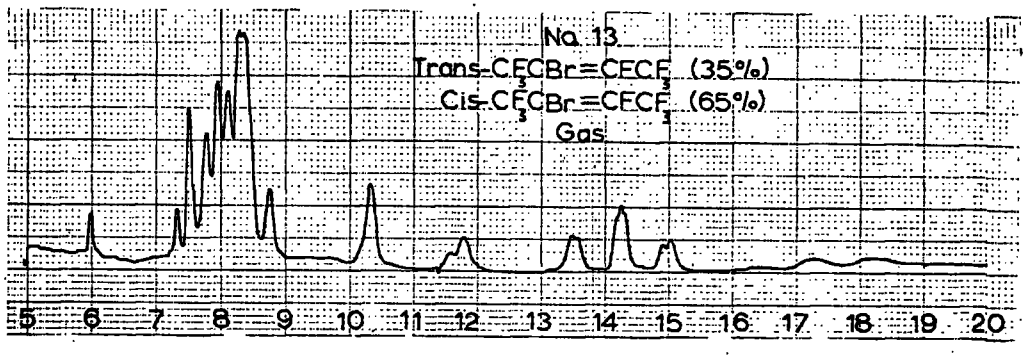

No. 8
$CF_3CHBrCFBrCF_3$ (2)
Liquid, contact film
25
35
50
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

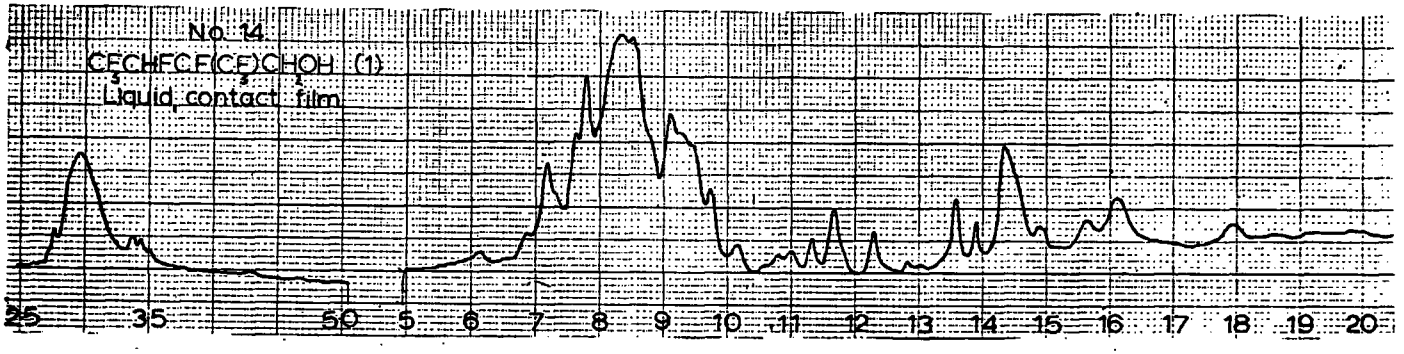

No. 9
Trans-$CF_3CF{=}CFCF_3$
Gas
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

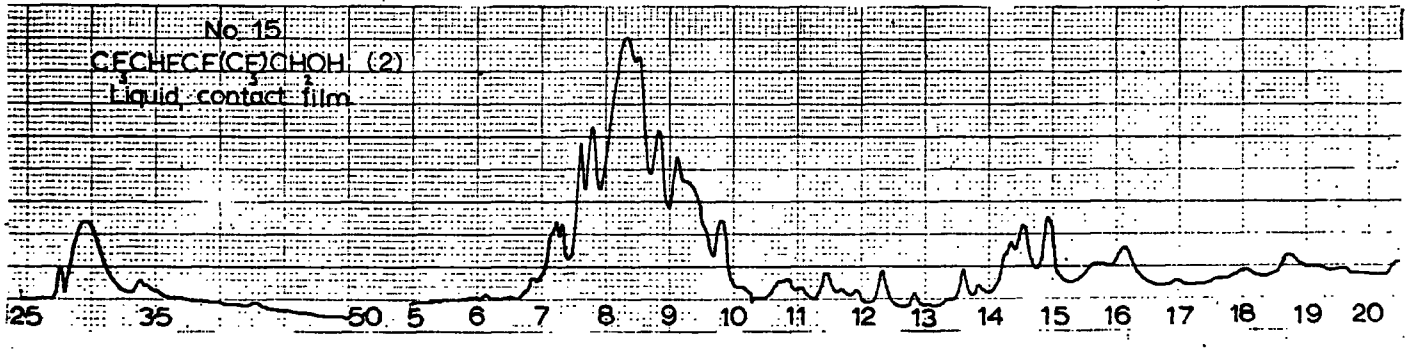

No. 10
Cis-CFCF=CFCF3
Gas
5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

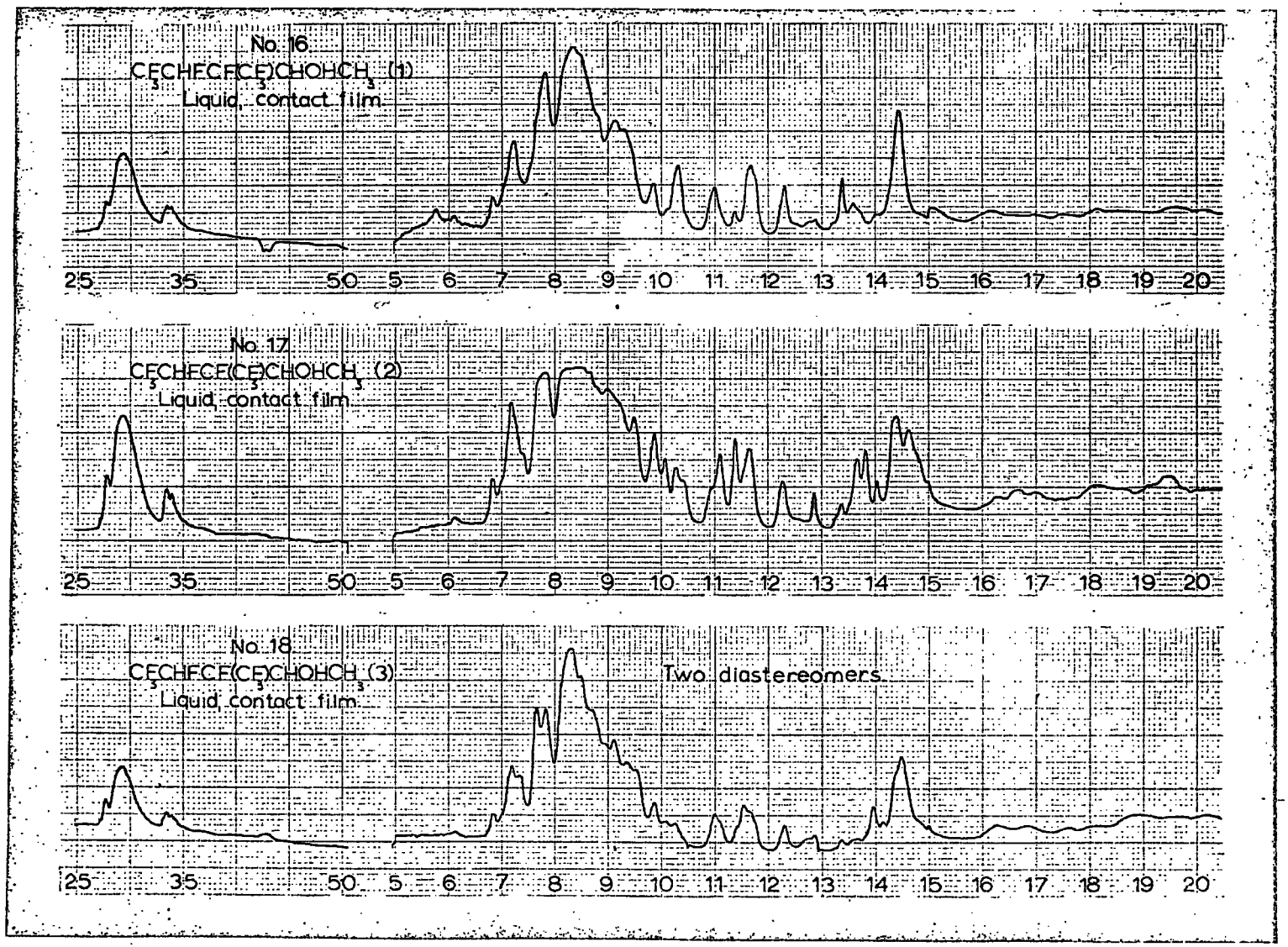

No. 11
Trans-CFCCl=CFCF3
Gas
5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

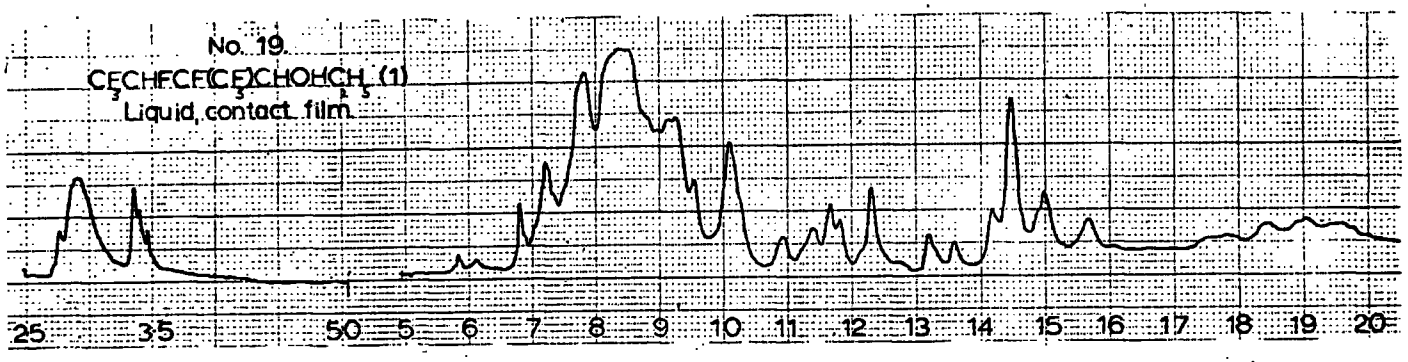

No. 12
Cis-CFCCl=CFCF3
Gas
5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

