

"FREE-RADICAL ADDITION TO OLEFINS"

by

R. Gregory B.Sc. Tech.

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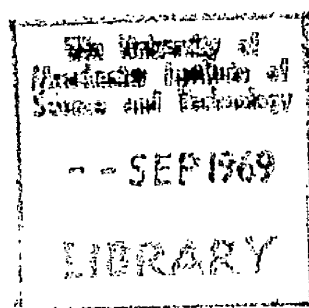
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October 1966.

University of Manchester
Institute of Science and Technology.

The work described in this thesis was carried out under the direction of Professor R.N. Haszeldine and supervision of Dr. A.E. Tipping to whom I express my sincere gratitude for their continued advice and encouragement.

I also thank members of the Chemistry Department, both past and present, for many helpful discussions and their generous gifts of chemicals.

Thanks are also due to the Science Research Council for the award of a Research Studentship which made this work possible.

The author graduated from the University of Manchester Institute of Science and Technology in 1963. Since then, the author has been engaged in research in the Department of Chemistry under the direction of Professor R.N. Haszeldine and Doctor A.E. Tipping.

T O _ M _ Y _ P _ A _ R _ E _ N _ T _ S

Summary.

The present work is mainly concerned with the photochemically initiated free-radical additions of trifluoroiodomethane and hydrogen bromide to the olefins, chloro-1,1-difluoroethylene, 1,1,3,3,3-pentafluoropropene, 1,3,3,3-tetrafluoropropene and 1,1,1-trifluorobut-2-ene. In each instance, except with the addition of hydrogen bromide to chloro-1,1-difluoroethylene, bidirectional addition occurred. With chloro-1,1-difluoroethylene and 1,1,3,3,3-pentafluoropropene, thermal additions of trifluoroiodomethane were also attempted, but only low yields of the 1:1 adducts were obtained.

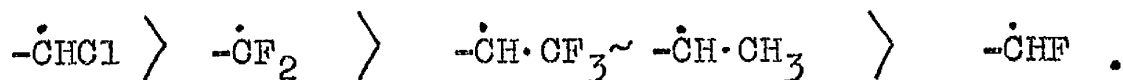
In the addition reactions of hydrogen bromide with 1,1,3,3,3-pentafluoropropene and 1,3,3,3-tetrafluoropropene, the corresponding olefin dibromides were also formed, but with 1,1,1-trifluorobut-2-ene, the major side-product was 4-bromo-1,1,1-trifluorobut-2-ene. The ionic addition of bromine to 1,1,1-trifluorobut-2-ene gave the diastereomeric olefin dibromides.

The results are discussed in terms of the factors which are known to affect the orientation of free-radical addition. Attempts to correlate the orientation of addition with the relative electrophilicities of the bromine atom and the trifluoromethyl radical indicate that the bromine atom is

the more electrophilic, although the orientations of addition of these two radicals are, in some cases, inconsistent.

The addition of trifluoroiodomethane to the olefins, 1,3,3,3-tetrafluoropropene and 1,1,1-trifluorobut-2-ene, gave, in each case, three 1:1 adducts; one resulting from the addition of the trifluoromethyl radical to the $-\text{CH}\cdot\text{CF}_3$ groups of the olefins, and the other two resulting from addition to the $-\text{CHF}\cdot$ and $-\text{CH}\cdot\text{CH}_3$ groups respectively, i.e., erythro- and threo- $\text{CF}_3\cdot\text{CHI}\cdot\text{CHF}\cdot\text{CF}_3$, and erythro- and threo- $\text{CF}_3\cdot\text{CHI}\cdot\text{CH}(\text{CF}_3)\cdot\text{CH}_3$. Attempts are made to determine the absolute stereochemical configurations of the isomers by n.m.r. spectroscopy and by elimination reactions with potassium hydroxide. It is suggested that the major diastereomer of formula $\text{CF}_3\cdot\text{CHI}\cdot\text{CHF}\cdot\text{CF}_3$ has the erythro configuration, and the major diastereomer of formula $\text{CF}_3\cdot\text{CHI}\cdot\text{CH}(\text{CF}_3)\cdot\text{CH}_3$ has the threo configuration. These results are explained on the basis of electrostatic and steric effects in the transition state of the chain-transfer reaction.

The group order of radical stability has been found to be:-



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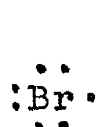
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I N T R O D U C T I O N

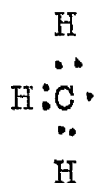
INTRODUCTION

The chemistry of organic free radicals dates from the beginning of this century when Gomberg isolated the first free radical, triphenylmethyl¹, but it was not until Paneth's study ² of the free methyl radical, in 1929, that such species were considered as having a significant role in certain organic chemical reactions.

The modern definition states that a free radical is an atom or molecule in which the normal chemical binding is modified so that an unpaired electron is left associated with the system³. The bromine atom (I) and the methyl radical (II) are two such examples, both having six paired electrons and an unpaired, or lone, electron.

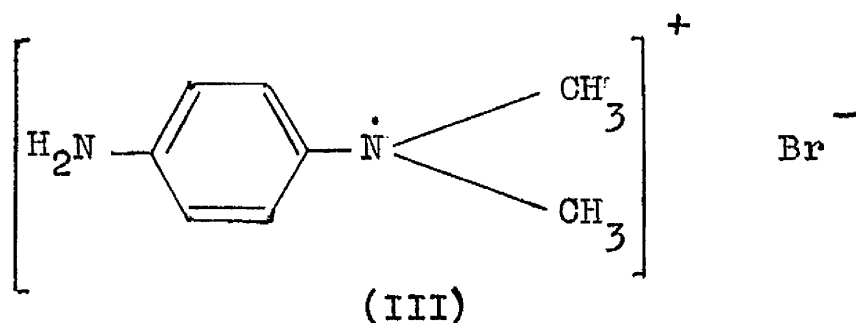


(I)



(II)

As a result of such unpaired electrons, free radicals are paramagnetic; a fact which has been made use of in their detection and estimation. Free radicals generally exist as neutral entities although complex 'radical ions' such as the Würster salt (III) are known, and their reactions are usually unaffected by variations in the ionising power of the solvents.



Homolytic reactions are defined as those reactions which pass through free-radical intermediates, and many of these consist, not of a single reaction, but a chain reaction, i.e., several reactions each taking place as a consequence of a previous one.

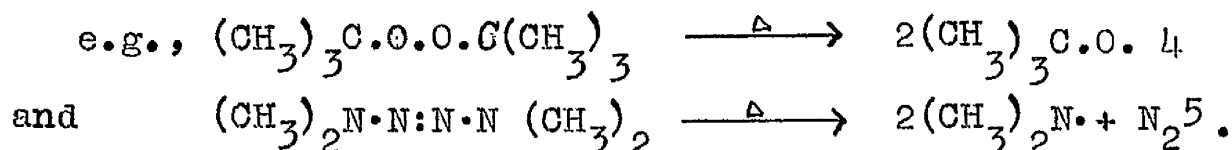
General Methods of Free-Radical Preparation.

The homolytic cleavage of a covalent bond results in the formation of two free radicals,



and may be effected in the following ways:

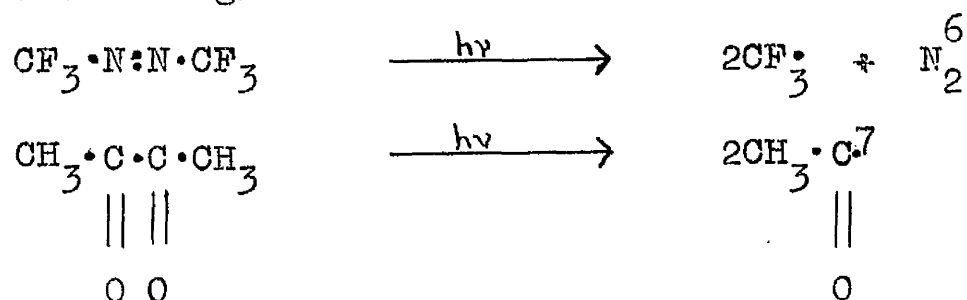
(i) Thermally. On moderate heating (up to 100°) numerous compounds break down homolytically, notably organic peroxides and azo compounds,



The most general way of starting a free-radical chain reaction is by the use of these compounds as initiators, which under reaction conditions furnish a sufficient number of radicals

to begin the chain reaction.