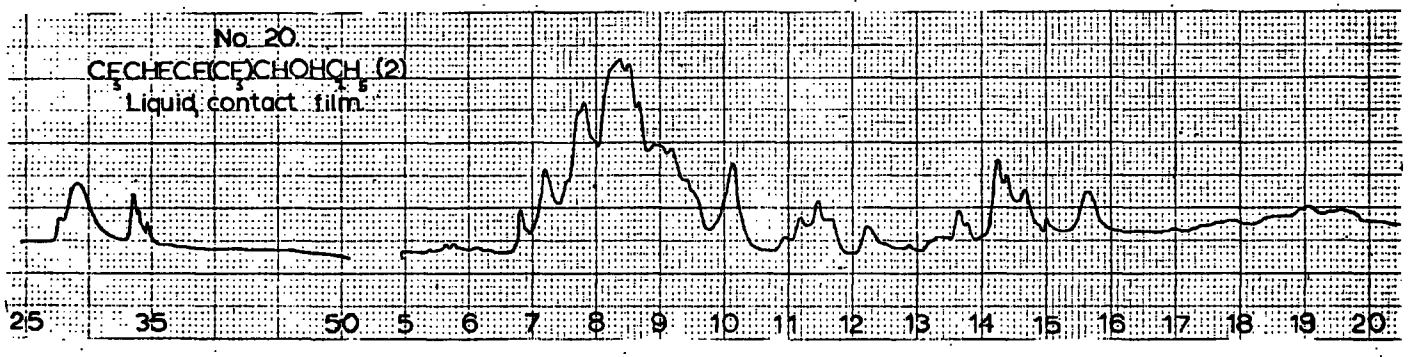

No. 13
Trans-$CF_3CBr{=}CFCF_3$ (35%)
Cis-$CF_3CBr{=}CFCF_3$ (65%)
Gas
5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

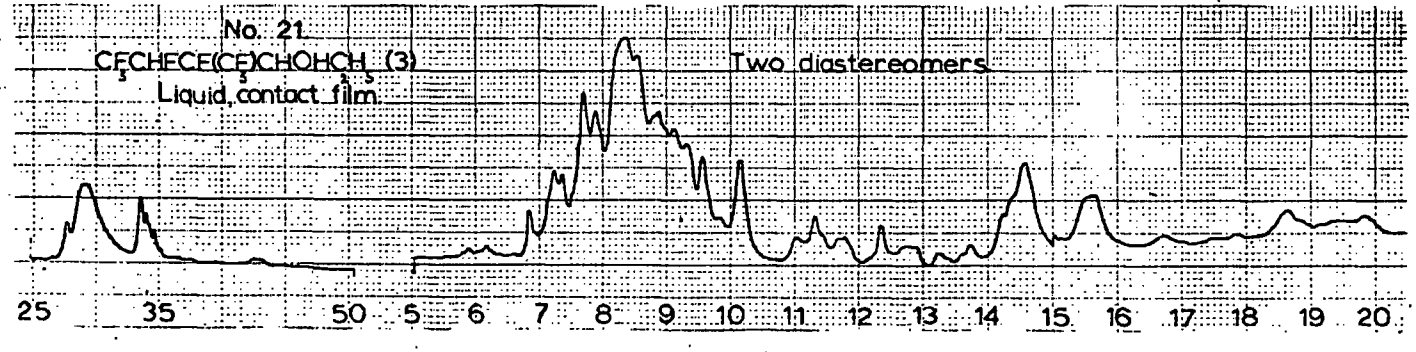

No. 14
$CF_3CHFCF(CF_3)CH_2OH$ (1)
Liquid contact film
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

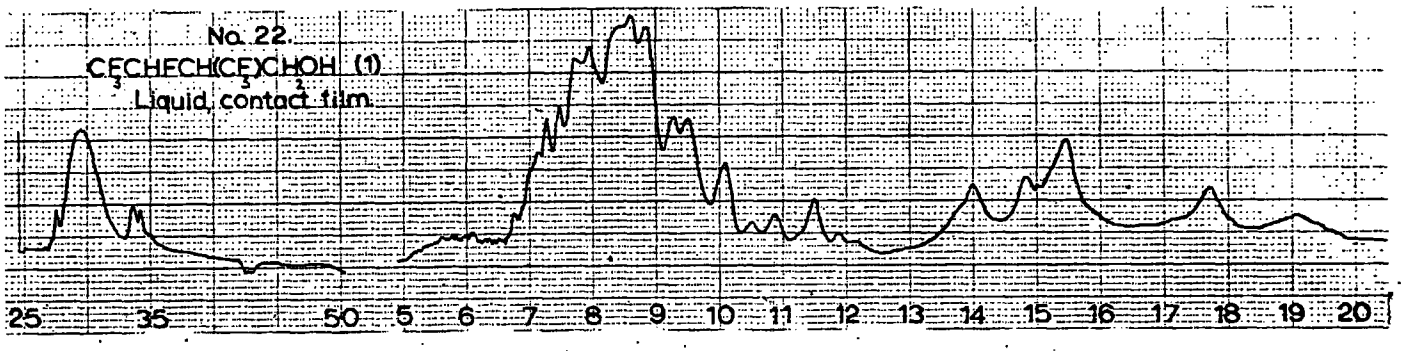

No. 15
$CF_3CHFCF(CF_3)CH_2OH$ (2)
Liquid contact film
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

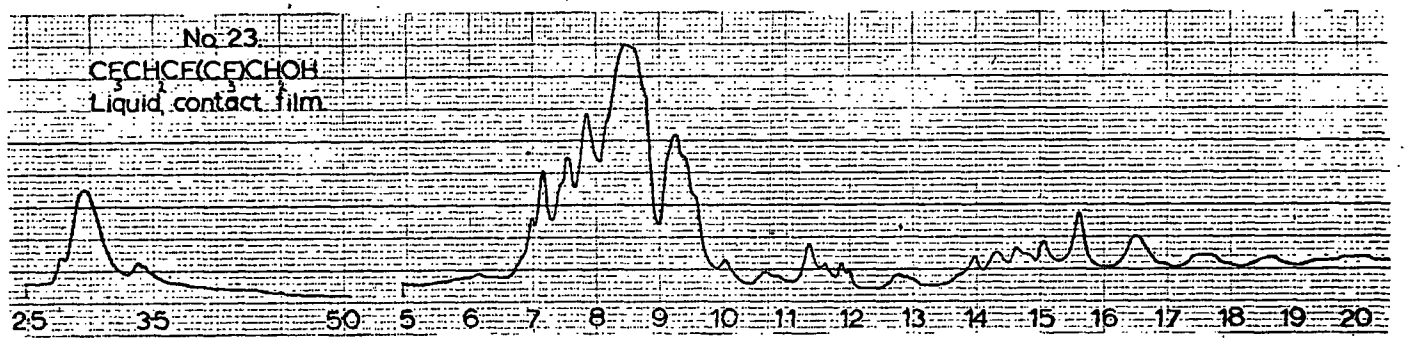

No. 16
$CF_3CHFCF(CF_3)CHOHCH_3$ (1)
Liquid contact film
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
No. 17
$CF_3CHFCF(CF_3)CHOHCH_3$ (2)
Liquid contact film
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
No. 18
$CF_3CHFCF(CF_3)CHOHCH_3$ (3)
Liquid contact film
Two diastereomers
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

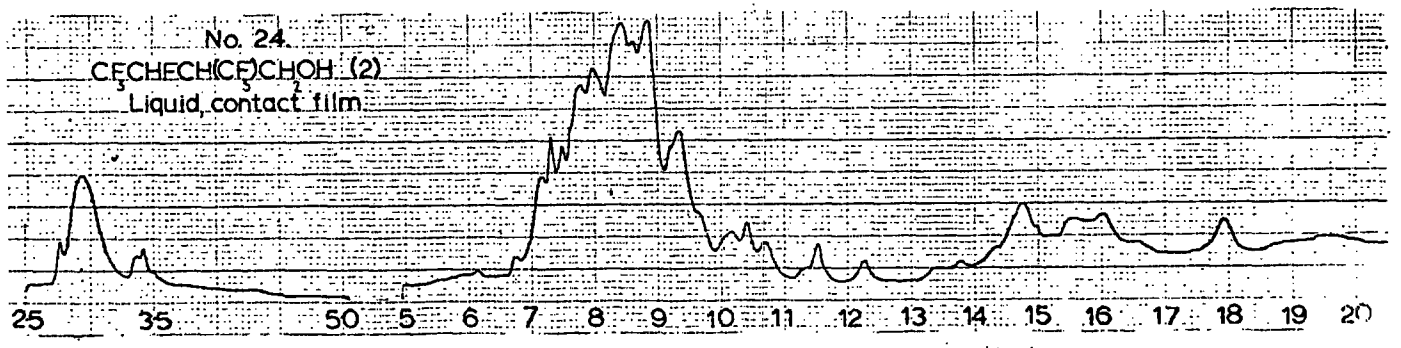

No. 19.
$CF_3CHFCF(CF_3)CHOHCH_2CH_3$ (1)
Liquid, contact film
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