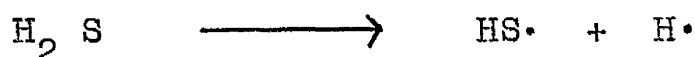
(ii) Photochemically. A quantum of light of wavelength $3,000\text{\AA}$ has an associated energy of 96 kcal./mole which is comparable to the dissociation energy of many covalent bonds. Thus energy transferred to a molecule by absorption of light can result in bond fission.



(iii) By oxidation - reduction. Many oxidation-reduction processes occur by one-electron transfer steps and result in the formation of free radicals, especially when organic substrates are used. A reaction of this type which has found wide use in the manufacture of synthetic rubber is the ferrous ion/hydroperoxide system⁸.

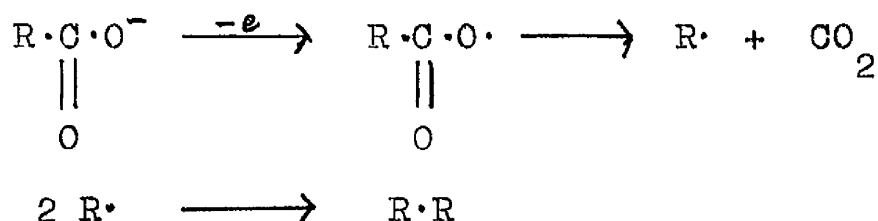


(iv) By miscellaneous cleavage reactions. Irradiation of organic material with α , β , γ or X-rays can result in homolytic fission of covalent bonds. For example, irradiation of hydrogen sulphide with X-rays⁹ cleaves the hydrogen-sulphur bond.



In many cases the cleavage occurs in an indiscriminate manner.

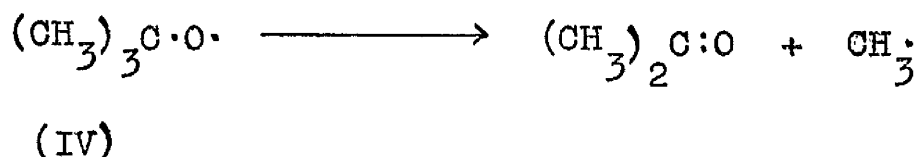
The electrolysis of salts of carboxylic acids¹⁰ has been shown to produce radicals.



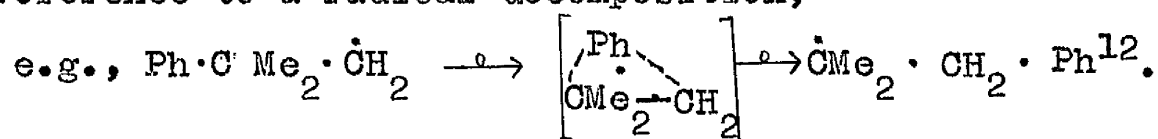
Radical Reactions.

The majority of free radicals, by virtue of their electron deficiency, are very reactive and capable of undergoing a wide variety of reactions which can be classified as follows:

(i) Radical decompositions and rearrangements. Radical decompositions, resulting in the formation of a simpler radical and an unsaturated molecule, are well known. The t-butoxy radical (IV), for example, decomposes to acetone and a methyl radical¹¹.

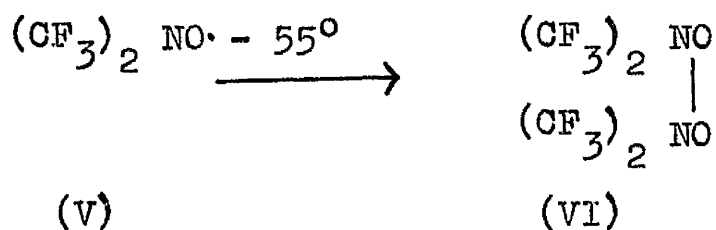


Alternatively, a radical rearrangement may occur in preference to a radical decomposition,

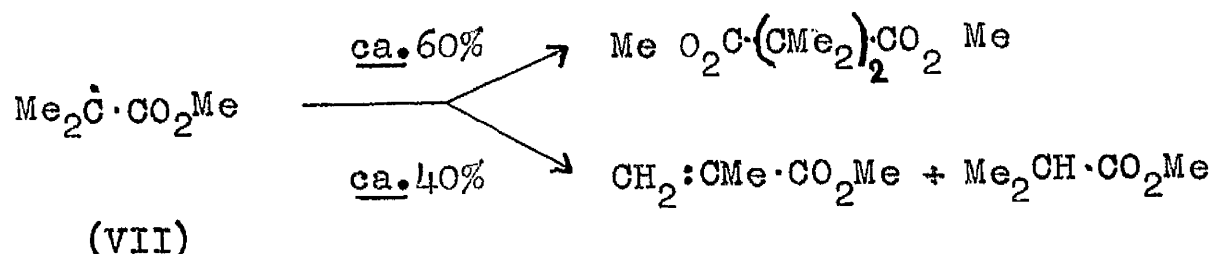


(ii) Radical coupling reactions. These reactions usually occur with great speed and are characteristic of almost all radicals. However, bistrifluoromethyl nitroxide

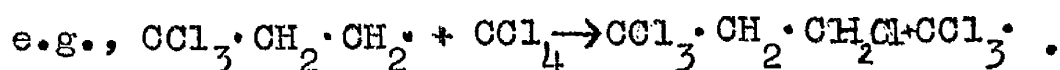
(V)¹³ is a stable purple gas at room temperature and only at low temperatures (-55°)¹⁴ are yellow crystals of the dimer (VI) formed.



(iii) Radical Disproportionations. These reactions result in the formation of a saturated and an unsaturated molecule. Such a reaction may occur in competition with a radical coupling reaction; thus the 2-methyl-2-carbomethoxyethyl radical (VII)¹⁵ decomposes by two separate mechanistic paths.

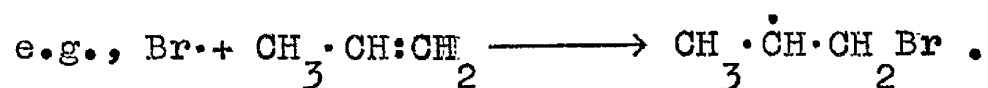


(iv) Radical displacement or transfer reaction¹⁶ In these reactions a free radical abstracts an atom (usually hydrogen or halogen) from another molecule, thereby creating a new radical,



(v) Radical additions to olefins¹⁷ Free radicals add readily to most unsaturated systems, especially electron-rich

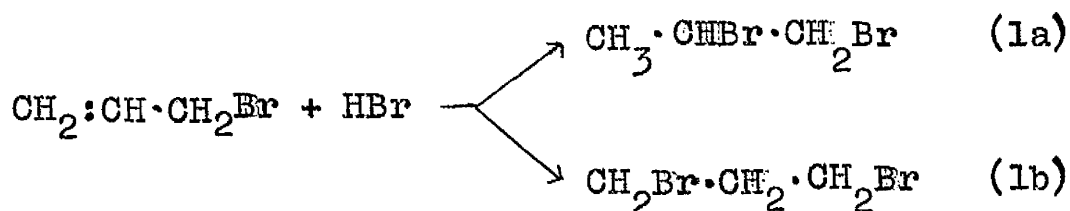
olefinic double bonds, to form new radicals,



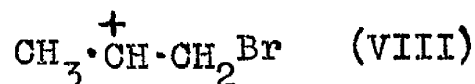
This review is primarily concerned with such radical additions to olefins, and they are now discussed in detail.

Free-Radical Addition to Olefins.

Before 1930 much confusion existed concerning hydrogen halide additions to unsaturated compounds¹⁸, and many hypotheses were put forward to account for the products formed. The addition of hydrogen bromide to allyl bromide was particularly ambiguous as the reported products were either 1,2-dibromopropane or 1,3-dibromopropane under supposedly identical experimental conditions. The so-called "peroxide effect" was discovered by Kharasch and Mayo¹⁹ during an attempt to rationalise the reaction.

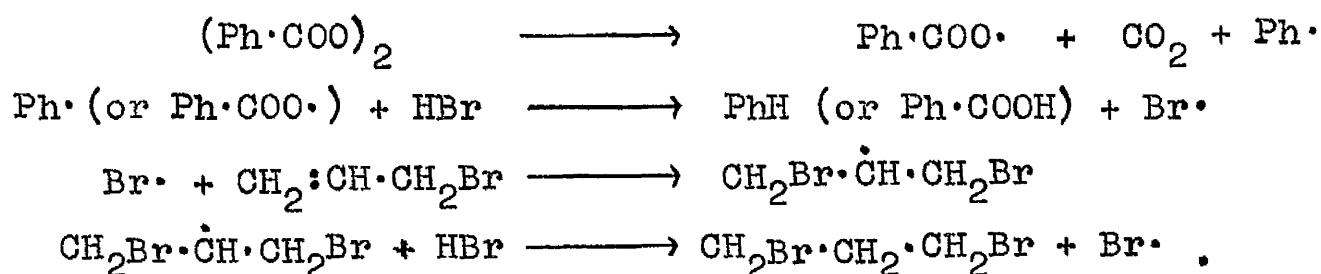


They found that, in the dark and using rigorously purified reagents, reaction (1a) took place exclusively, though slowly, but in the presence of small quantities of oxygen, or peroxides, reaction (1b) occurred rapidly²⁰. Reaction (1a) is the normal heterolytic addition, in accordance with the Markownikoff rule²¹, which goes via the formation of the more stable intermediate carbonium ion (VIII). Reaction (1b) is the abnormal one showing the "peroxide effect".



It was a further six years before a theoretical interpretation of reaction (1b) was put forward^{22,23}.

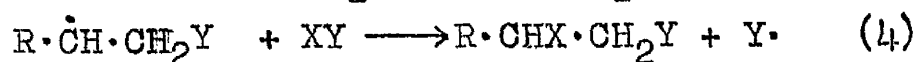
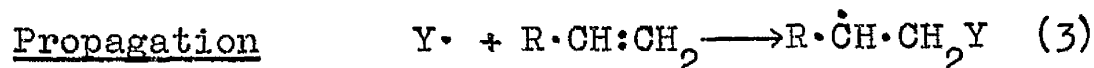
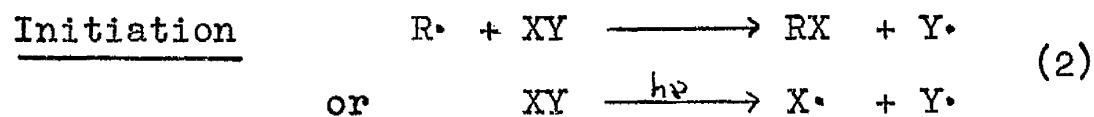
It was proposed that the fast abnormal reaction was a self-propagating chain reaction involving a free-radical intermediate and atomic bromine, initiated by oxygen or peroxide impurities. When benzoyl peroxide is used as initiator the reaction proceeds as follows:



A few years after this free-radical theory was proposed it received additional support²⁴ when it was found that a photochemical reaction could also produce an abnormal product in the absence of initiators.

The Mechanism of the Addition Reaction.

A general scheme for free-radical addition to olefins may be represented as follows:-



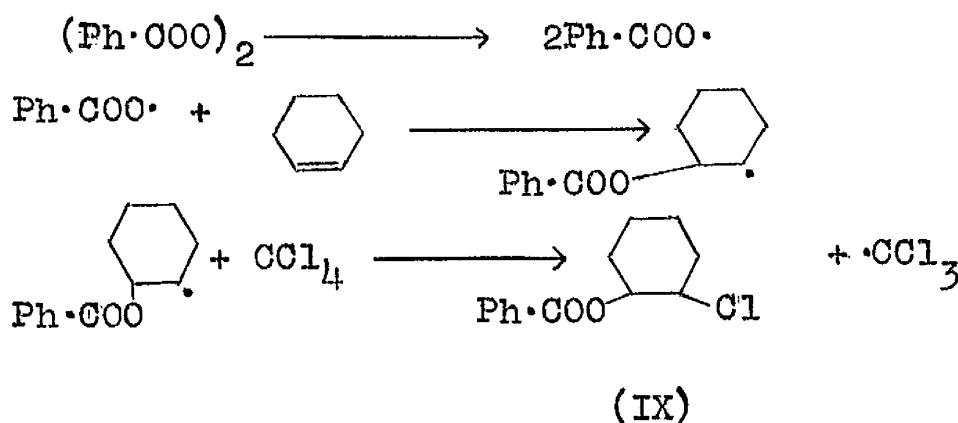
Termination

By dimerisation or disproportionation of radicals.

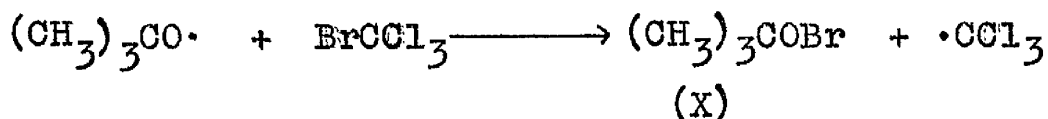
(i) Chain Initiation. In many chain reactions the average kinetic chain lengths are very large and only small amounts of initiators are required.

This is of great importance since it means that the required products are not contaminated with large amounts of impurities from the decomposition of the initiator.

In the addition of carbon tetrachloride to cyclohexene, however, it has been reported²⁵ that only 20 to 40 moles of addition product were formed per mole of initiator, and decomposition products from the initiator were isolated. The results from this investigation indicate that the major initiation process is one of addition, since 55% of the phenylcarboxy radicals from the peroxide appeared as 2-chlorocyclohexyl benzoate (IX).



In the addition of bromotrichloromethane to trans-stilbene, initiated by di-t-butylperoxide, the main initiation process is one of abstraction, since 64% of the peroxide reacts to form t-butyl hypobromite (X)²⁶.

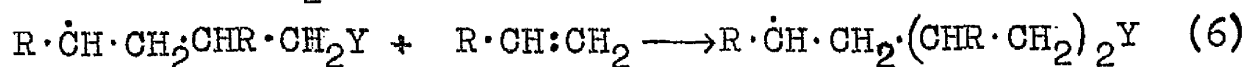
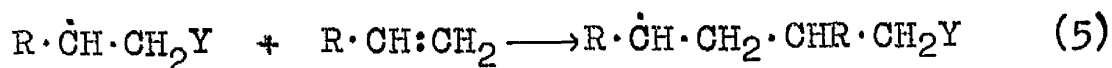


The presence of trace metals, e.g., tin²⁷, cobalt, and silver²⁸, allow the peroxide-initiated additions to

olefins to proceed under milder conditions than when peroxides are used alone, but the mechanism of these reactions is still obscure.

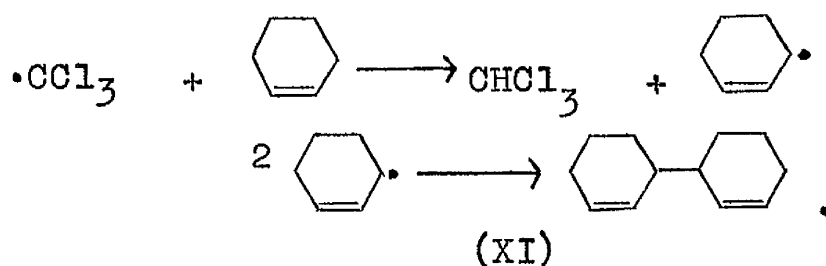
(ii) Chain-Propagation. This consists of two steps: an addition reaction (equation 3) and a radical displacement reaction (equation 4).

Radical bimolecular reactions invariably have a very high rate constant, showing that the time interval between initiation and termination is short and that propagation is rapid. Low activation energies are involved and so small changes in the reactants can have large effects on the overall rates and yields. For a high addend to olefin ratio, reaction (3) is the rate-determining step; radical Y. accumulates and the rate becomes first order in olefin. At low addend to olefin ratios, reaction (4) is the slow propagation step, and further reactions (5) and (6) may occur to form telomers, i.e., products containing more than one molecule of olefin per molecule of addend.



Chain Termination. In general, chain termination occurs either by radical dimerisation or, to a lesser extent, by disproportionation. In the addition of bromotrichloromethane to cyclohexene²⁹, for example, using a 10:1 ratio, chain termination results exclusively by the dimerisation of the trichloromethyl radicals.