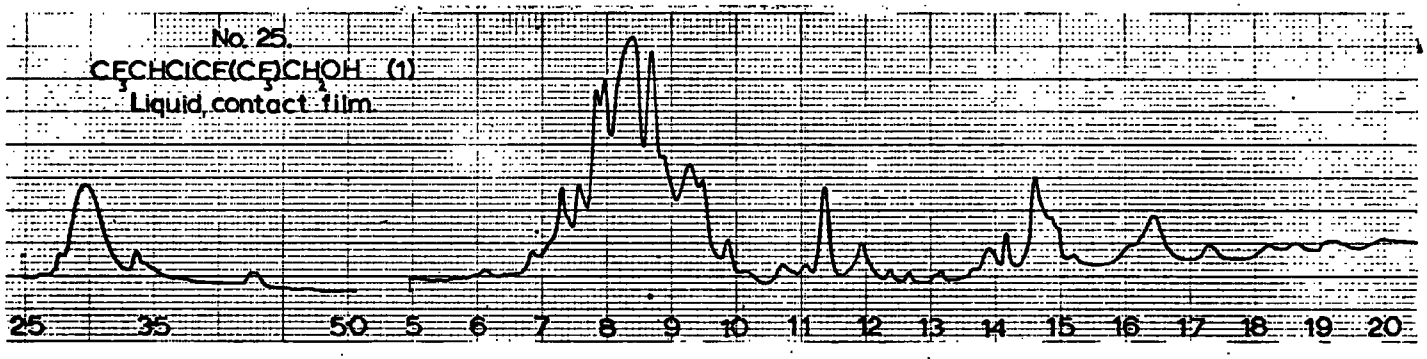

No. 20.
$CF_3CHFCF(CF_3)CHOHCH_2CH_3$ (2)
Liquid, contact film
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

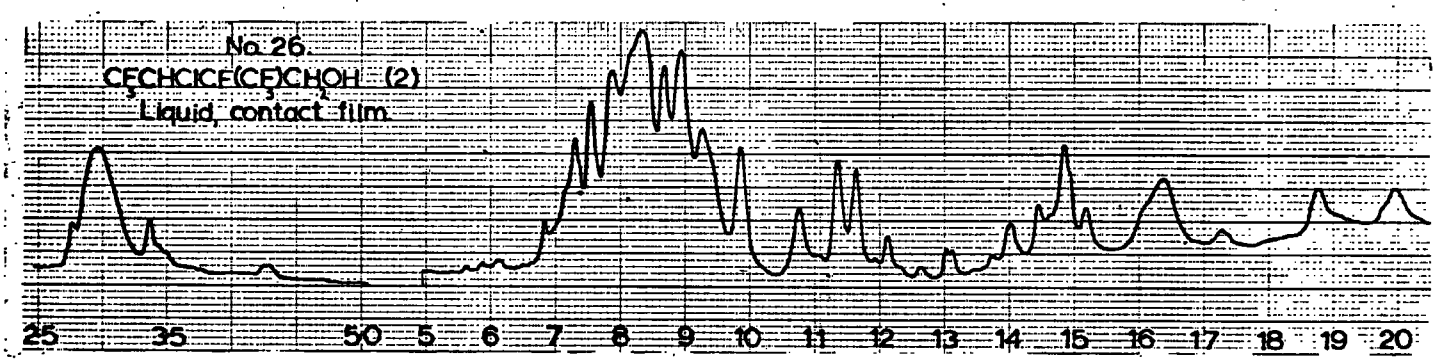

No. 21.
$CF_3CHFCF(CF_3)CHOHCH_2CH_3$ (3)
Liquid, contact film
Two diastereomers
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

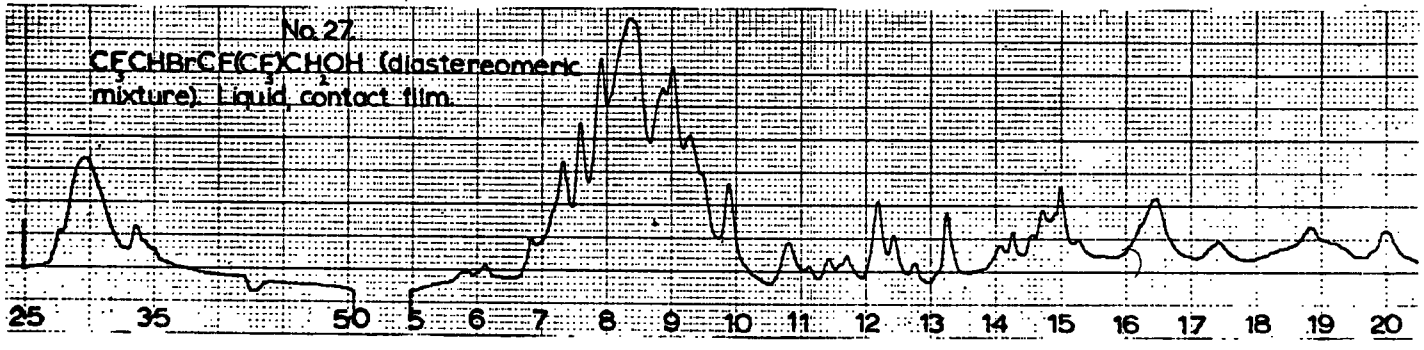

No. 22.
$CF_3CHFCH(CF_3)CH_2OH$ (1)
Liquid, contact film.
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

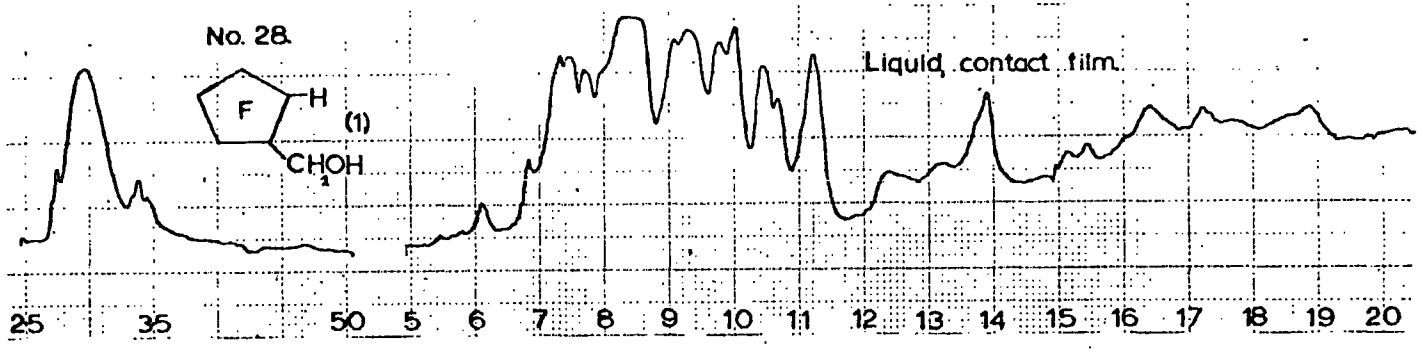

No. 23.
$CF_3CH_2CF(CF_3)CH_2OH$
Liquid, contact film.
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

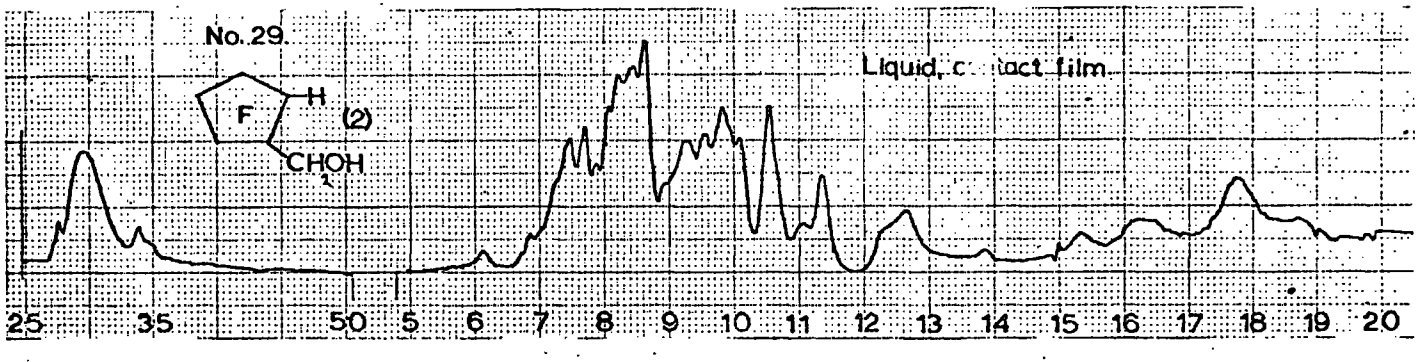

No. 24.
$CF_3CHFCH(CF_3)CH_2OH$ (2)
Liquid, contact film.
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

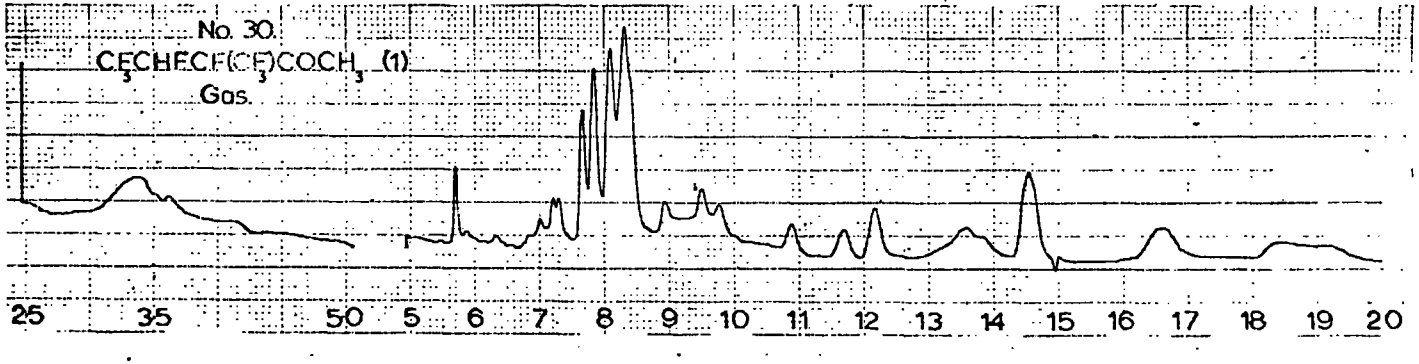

No. 25.
$CF_3CHClCF(CF_3)CH_2OH$ (1)
Liquid contact film.
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

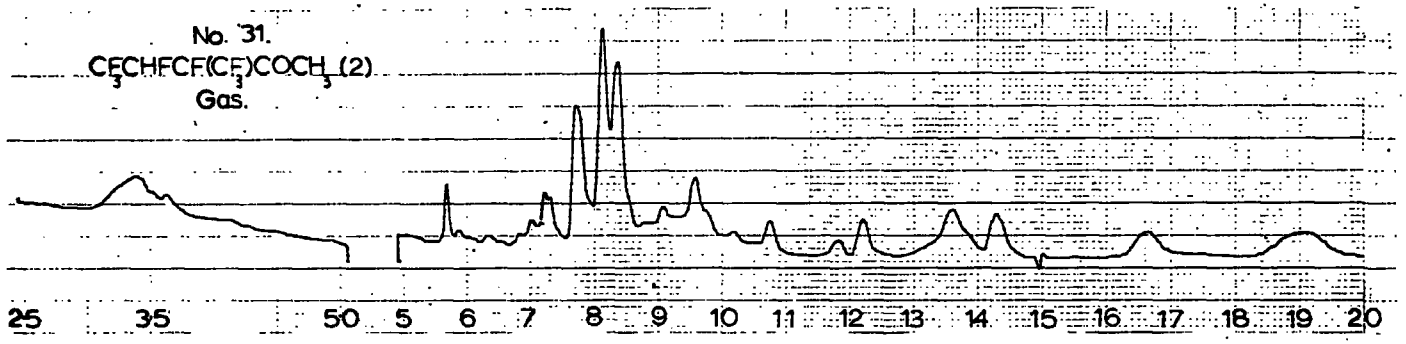

No. 26.
$CF_3CHClCF(CF_3)CH_2OH$ (2)
Liquid contact film.
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

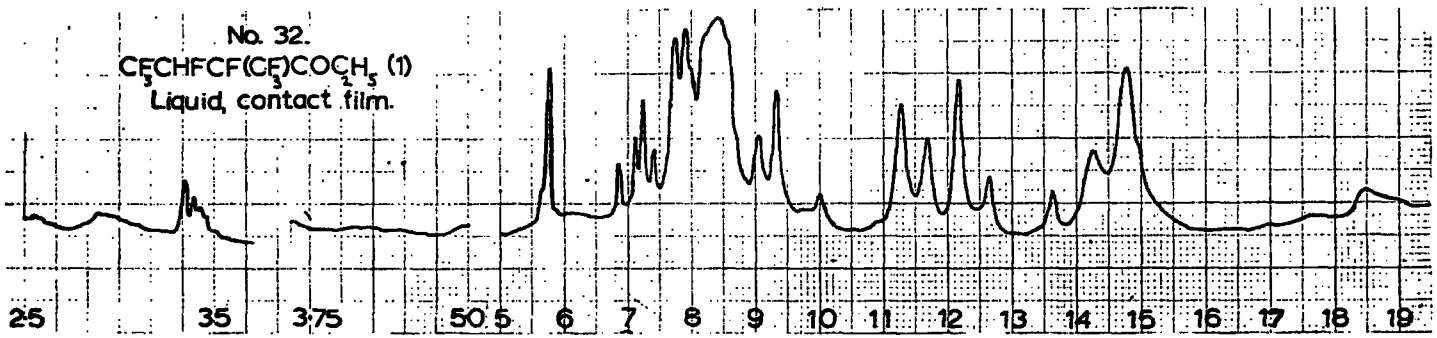

No. 27.
$CF_3CHBrCF(CF_3)CH_2OH$ (diastereomeric mixture). Liquid contact film.
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

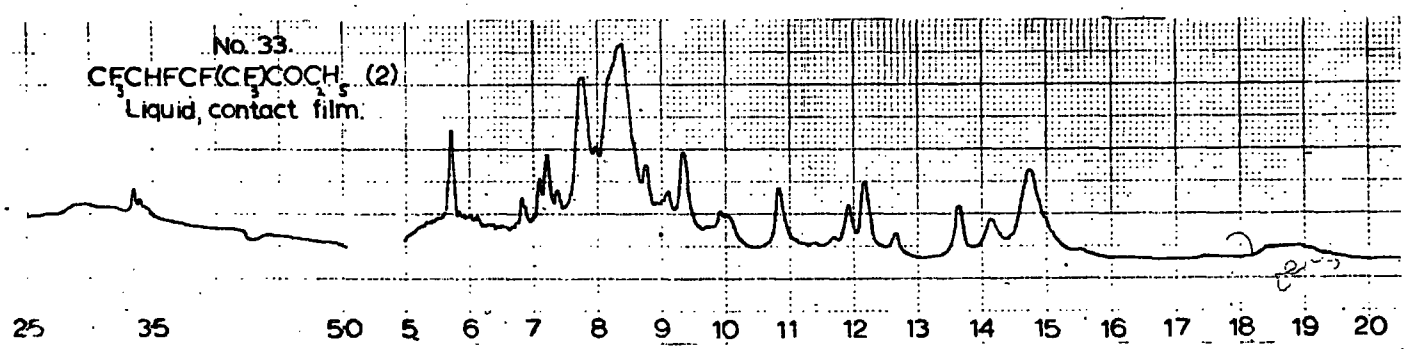

No. 28.
F
H
(1)
CH2OH
Liquid, contact film.
25
35
50
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

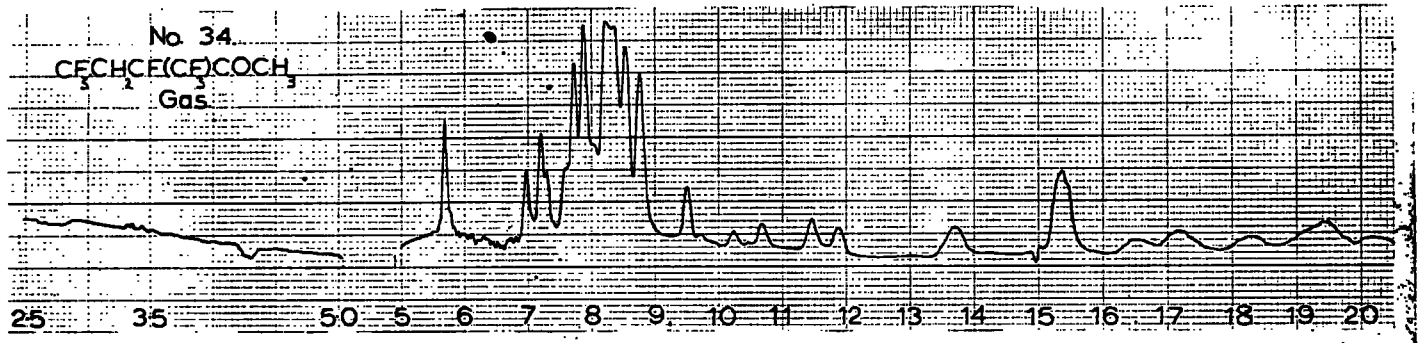

No. 29.
F
H
(2)
CH2OH
Liquid, contact film.
25
35
50
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

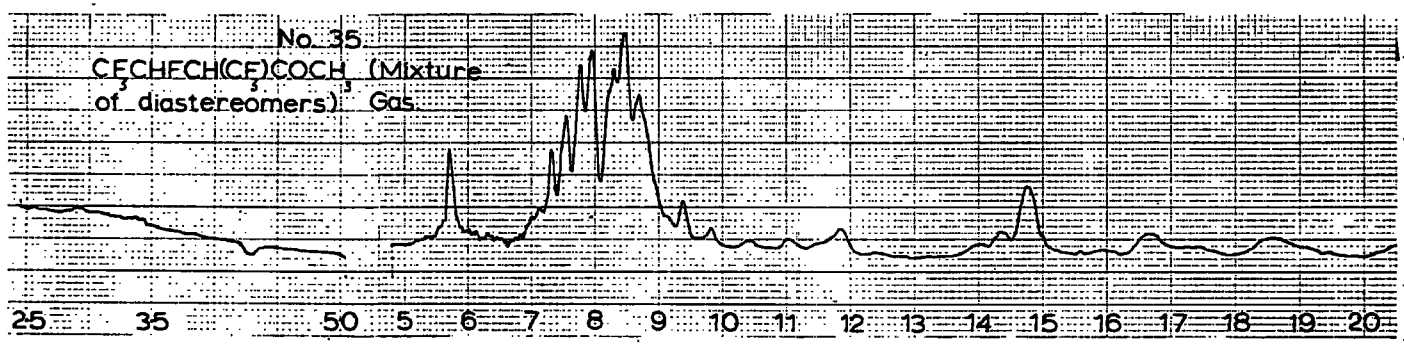

No. 30.
C3CHFCF(CF3)COCH3 (1)
Gas.
25
35
50
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