Termination by abstraction of a hydrogen or halogen atom from an olefin, resulting in the formation of a stable molecule and a new radical of low reactivity (which is unable to continue the chain), has been reported. In the reaction of carbon tetrachloride with cyclohexene²⁵, the isolation of chloroform and bicyclohexene-2-yl (XI) suggests the following scheme for allylic termination:



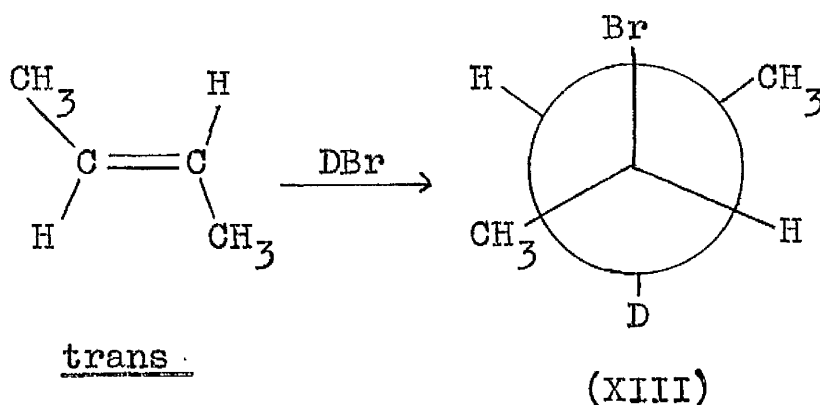
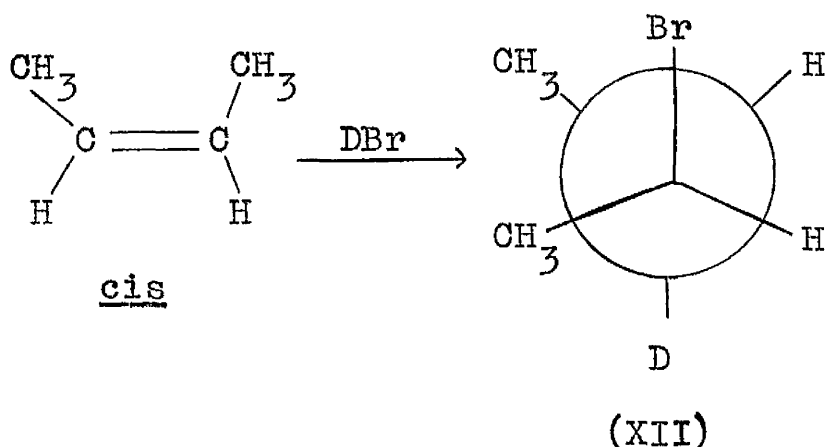
Stereochemistry of Addition Reactions.

The proposed mechanism of free-radical addition to olefins gives no expectations of stereospecificity, but, infact, trans-addition occurs in most cases, though evidence is sparse. It is considered that free-radical attack on an olefin is perpendicular to the π -bond of the unsaturated carbons; a view supported by the molecular orbital theory³⁰.

Recently the transition state of reaction (3)³¹ has been considered to involve an incipient sigma-bond between the radical and the reaction centre to form a sigma-complex, and not an association with the entire pi-electron cloud.

Szwarc had postulated³² that the attacking methyl radical approached along the pi-bond of the olefin, but this was later retracted³³.

Stereospecific trans-addition has been observed when deuterium bromide adds to cis-and trans-but-2-ene³⁴, between -60 and -78°, to give pure threo- and erythro-3-deutero-2-bromobutane, (XII) and (XIII), respectively.



Additions of deuterium bromide and hydrogen bromide to cis-and trans-2-bromo-but-2-ene³⁵ are trans-stereospecific in a large excess of liquid halide at -80°. The stereospecificity decreases with decreasing addend to olefin ratio and with increasing reaction temperature. The high degree of selectivity in the addition of hydrogen bromide and deuterium bromide requires that the rate of chain transfer [reaction (4)] is faster than rotation about what was

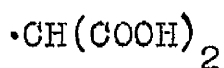
previously the unsaturated carbon-carbon bond, or in the case of cyclic compounds, than conformational isomerisation; both of which would produce the stereoisomers. Since low temperatures, when rotation is much reduced, and high concentrations of hydrogen bromide and deuterium bromide have to be used to achieve stereospecificity in their additions to olefins, it would suggest that stereospecific addition reactions are unlikely to be observed with addenda which are inferior transfer agents, e.g., the addition of deuteromethylmercaptan to cis- and trans-but-2-ene³⁶ at -70° is non-specific, though trans-stereospecificity has been obtained with this mercaptan using deuterium bromide as the transfer agent.

Trans-addition is observed with the homolytic additions of hydrogen bromide to 1-chloro-, 1-bromo-, and 1-methylcyclohexene^{37,38} to give cis-1-bromo-2-chlorocyclohexane, cis-1,2-dibromohexane, and cis-1-bromo-2-methylcyclohexane respectively.

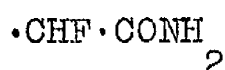
Recently much discussion has taken place on the conformation of the intermediate free radical. Skell and coworkers³⁹ favoured a pyramidal intermediate suggested by the mode of addition of bromotrichloromethane to the but-2-enes, while Goering and coworkers³⁵ postulated a planar intermediate in the reaction of hydrogen bromide with 2-bromobut-2-ene. It has since been shown by electron-spin resonance measurements that certain radicals, e.g., (XIV), (XV), (XVI), and (XVII) are planar or almost so.



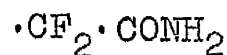
(XIV)



(XV)



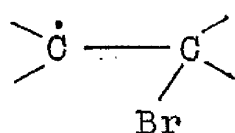
(XVI)



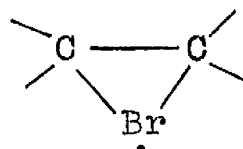
(XVII)

Since the trifluoromethyl and the difluoromethyl radicals are reported to be non-planar⁴⁵, both fluorine containing (XVI) and (XVII) could also be expected to be non-planar, and since this is not the case, it would suggest that most other radicals are planar.

Several rationalisations have been put forward to account for the preference of trans-addition with hydrogen bromide. Goering, Abell, and Aycock³⁷ suggested a bridged, or at least a resonating bromine atom, holding both carbon atoms of the double bond in a fixed conformation until hydrogen abstraction completes the addition from the side opposite to the bromine bridge. The contributing structures, (XVIII) to (XXII), involve three electron bonds.



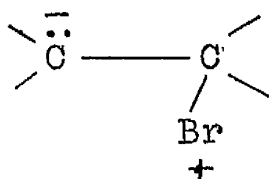
(XVIII)



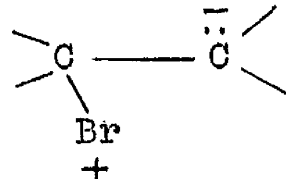
(XIX)



(XX)



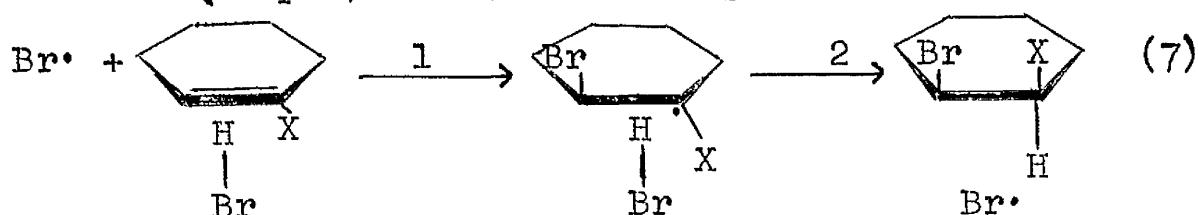
(XXI)