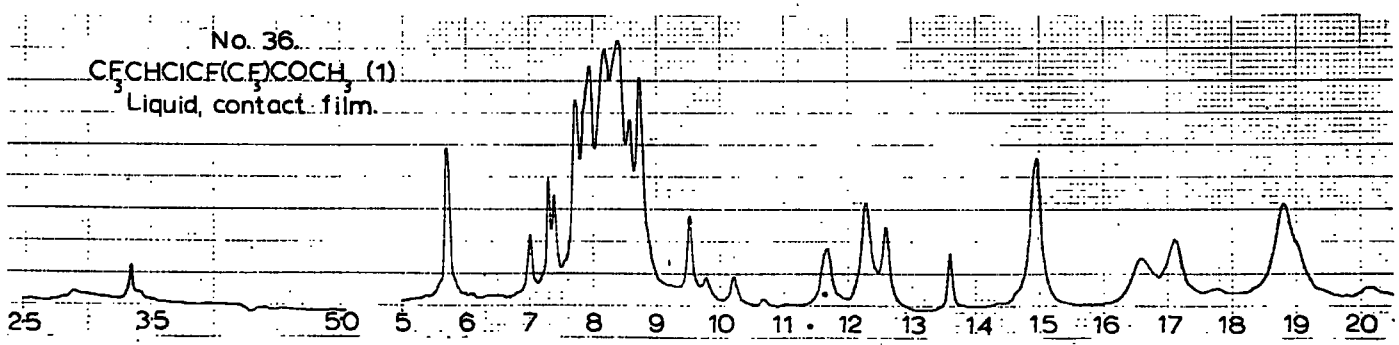

No. 31.
$CF_3CHFCF(CF_3)COCH_3$ (2)
Gas.
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

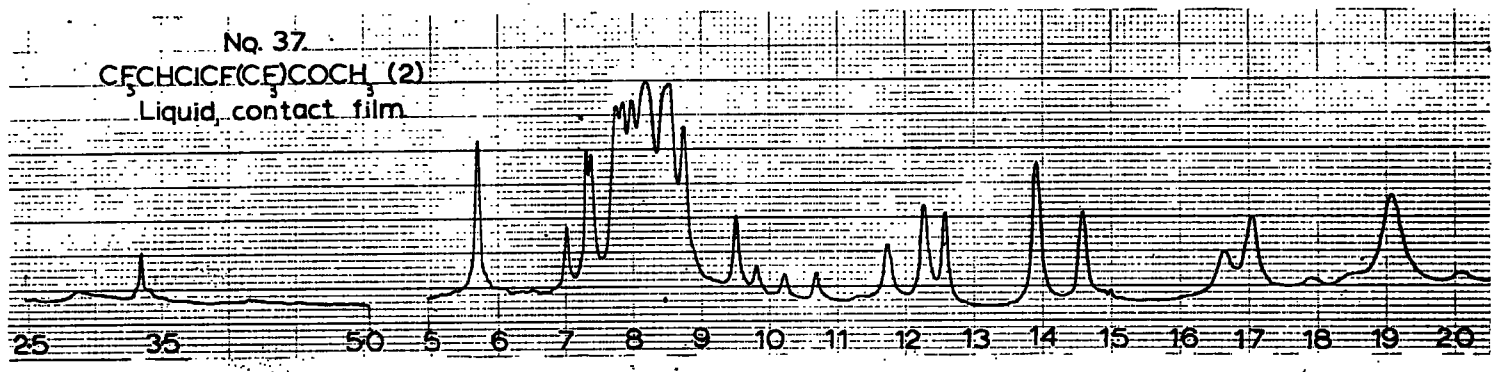

No. 32.
$CF_3CHFCF(CF_3)COC_2H_5$ (1)
Liquid, contact film.
25 35 3·75 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19

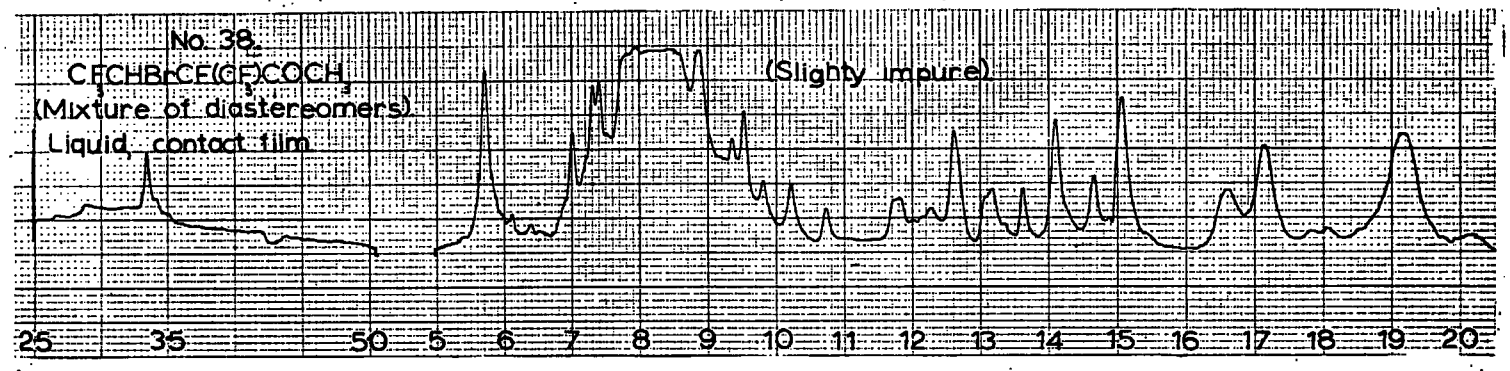

No. 33.
$CF_3CHFCF(CF_3)COC_2H_5$ (2)
Liquid, contact film.
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

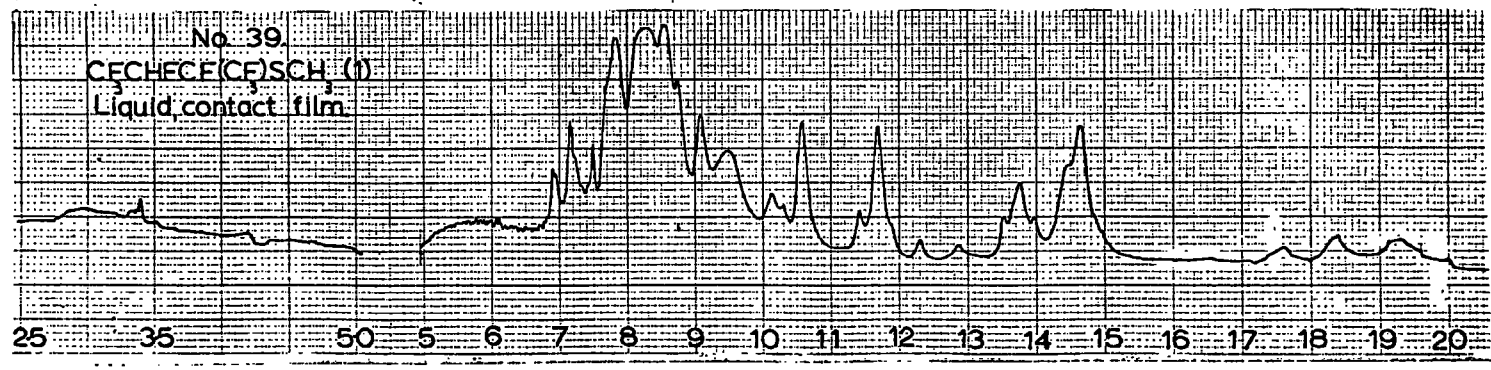

No. 34.
$CF_3CH_2CF(CF_3)COCH_3$
Gas.
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

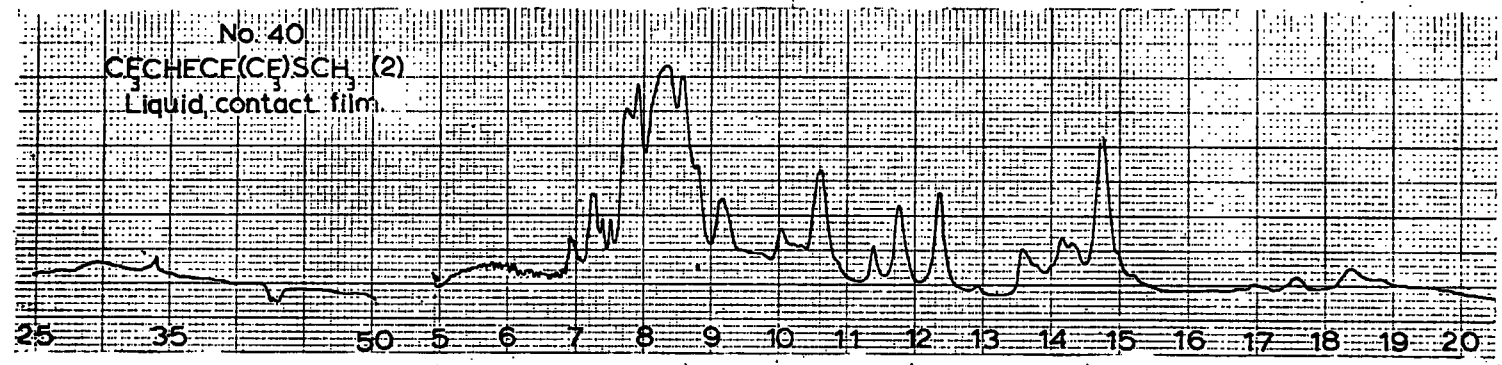

No. 35.
$CF_3CHFCH(CF_3)COCH_3$ (Mixture of diastereomers) Gas.
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