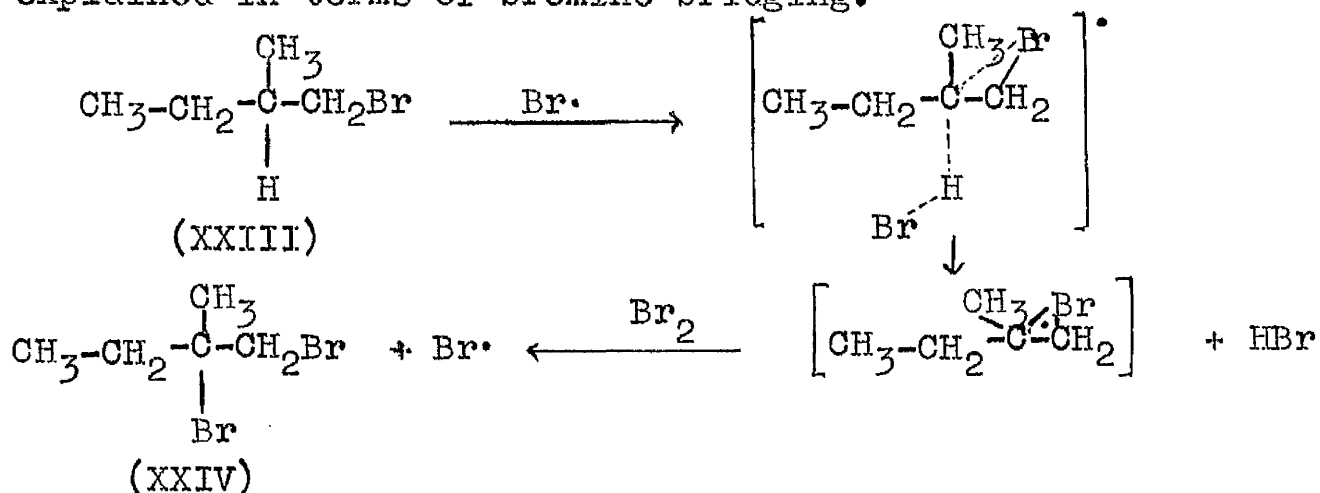
(XXII)

A second possibility is that the hydrogen abstraction step follows the addition of bromine so closely that changes in conformation of the initially formed bromoalkyl radical do not take place. Thirdly, it has been suggested that

the olefin complexes with the hydrogen bromide; collision with a bromine atom then gives a simultaneous attachment of this attacking bromine radical and a breaking of the hydrogen-bromine bond of the complexed hydrogen bromide. This bonds the hydrogen and frees a new bromine atom to continue the chain. Such a scheme is depicted below (reaction 7); the process may be visualised as a two-step process or as a concerted one in which addition (step 1) and transfer (step 2) are simultaneous.



Support for the bridged bromine theory has recently been published by Skell⁴⁶ who found that the free-radical bromination of (+)-1-bromo-2-methylbutane (XXIII) yielded (-)-1,2-dibromo-2-methylbutane (XXIV) at 0°; a result best explained in terms of bromine bridging.



Electron paramagnetic resonance spectroscopy studies⁴⁷ of the intermediate radical derived from the addition of hydrogen bromide to several olefins lend support to the bridged structure theory. The hydrogen bromide-olefin

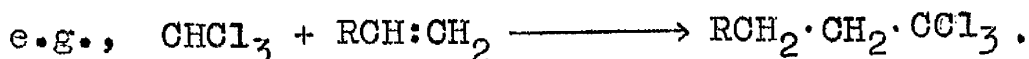
complex hypothesis has not yet been shown to be significant in free-radical reactions.

Scope of Addition Reactions.

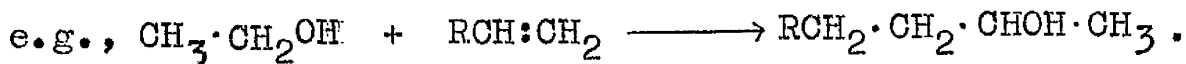
Additions of Carbon Radicals.

Many classes of compounds have been added to a wide variety of olefins according to the scheme previously outlined (page 8).

Polyhalogenoalkanes⁴⁸⁻⁵¹ add readily to olefins by a free-radical process to give 1:1 adducts and telomers. Telomer formation^{49,52} is reduced when more reactive halides (containing a >C-Br or a >C-I bond) are used. Chloroform⁵³ generally is displaced at the >C-H bond. This is due to the greater difference between the resonance energy of the trichloromethyl radical⁵⁴ formed and the resonance energy of the dichloromethyl radical than the difference between the energy required to break a >C-H and a >C-Cl bond,

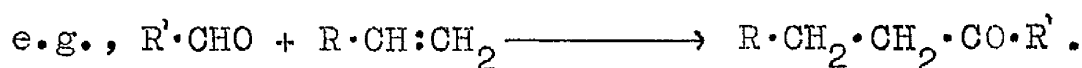


Free-radical additions of both primary and secondary alcohols⁵⁵⁻⁵⁷ to olefins and perfluoro-olefins⁵⁸⁻⁶⁰, to give high yields of the 1:1 adducts, are well known, but require a high alcohol to olefin ratio owing to the low transfer constants for such reactions,

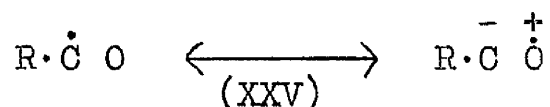


Aldehydes, under the influence of peroxides or light, also add to olefins to give ketones, but again telomer

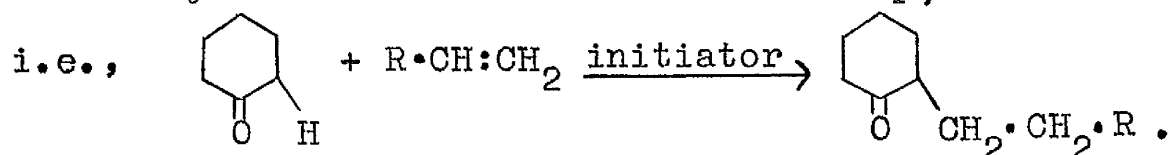
formation may be appreciable,



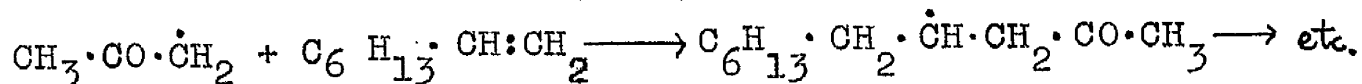
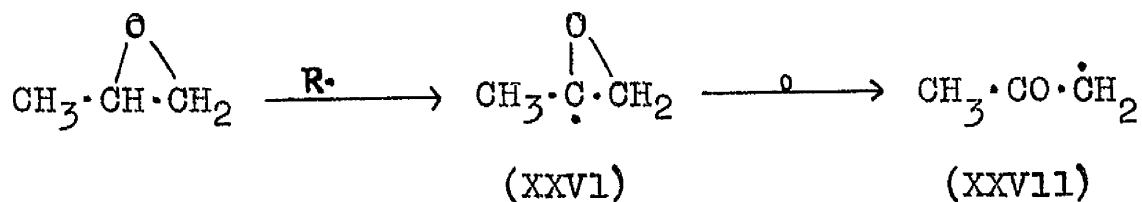
The high yields of 1:1 adducts with perfluoro-olefins, where the olefin is more susceptible to nucleophilic attack, suggests that the acyl radical (XXV) is nucleophilic in character.



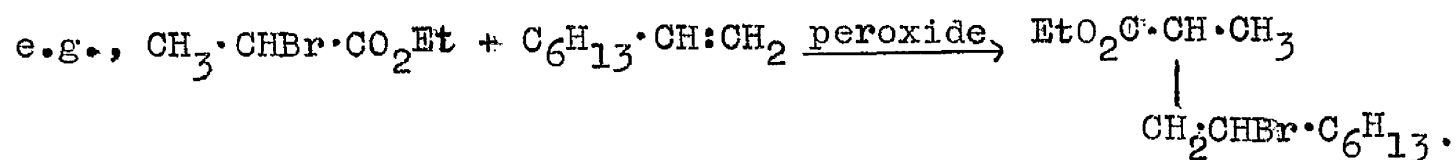
Cyclohexanone ⁶⁴ is the most reactive ketone in free-radical additions to olefins due to the ease of hydrogen abstraction from the cyclohexanone in the transfer step,



Epoxides ⁶⁵ add to oct-1-ene to form ketones in low yields; the intermediate epoxy radical (XXVI) which is formed rearranges to an α -keto radical (XXVII) which then adds to the olefin.