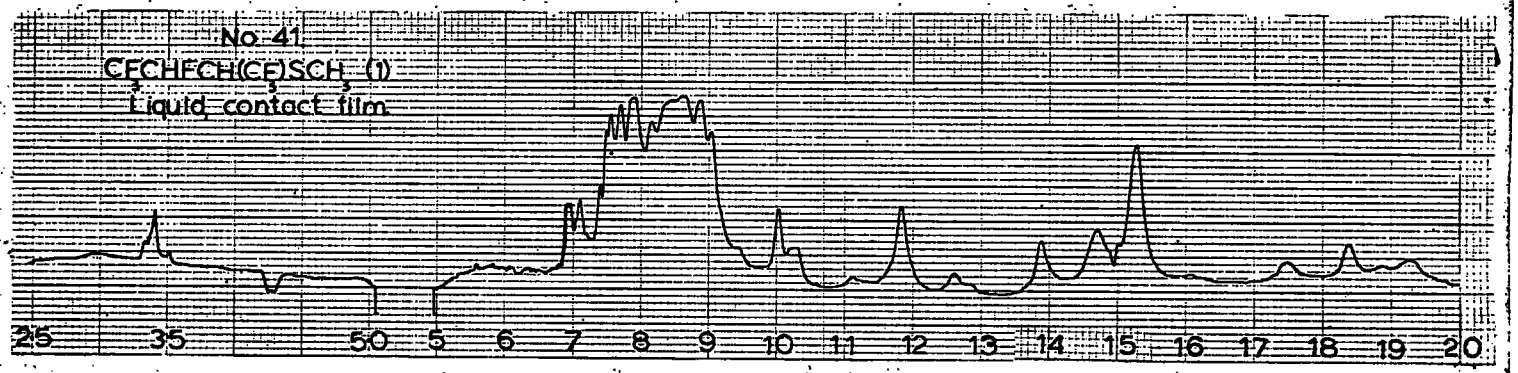

No. 36.
$CF_3CHClCF(CF_3)COCH_3$ (1)
Liquid, contact film.
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

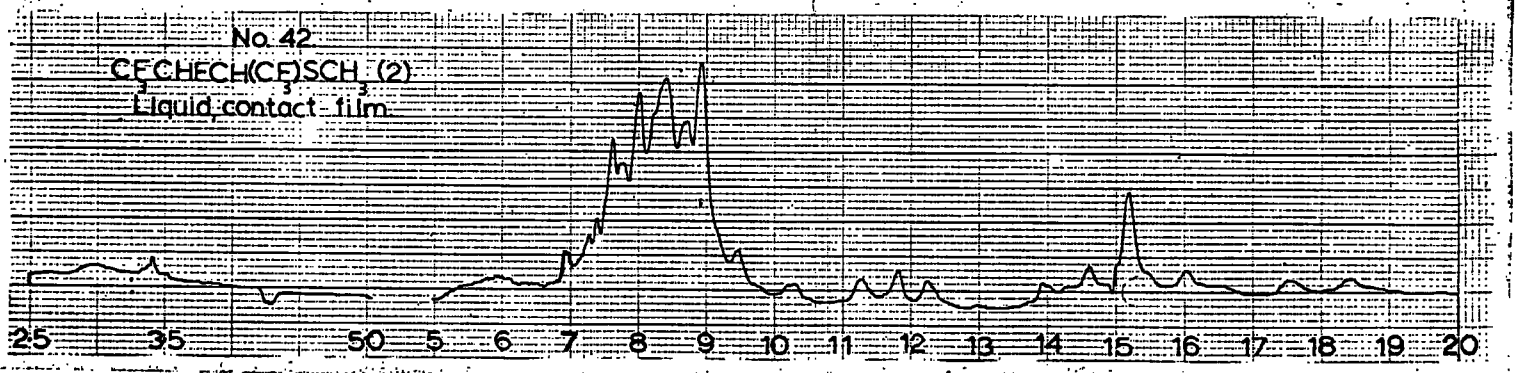

No. 37
$CF_3CHClCF(CF_3)COCH_3$ (2)
Liquid contact film
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

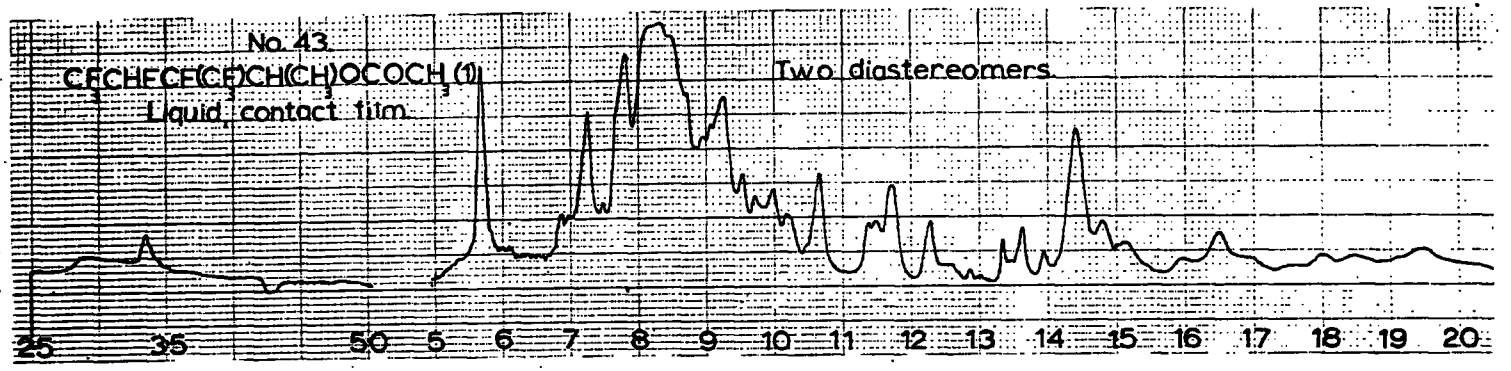

No. 38
$CF_3CHBrCF(CF_3)COCH_3$
(Mixture of diastereomers)
Liquid contact film
(Slighty impure)
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

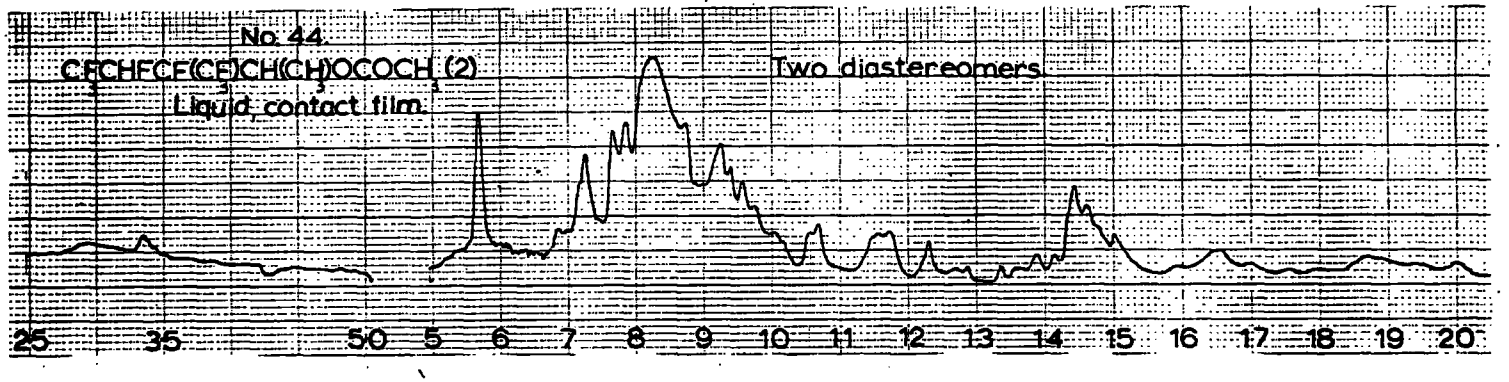

No. 39
$CF_3CHFCF(CF_3)SCH_3$ (1)
Liquid contact film
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

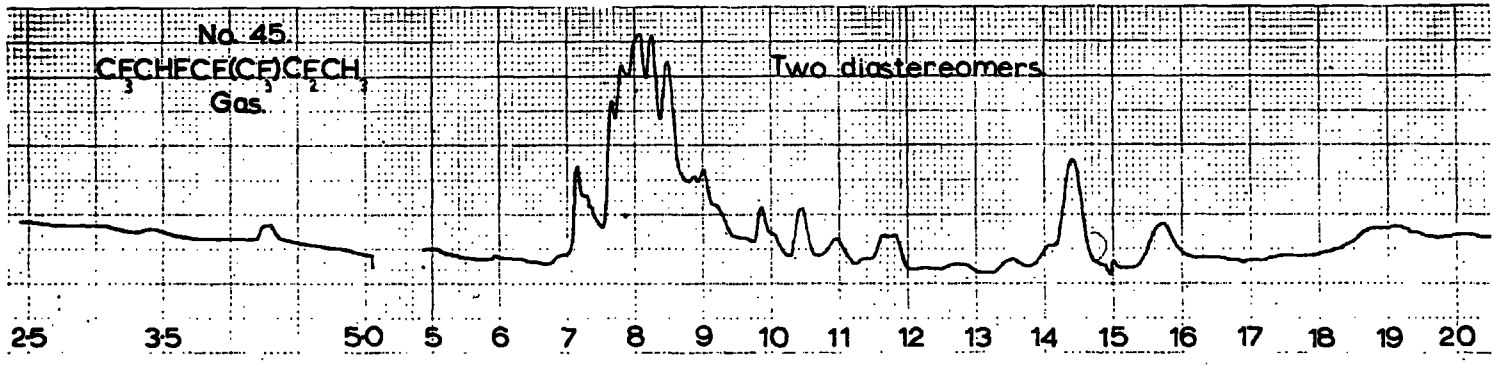

No. 40
$CF_3CHFCF(CF_3)SCH_3$ (2)
Liquid contact film
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20


No. 41
$CF_3CHFCH(CF_3)SCH_3$ (1)
Liquid contact film
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20


No. 42
$CF_3CHFCH(CF_3)SCH_3$ (2)
Liquid contact film
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20


No. 43.
$CF_3CHFCF(CF_3)CH(CH_3)OCOCH_3$ (1)
Liquid, contact film.
Two diastereomers.
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20


No. 44.
$CF_3CHFCF(CF_3)CH(CH_3)OCOCH_3$ (2)
Liquid, contact film.
Two diastereomers.
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20


No. 45.
$CF_3CHFCF(CF_3)CF_2CH_3$
Gas.
Two diastereomers.
25 35 50 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

FUTURE WORK

1. It should be possible to determine the structures of the diastereomers of the alcohol and thiol adducts by dehydrofluorination reactions (Pages 132 and 136).

2. The polyfluorobut-2-enes used in this work should be suitable for a study of the stereochemistry of nucleophilic addition reactions.

3. It should be possible to prepare the lithio derivative $CF_3CLi{=}CFCF_3$ from 2-bromoheptafluorobut-2-ene and reactions of this, together with its configurational stability when prepared from a pure geometrical isomer give scope for study. It may also be possible to prepare the lithio derivative from an exchange reaction with 2H-heptafluorobut-2-ene.

REFERENCES

REFERENCES

1. T. Posner, Ber, 1905, 38, 646.
2. F. Ashworth and G.N. Burkhardt, J. Chem. Soc., 1928, 1791.
3. M.S. Kharasch and F.R. Mayo, J. Amer. Chem. Soc., 1933, 55, 2468.
4. M.S. Kharasch and F.R. Mayo, J. Amer. Chem. Soc., 1938, 60, 3097.
5. M.S. Kharasch, W.R. Haefele and F.R. Mayo, J. Amer. Chem. Soc., 1940, 62, 2047.
6. F.R. Mayo and C. Walling, Chem. Rev., 1940, 27, 351.
7. J.C. Smith, Chem. and Ind., 1937, 56, 833.
8. J.C. Smith, Chem. and Ind., 1938, 57, 461.
9. J.C. Smith, Ann. Reports, (for 1939), 1940, 36, 219.
10. M.S. Kharasch, H. Engelmann and F.R. Mayo, J. Org. Chem., 1937, 2, 288, 400, 577.
11. D.H. Hey and W.A. Waters, Chem. Rev., 1937, 21, 169.
12. M.S. Kharasch, A.T. Read and F.R. Mayo, Chem. and Ind., 1938, 57, 752.
13. M.S. Kharasch, E.M. May and F.R. Mayo, J. Org. Chem., 1939, 3, 175.
14. G.N. Burkhardt, Trans. Faraday Soc., 1934, 30, 18.
15. M.S. Kharasch, E.V. Jensen and W.H. Urry, Science, 1945, 102, 128; Chem. Abs. 1945, 39, 4837[6].
16. F.R. Mayo, J. Amer. Chem. Soc., 1943, 65, 2324.
17. C. Walling and E.S. Huyser, Org. Reactions, 1963, Vol.13, Chapter 3, 91.
18. F.W. Stacey and J.F. Harris Jr., Org. Reactions, 1963, Vol.13, Chapter 4, 150.