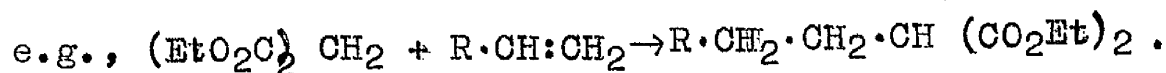


α -Bromoesters and diesters ⁶⁶ add readily to oct-1-ene to give the corresponding 1:1 adducts in high yields,



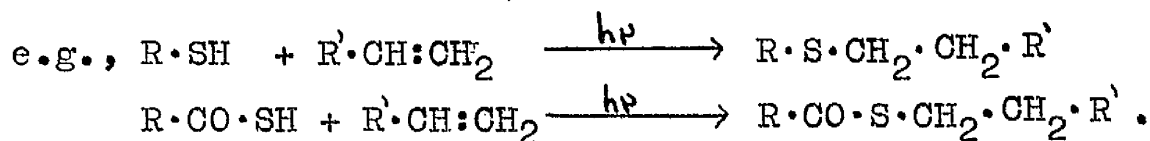
The addition of unsubstituted esters ⁶⁷ (diethyl malonate, ethyl cyanoacetate, and ethyl acetoacetate) to various olefins affords

a new synthetic route to long chain esters,

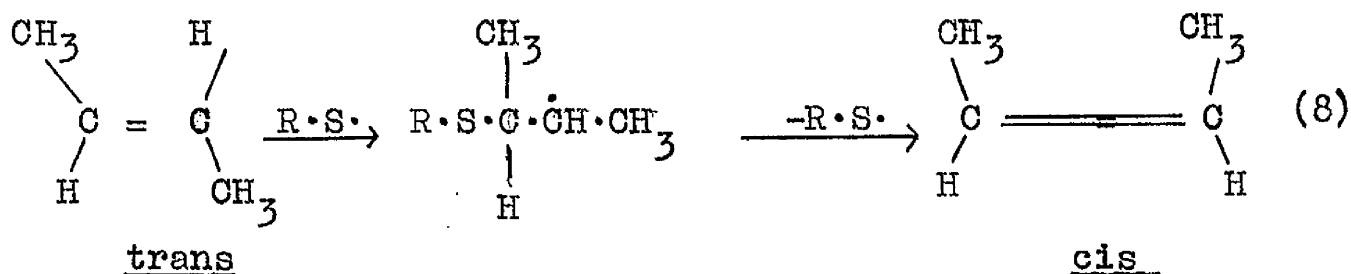


Additions of Non-carbon Radicals.

Thiols^{55,68} and thioacids⁶⁹ add to olefins by a free-radical mechanism to give, in most cases, excellent yields of the corresponding 1:1 adducts, and such reactions have been studied in considerable detail,



The addition step⁷⁰ can be reversible in certain cases because cis-trans isomerisation of the unreacted olefin may occur during thiol or thioacid addition, e.g., cis- and trans-but-2-ene can be isolated from the reaction of trans-but-2-ene with methanethiol, probably by the route shown in equation (8).

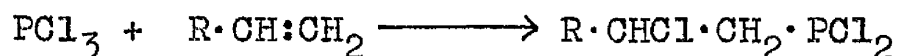


Hydrogen sulphide^{71,72} also adds homolytically to olefins to give mercaptans, though a high ratio of hydrogen sulphide to olefin is required to minimise subsequent addition of the mercaptan to the unreacted olefin,

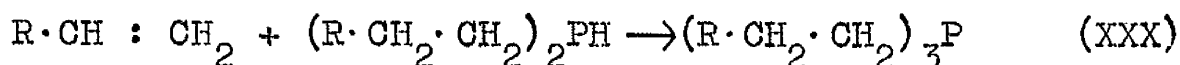
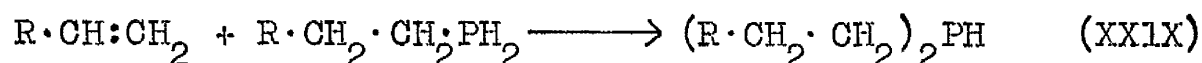
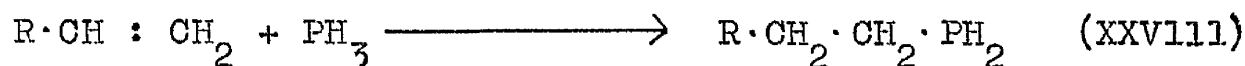


The addition of various other sulphur compounds, e.g., sulphenyl halides⁷³, organo-sulphonyl chlorides,^{74,75} bisulphite⁷⁶, and sulphur dioxide,⁷⁷ each with the lone electron associated with the sulphur atom of the attacking radical, have been reported.

The first free-radical addition of a phosphorus compound to an olefin was that of phosphorus trichloride⁷⁸ using peroxide initiation.

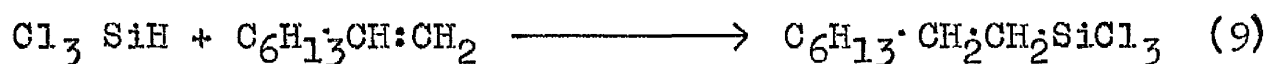


Since then the addition of phosphine⁷⁹⁻⁸² to various olefins, using varied initiation techniques, has been investigated, to give products ranging from primary (XXV111), to secondary (XX1X), and to tertiary phosphines (XXX); the relative amounts of which are dependent upon the original ratio of reactants.



The homolytic addition of dialkyl phosphites⁸³ and phosphonates^{84,85} occurs readily, by the cleavage of the P-H bond to give good yields of 1:1 adducts.

Homolytic scission of the silicon-hydrogen bond in silanes⁸⁶ can be readily brought about photochemically, thermally, or by added peroxides, and the addition of such compounds to olefins gives excellent yields of the 1:1 adducts, e.g., trichlorosilane⁸⁷ adds to oct-1-ene to give a 99% yield of *n*-octyl-trichlorosilane (equation 9).



Addition reactions of nitrogen compounds are rare though nitryl chloride⁸⁸, nitrogen dioxide⁸⁹, dinitrogen tetroxide⁹⁰, and N-bromo-bis(trifluoromethyl)amine⁹¹ undergo radical-chain additions with olefins.

Reactivity of Olefinic Double Bonds towards Free Radicals.

Competitive reactions have given much information on the relative reactivities of olefinic double bonds towards free radicals. An equimolecular mixture of two olefins is allowed to react with a large excess of addend until 20-30% conversion of the olefin is achieved, and the ratio of the products compared.

A series of competitive reactions⁹² with various olefins using bromotrichloromethane as the addend was carried out by Kharasch, and a similar series of olefins⁹³ using dodecanethiol as the addend was investigated by Walling. In the latter work, corrections for the reversibility of the addition step had to be made so that the reactivities of the various olefins could be compared with the results obtained by Kharasch. The results of both investigations are given in Table 1.

Table 1. Relative Reactivities of Olefins towards the $\cdot\text{CCl}_3$ and $\text{RS}\cdot$ Radicals.

Olefin	Relative Rate		Olefin	Relative Rate	
	$\cdot\text{CCl}_3$	$\text{RS}\cdot$		$\cdot\text{CCl}_3$	$\text{R}\cdot\text{S}\cdot$
oct-1-ene	1.0	1.0	ethyl cinnamate	0.8	-
β -methylstyrene	1.4	1.5	vinyl acetate	0.8	0.8
butadiene	18	-	allyl benzene	0.7	1.0
methallyl chloride	1.6	-	allyl chloride	0.5	0.7
2-methyl-but-1-ene	0.9	1.2	allyl cyanide	0.3	0.4
2-ethyl-but-1-ene	1.4	-	cyclohexene	0.24	0.25
vinyl butyl ether	-	3.9	cyclopentene	0.8	0.6
styrene	100	17	4,4,4-trichloro- -but-1-ene	0.3	-

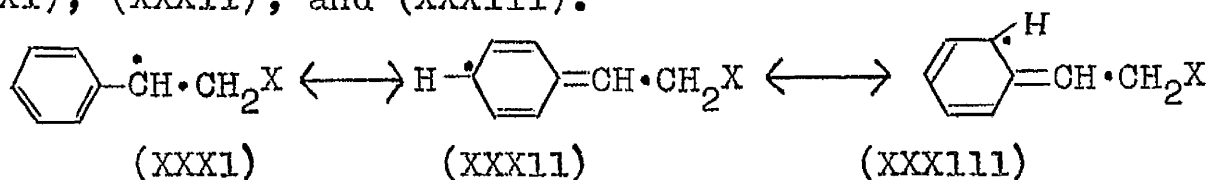
Table 2 shows the reactivities of various "simple" olefins towards certain free radicals.

Table 2. Relative Reactivities of Olefins towards certain Radicals

Olefin	H•	CH ₃ •	CF ₃ •	S•	O•	Br•
ethylene	1.0	1.0	1.0	1.0	1.0	1.0
propene	1.53	1.3	2.8	3.6	5.8	17.7
but-1-ene	-	1.6	3.1	-	5.8	22.6
isobutene	4.5	2.1	1.6	-	25.0	384
<u>cis</u> -but-2-ene	0.9	0.08	0.60	-	23.8	95
<u>trans</u> -but-2-ene	1.1	0.15	0.60	-	28.3	98.5
References	94	95	95	96	97,98	99

Several conclusions can be drawn from the above results:

i) The high reactivity of styrene and butadiene show that olefins yielding a resonance stabilised radical are much more reactive than those that do not, e.g., when radical X• adds to styrene the intermediate radical is a hybrid of structures (XXX1), (XXX11), and (XXX111).



ii) The rate of addition of the thiyl and trichloromethyl radicals is increased by electron-donating groups in the olefin and decreased by electron-withdrawing groups, thus illustrating the electrophilic character of these radicals.

iii) Terminal double bonds are more reactive towards addition than internal ones.

iv) The addition of the bromine and oxygen radicals is greatly increased when more complex olefins than ethylene are used, whereas such a notable increase is not obtained with the addition of other radicals. A bridged structure (see Page 14) has been proposed for the intermediate in the addition of bromine and oxygen to cis-and trans-but-2-ene.

Further evidence that electron-donating groups in the olefin facilitate the addition of most radicals is supplied by the relative reactivities of several para-substituted α -methylstyrenes¹⁰⁰ towards the thiyl radical produced from thioglycollic acid (Table 3).

Table.3. Relative Reactivities of Para-substituted
 α -Methylstyrenes.
Towards the $\cdot\text{SCH}_2\text{COOH}$ Radical

Substituent	Reactivity
p-H	1.00
p-F	0.51 \pm 0.13
p-Br	0.90 \pm 0.56
p-Cl	0.96 \pm 0.56
p-CH ₃	2.28 \pm 0.54
p-OCH ₃	215 \pm 100

From these results, it can be seen that the introduction of the electron-releasing p-methoxy group increases the

reactivity of the olefin by a factor of 200, whereas the electron-withdrawing p-fluorine decreases the reactivity by a factor of 2.

Cuneen ¹⁰¹ has shown that electron-withdrawing groups on the thiol generally enhance the rate of addition to olefins by making the radical more electrophilic.

These results are in general agreement with those of other workers¹⁰²⁻¹⁰⁵ and with the considerable evidence derived from copolymerisation studies^{106,107}.

Steric Factors Affecting The Reactivity of Olefins.

It has already been noted that internal double-bonds of olefins are less reactive towards addition than terminal ones (see Page 22), and the substitution of bulky groups for atoms, or small groups, at the position of radical attack on olefins produces a marked decrease in the reactivity of the olefins. These effects are attributed to steric crowding in the transition state of the addition-propagation step in the chain reaction (which must, of course, be rate-determining).

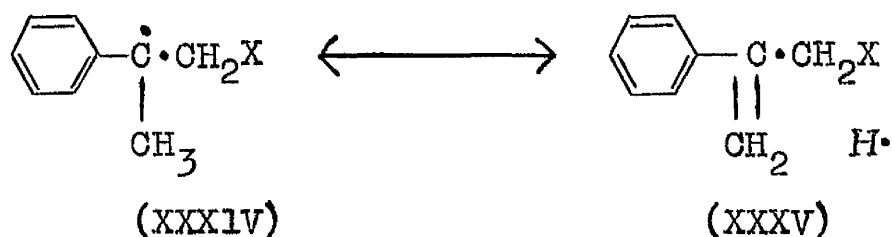
Styrene derivatives methylated in the α - and β -positions of the vinyl group have been studied by Szwarc¹⁰⁸ and the results are summarised in Table 4.

Table 4. Effect of Methyl Substituents on the Reactivity of
Styrene

Towards Methyl Radicals.

Olefins	Reactivity
Styrene	100
α -methylstyrene	118
β -methylstyrene (<u>trans</u>)	12
β -methylstyrene (<u>cis</u>)	5
α,β -dimethylstyrene	8
α,β -trimethylstyrene	2.5

α -Methyl substitution enhances the reactivity of the olefin towards radical attack because it produces an intermediate radical which can be stabilised by hyperconjugation^{109,110}, (XXXIV) and (XXXV). β -Methyl substitution at the reaction centre decreases the reactivity of the olefin.

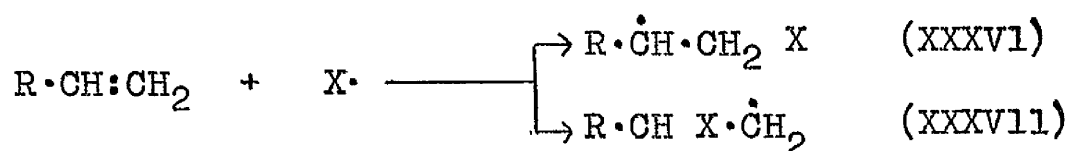


Orientation of Free-Radical Addition.

It will already be apparent that initial attack of a radical on an olefin $\text{R}\cdot\text{CH}=\text{CH}_2$ generally occurs on the terminal methylene group, and an empirical rule¹¹¹ has long been employed stating that, in non-polar additions, the intermediate radical

formed will be the one in which the lone electron is situated on the carbon atom carrying the smallest number of hydrogen atoms. This specificity of attack has been accounted for by several theories, but that of the relative stabilities of the two possible intermediate radicals is the sole survivor.

i) Intermediate radical stability. Present evidence shows that orientation in free-radical addition reactions can be generally predicted by considering the relative stabilities of the two possible intermediate radicals formed by the addition of the initial attacking radical. The more stable intermediate will be formed, and the products of the reaction will be derived from this intermediate, e.g., either (XXXVI) or (XXXVII) is the more stable intermediate when radical $X\cdot$ adds.

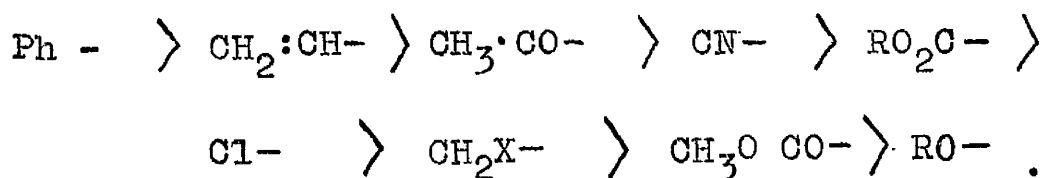


The order of stability of free radicals¹¹² is, in general, tertiary $\text{>}\dot{C}\cdot$ > secondary $\text{>}\dot{C}H\cdot$ > primary $\text{>}\dot{C}H_2$ where tertiary, secondary, and primary refer to the number of substituents other than hydrogen and not to the carbon skeleton. Substituents vary in their stabilising power and certain primary and secondary radicals may be more stable than certain secondary and tertiary radicals respectively, e.g., $R\dot{C}HCl$ is more stable than $R\dot{C}F_2$.

The direction of radical attack on olefins can thus be rationalised on this basis; attack on the terminal methylene group of an olefin $R\cdot CH:CH_2$ yields the more stable secondary

intermediate radical (XXXV1), in preference to the alternative primary radical (XXXV11).