19. C. Walling, "Free Radicals in Solution", John Wiley and Sons Inc., New York, 1957, p.243.

20. F.M. Lewis and F.R. Mayo, J. Amer. Chem. Soc., 1954, 76, 457.

21. Reference 19, p.121.

22. Reference 19, p.241.

23. Reference 19, p.242.

24. F. Leavitt, M. Levy, M. Szwarc and V. Stannett, J. Amer. Chem. Soc., 1955, 77, 5493.

25. F.M. Lewis and F.R. Mayo, J. Amer. Chem. Soc., 1948, 70, 1533.

26. J.I.G. Cadogan and I.H. Sadler, J. Chem. Soc.,(B), 1966, 1191.

27. R.N. Haszeldine and J.E. Osborne, J. Chem. Soc., 1956, 61.

28. Reference 19, p.134.

29. C. Walling, E.R. Briggs, K.B. Wolfstirn and F.R. Mayo, J. Amer. Chem. Soc., 1948, 70, 1537.

30. Reference 19, p.277.

31. H.P. Treffers and L.P. Hammett, J. Amer. Chem. Soc., 1937, 59, 1708.

32. R.E. Banks, "Fluorocarbons and their Derivatives", Oldbourne Book Co. Ltd., London, 1964, p.32.

33. R.P. Buck, F. Leavitt and M. Szwarc, J. Amer. Chem. Soc., 1956, 78, 5557.

34. E.S. Huyser, J. Org. Chem., 1961, 26, 3261.

35. R.N. Haszeldine and B.R. Steele, J. Chem. Soc., 1953, 1199.

36. J.I.G. Cadogan, E.G. Duell and P.W. Inward, J. Chem. Soc., 1962, 4164.

37. R.N. Haszeldine, J. Chem. Soc., 1953, 1764.

38. R.L. Huang, J. Chem. Soc., 1956, 1749.

39. R.L. Huang, J. Chem. Soc., 1957, 1342.

40. G.M. Burch, H. Goldwhite and R.N. Haszeldine, J. Chem. Soc., 1963, 1083.

41. J.F. Harris Jr., and F.W. Stacey, J. Amer. Chem. Soc., 1961, 83, 840.

42. R.N. Haszeldine, J. Chem. Soc., 1953, 3559.

43. F.W. Stacey and J.F. Harris Jr., J. Org. Chem., 1962, 27, 4089.

44. J.D. LaZerte and R.J. Koshar, J. Amer. Chem. Soc., 1955, 77, 910.

45. J. Kisby, Ph.D. Thesis, University of Durham, 1964.

46. R.N. Haszeldine and B.R. Steele, J. Chem. Soc., 1957, 2800.

47. J.C. Allen, J.I.G. Cadogan, B.W. Harris and D.H. Hey, J. Chem. Soc., 1962, 4468.

48. J.M. Tedder and J.C. Walton, Proc. Chem. Soc., 1964, 420.

49. J.M. Tedder and J.C. Walton, Trans. Faraday Soc., 1966, 62, 1859.

50. H. Muramatsu, S. Moriguchi and K. Inukai, J. Org. Chem., 1966, 31, 1306.

51. H. Muramatsu, J. Org. Chem., 1962, 27, 2325.

52. H. Muramatsu, K. Inukai and T. Ueda, J. Org. Chem., 1965, 30, 2546.

53. H. Muramatsu and K. Inukai, Kogyo Kagaku Zasshi, 1962, 65, 1992; Chem. Abs., 1963, 69, 2637d.

54. H. Muramatsu, K. Inukai and T. Ueda, J. Org. Chem., 1964, 29, 2220.

55. H. Muramatsu and K. Inukai, J. Org. Chem., 1965, 30, 544.

56. K. Inukai, T. Ueda and H. Muramatsu, Bull. Chem. Soc. Japan, 1966, 39, 2191; Chem. Abs., 1967, 66, 75613y.

57. M.S. Kharasch, W.H. Urry and B.M. Kuderna, J. Org. Chem., 1949, 14, 248.

58. T.M. Patrick Jr., J. Org. Chem., 1952, 17, 1009.

59. T.M. Patrick Jr., J. Org. Chem., 1952, 17, 1269.

60. H. Muramatsu and K. Inukai, J. Org. Chem., 1962, 27, 1572.

61. J.F. Harris Jr. and D.D. Coffman, J. Amer. Chem. Soc., 1962, 84, 1553.

62. G. Buchi, C.G. Inman, and E.S. Lipinsky, J. Amer. Chem. Soc., 1954, 76, 4327.

63. E.R. Bissell and D.B. Fields, J. Org. Chem., 1964, 29, 249.

64. W.H. Urry, F.W. Stacey, O.O. Juveland and C.H. McDonnell, J. Amer. Chem. Soc., 1953, 75, 250.

65. Reference 19, p.286.

66. U.S.P. 2,559,628/1951; Chem. Abs., 1952, 46, 3063b.

67. W.H. Urry, F.W. Stacey, E.S. Huyser and O.O. Juveland, J. Amer. Chem. Soc., 1954, 76, 450.

68. U.S.P. 2,585,723/1952; Chem. Abs., 1953, 47, 2767e.

69. J.C. Allen, J.I.G. Cadogan and D.H. Hey, Chem. and Ind., 1962, 1621.

70. J.C. Allen, J.I.G. Cadogan, B.W. Harris and D.H. Hey, Chem. and Ind., 1961, 830.

71. M.S. Kharasch, P.S. Skell and P. Fisher, J. Amer. Chem. Soc., 1948, 70, 1055.

72. U.S.P. 2,411,158/1946; Chem. Abs., 1947, 41, 985f.

73. U.S.P. 2,562,547/1951; Chem. Abs., 1952, 46, 1578i.

74. J.F. Harris Jr., and F.W. Stacey, J. Amer. Chem. Soc., 1963, 85, 749.

75. U.S.P. 2,433,844/1948; Chem. Abs., 1948, 42, 2266a.

76. M. Hauptschein and J.M. Lesser, J. Amer. Chem. Soc., 1956, 78, 676.

77. H.L. Goering, P.I. Abell and B.F. Aycock, J. Amer. Chem. Soc., 1952, 74, 3588.

78. H.L. Goering and L.L. Sims, J. Amer. Chem. Soc., 1955, 77, 3465.

79. M.S. Kharasch, J.S. Sallo and W. Nudenberg, J. Org. Chem., 1956, 21, 129.

80. P.I. Abell and B.A. Bohm, J. Org. Chem., 1961, 26, 252.

81. P.I. Abell and C. Chiao, J. Amer. Chem. Soc., 1960, 82, 3610.

82. P.D. Readio and P.S. Skell, J. Org. Chem., 1966, 31, 753.

83. H.L. Goering and D.W. Larsen, J. Amer. Chem. Soc., 1957, 79, 2653.

84. H.L. Goering and D.W. Larsen, J. Amer. Chem. Soc., 1959, 81, 5937.

85. P.S. Skell and R.G. Allen, J. Amer. Chem. Soc., 1959, 81, 5383.

86. P.S. Skell and P.K. Freeman, J. Org. Chem., 1964, 29, 2524.

87. P.S. Skell and R.G. Allen, J. Amer. Chem. Soc., 1958, 80, 5997.

88. C. Walling, M.S. Kharasch and F.R. Mayo, J. Amer. Chem. Soc., 1939,61,1711.

89. Reference 19, p.295.

90. L.D. Bergel'son, Izvest. Akad. Nauk. S.S.S.R. Otdel khim. Nauk. 1960, 1235; Chem. Abs., 1960, 54, 24334g.

91. B.A. Bohm and P.I. Abell, Chem. Rev., 1962, 62, 599.

92. W.A. Pryor "Free Radicals", McGraw-Hill Inc., 1966, p.30.

93. Reference 92, p.210

94. P.S. Skell, Chem. Soc. Special Publ., 1964, 19, 131.

95. N.A. LeBel, J. Amer. Chem. Soc., 1960, 82, 623.

96. H. Kwart and J.L. Nyce, J. Amer. Chem. Soc., 1964, 86, 2601.

97. P.S. Skell and P.D. Readio, J. Amer. Chem. Soc., 1964, 86, 3334.

98. P.S. Skell, D.L. Tuleen and P.D. Readio, J. Amer. Chem. Soc., 1963, 85, 2849.

99. P.S. Skell, R.G. Allen and N.D. Gilmour, J. Amer. Chem. Soc., 1961, 83, 504.

100. P.I. Abell and L.H. Piette, J. Amer. Chem. Soc., 1962, 84, 916.

101. M.C.R. Symons, J. Phys. Chem., 1963, 67, 1566.

102. Reference 92, p.36.

103. G.H. Williams, Progr. Stereochem., 1958, Vol.2, Chapter 2, 39.

104. N.P. Neureiter and F.G. Bordwell, J. Amer. Chem. Soc., 1960, 82, 5354.

105. P.S. Fredricks and J.M. Tedder, J. Chem. Soc., 1961, 3520.

106. P.S. Skell and R.G. Allen, J. Amer. Chem. Soc., 1960, 82, 1511.

107. H.L. Goering, D.I. Relyea and D.W. Larsen, J. Amer. Chem. Soc., 1956, 78, 348.

108. F.G. Bordwell and W.A. Hewett, J. Amer. Chem. Soc., 1957, 79, 3493.

109. F.G. Bordwell, P.S. Landis and G.S. Whitney, J. Org. Chem., 1965, 30, 3764.

110. P.D. Readio and P.S. Skell, J. Org. Chem., 1966, 31, 759.

111. J.F. Ford, R.C. Pitkethly and V.O. Young, Tetrahedron, 1958, 4, 325.

112. S.J. Cristol and G.D. Brindell, J. Amer. Chem. Soc., 1954, 76, 5699.

113. S.J. Cristol and R.P. Arganbright, J. Amer. Chem. Soc., 1957, 79, 6039.

114. S.J. Cristol and J.A. Reeder, J. Org. Chem., 1961, 26, 2182.

115. S.J. Cristol, G.D. Brindell and J.A. Reeder, J. Amer. Chem. Soc., 1958, 80, 635.

116. D.J. Trecker and J.P. Henry, J. Amer. Chem. Soc., 1963, 85, 3204.

117. S.J. Cristol and D.I. Davies, J. Org. Chem., 1964, 29, 1282.

118. J.A. Claise, D.I. Davies and (in part) C.K. Alden, J. Chem. Soc. (C), 1966, 1498.

119. J.A. Kampmeier and G. Chen, J. Amer. Chem. Soc., 1965, 87, 2608.

120. A.A. Oswald, K. Griesbaum, B.E. Hudson Jr. and J.M. Breaman, J. Amer. Chem. Soc., 1964, 86, 2877.

121. P.S. Skell and J.H. McNamara, J. Amer. Chem. Soc., 1957, 79, 85.

122. P.S. Skell, R.C. Woodworth and J.H. McNamara, J. Amer. Chem. Soc., 1957, 79, 1253.

123. M.S. Kharasch and H.N. Friedlander, J. Org. Chem., 1949, 14, 239.

124. F.S. Fawcett, Chem. Rev., 1950, 47, 219.

125. E. Tobler and D.J. Foster, J. Org. Chem., 1964, 29, 2839.

126. P.S. Skell and R.C. Woodworth, J. Amer. Chem. Soc., 1955, 77, 4638.

127. J.I.G. Cadogan and E.G. Duell, J. Chem. Soc., 1962, 4154.

128. L.D. Bergel'son and L.P. Badenkova, Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk., 1960, 887; Chem. Abs., 1960, 54, 24334b.

129. I.N. Nazarov and L.D. Bergel'son, Zhur. obshchei khim., 1957, 27, 1540; Chem. Abs., 1958, 52, 3660g.

130. I.N. Nazarov and L.D. Bergel'son, Izvest. Akad. Nauk. S.S.S.R., Otdel khim. Nauk., 1960, 887; Chem. Abs. 1960, 54, 24332f.

131. I.N. Nazarov and L.D. Bergel'son, Izvest. Akad. Nauk. S.S.S.R., Otdel, khim. Nauk., 1960, 896; Chem. Abs., 1960, 54, 24333d.

132. P.S. Skell and P.R. Pavlis, J. Amer. Chem. Soc., 1964, 86, 2956.

133. A.L. Henne and T.H. Newby, J. Amer. Chem. Soc., 1948, 70, 130.

134. E.W. Schlag and E.W. Kaiser,Jr., J. Amer. Chem. Soc., 1965, 87, 1171.

135. H. Rotzsche, Z. analyt. Chem., 1960, 175, 338; Chem. Abs., 1961,55,4233i.

136. M. Hudlicky, "Chemistry of Organic Fluorine Compounds" Pergamon Press, 1961, p.268.

137. R.E. Banks, W.I. Bevan and W.K.R. Musgrave, Chem. and Ind., 1959, 296.

138. A.M. Lovelace, D.A. Rausch and W. Postelnek, "Aliphatic Fluorine Compounds", Reinhold Publishing Corporation, New York, 1958.

139. D.V. Banthorpe, "Elimination Reactions", Elsevier Publishing Co., 1963, p.11.

140. J.T. Maynard, J. Org. Chem., 1963, 28, 112.

141. U.S.P. 2,436,357/1948; Chem. Abs., 1948, 42, 5465d.

142. K.O. Christe and A.E. Pavlath, J. Chem. Soc., 1963, 5549.

143. U.S.P. 2,885,449/1959; Chem. Abs., 1959, 53, 16962b.

144. U.S.P. 3,024,290/1962; Chem. Abs., 1962, 56, 15333i.

145. Reference 138, p.33.

146. M. Hauptschein and L.A. Bigelow, J. Amer. Chem. Soc., 1951, 73, 5591.

147. I. Galiba, J.M. Tedder and (in part) R.A. Watson, J. Chem. Soc., 1964,1321.

148. A.L. Henne and A.M. Whaley, J. Amer. Chem. Soc., 1942, 64, 1157.

149. P.S. Fredricks and J.M. Tedder, Chem. and Ind., 1959, 490.

150. P.S. Fredricks and J.M. Tedder, J. Chem. Soc., 1960, 144.

151. G.V.D. Tiers, J. Phys. Chem., 1962, 66, 1192.

152. Reference 138, p.36.

153. A.L. Henne and R.P. Ruh, J. Amer. Chem. Soc., 1947, 69, 279.

154. Reference 138, p.105.

155. S. Winstein, D. Pressman and W.G. Young, J. Amer. Chem. Soc., 1939, 61, 1645.

156. Reference 139, p.137.

157. W.M. Schubert, B.S. Rabinovitch, N.R. Larson and V.A. Sims, J. Amer. Chem. Soc., 1952, 74, 4590.

158. H.O. House and R.S. Ro, J. Amer. Chem. Soc., 1958, 80, 182.

159. Reference 139, p.138.

160. S. Andreades, J. Amer. Chem. Soc., 1964, 86, 2003.

161. H.G. Adolph and M.J. Kamlet, J. Amer. Chem. Soc., 1966, 88, 4761.

162. P. Tarrant, A.M. Lovelace and M.R. Lilyquist, J. Amer. Chem. Soc., 1955, 77, 2783.

163. R.N. Haszeldine, J. Chem. Soc., 1952, 3490.

164. K. Leedham and R.N. Haszeldine, J. Chem. Soc., 1954, 1634.

165. C.E. Stoops and C.L. Furrow, J. Org. Chem., 1961, 26, 3264.

166. D.T. Clark, J.N. Murrell and J.M. Tedder, J. Chem. Soc., 1963, 1250.

167. D.T. Clark, Chem. Comm., 1966, 390.

168. R.D. Chambers and R.H. Mobbs, "Ionic Reactions of Fluoro-olefins" Advances in Fluorine Chemistry, 1965, Vol.4.P.50. Butterworths, London, 1965.

169. A.T. Coscia, J. Org. Chem., 1961, 26, 2995.

170. J.W. Emsley, Private Communication.

171. R.N. Haszeldine, J. Chem. Soc., 1953, 1748.

172. E.T. McBee, D.H. Campbell, R.J. Kennedy and C.W. Roberts, J. Amer. Chem. Soc., 1956, 78,4597.

173. W.C. Smith, C.W. Tullock, E.L. Muetterties, W.R. Hasek, F.S. Fawcett, V.A. Engelhardt and D.D. Coffman, J. Amer. Chem. Soc., 1959,81,3165.

174. W.R. Hasek, W.C. Smith and V.A. Engelhardt, J. Amer. Chem. Soc., 1960, 82, 543.

175. L.J. Bellamy, "The Infra-red Spectra of Complex Molecules", Methuen and Co. Ltd., London, 2nd. Ed., 1958, p.42.

176. P. Johncock, W.K.R. Musgrave and A. Wiper, Analyst, 1959, 84, 245.

177. M.E.J. Vince, Ph.D. Thesis, University of Durham, 1965.

178. J. Weiss, Nucleonics, 1952, 10, (7), 28.

179. J.W. Emsley, J. Feeney and L.H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy" Pergamon Press, 1966, Vol.2. p.909.

180. Reference 179, p.886.

181. E.G. Brame, Jr., Analyt. Chem., 1962, 34, 591.

DURHAM UNIVERSITY
21 SEP 1967
LIBRARY