A great deal of evidence has been collected from copolymerisation studies^{106,107} of styrene with certain olefins, and an order for the stabilising powers of various substituents on the eventual radical site of the intermediate has been determined:-



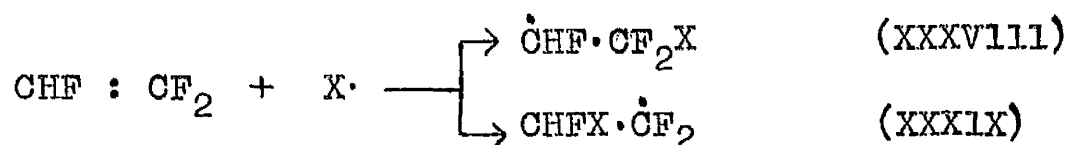
Spectroscopic studies on several halocarbon iodides¹¹³, and chemical evidence^{114,115} from various radical addition reactions have given the following order of stabilising effects:-



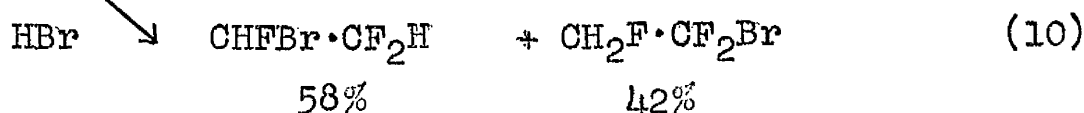
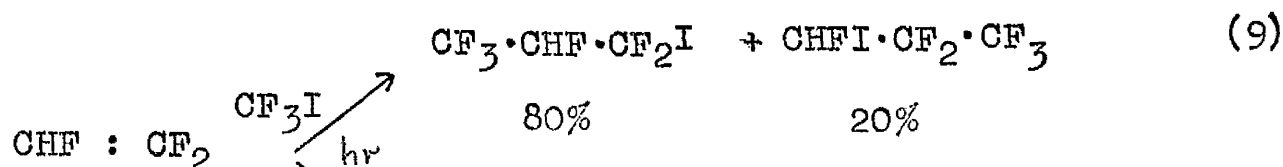
Radical stability appears to increase with the complexity of the substituent attached to the radical centre, presumably due to the increasing ability to delocalise the lone electron, and the following order of stabilities¹¹⁵ for halogeno-substituted radicals has been proposed:-



A consideration of such stabilising power led Haszeldine and Steele¹¹⁶ to predict two-way radical addition to trifluoroethylene, since the two possible intermediates (XXXV111) and XXX1X) were expected to have similar stabilities.



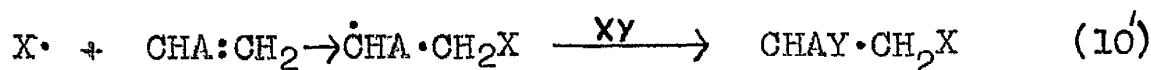
The isolation of both 1:1 adducts from the reaction with trifluoroiodomethane and with hydrogen bromide showed that bidirectional addition had indeed taken place (equations 9 and 10). The preponderance of the 1:1 adduct derived from the



intermediate radical (XXXIX) is in accordance with the order of stabilising power of hydrogen and fluorine (i.e., $-\dot{\text{C}}\text{F}_2 > -\dot{\text{C}}\text{HF}$).

Several examples of bidirectional radical addition have since been reported, especially with the olefins trifluoroethylene and perfluoropropene (Table 5), and the results interpreted on the basis that the two intermediate radicals have comparable stabilities.

Recently some doubt has been cast by Tedder and Walton¹²³ on the theory of intermediate radical stability; consider the two-way addition of radical $\text{X} \cdot$ to the olefin $\text{CH}_2 : \text{CHA}$ in equations (10') and (11). If the intermediate radical stability



(XL)

theory is correct then changes in A, where steric factors are at a minimum, should only have a small effect on the formation of radical (XL), since the rate of formation of this radical is

dependent on the stability of the $\dot{\text{C}}\text{H}_2$ group.

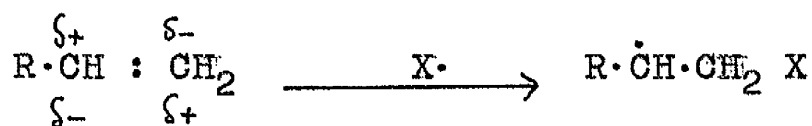
Table 5. Radical Additions to Trifluoroethylene and
Perfluoropropene.

Attacking Radical	CHF : CF ₂		CF ₃ ·CF : CF ₂		Reference
·CF ₃	80	20	20	80	116,117
·Br	58	42	38	62	116,118
·SH	85	15	-	-	119
·S·Me	75	25	9	91	120
·S·CH ₂ ·CF ₃	-	-	30	70	120
·S·CF ₃	98	2	55	45	120
·SF ₅	-	-	50	50	121
·PH ₂	-	-	34	66	82
·N(CF ₃) ₂	78	22	0	100	91
·SiH ₃	-	-	40	60	122
·SiH ₂ Me	-	-	24	76	122
·SiHMe ₂	-	-	5	95	122
·Si Me ₃	-	-	4	96	122

In order to test the theory, trichloromethyl radicals were added to the series of fluoroethylenes and ethylene, in the gas phase over a wide range of temperature, and the Arrhenius parameters for the rate of addition at each end of the olefins determined.

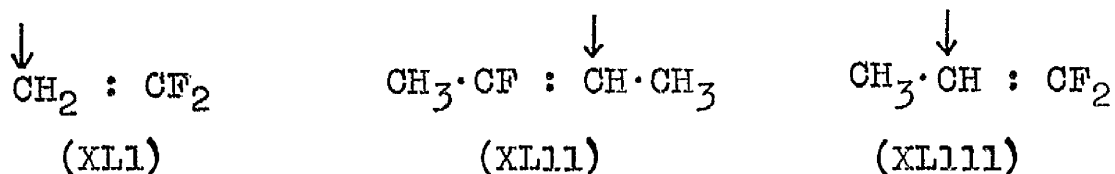
The results of this work were interpreted by the authors as showing that the rate of addition of the trichloromethyl radical is principally determined by substituents on the carbon atom attacked, and only to a lesser extent by the substituents attached to the carbon atom at which the unpaired electron is sited. It was, therefore, proposed that the orientation of radical addition is principally determined by the relative strengths of the two possible bonds initially formed. This, of course, leads to exactly the same prediction of orientation as arguments based on the stability of the intermediate radical.

ii) Polarisation of the olefinic double bond. It was suggested by Waters¹²⁴ that a free radical, being electrophilic in character, attacked the point of highest electron density in the olefin. Other workers¹²⁵⁻¹²⁷ have since found that this is not the case, as is clearly shown in the addition of trifluoriodomethane to various olefins. In the olefin $R \cdot CH : CH_2$ ($R = Me, Cl, \text{ or } F$) the olefin is polarised $\overset{\delta+}{R} \cdot CH : \overset{\delta-}{CH_2}$ for ionic additions, and where $R = CN, CO_2Me, \text{ or } CF_3$ it is polarised $\overset{\delta-}{R} \cdot CH : \overset{\delta+}{CH_2}$. Assuming that the same direction of polarisation holds for radical addition, then the attack on the terminal carbon of the double bond by the CF_3 radical shows clearly that the polarisation of the double bond is of little importance in directing the addition of free radicals.



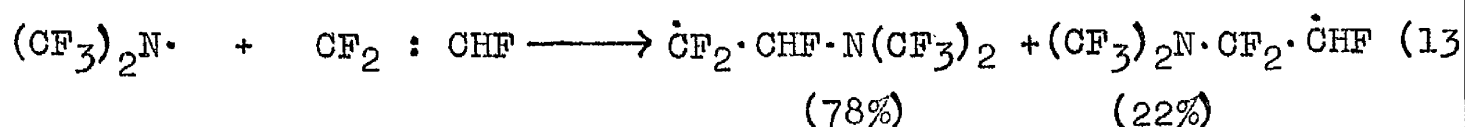
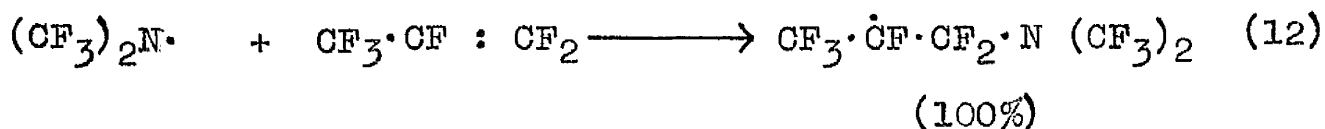
The polarisation of the olefin only plays an important part when the two possible intermediate radicals are of comparable stability. In such cases, the nucleophilicity or electrophilicity of the attacking radical will also influence the relative proportions of the products (see Page 31).

iii) Steric Factors. Much of the available evidence for the orientation of radical additions to olefins can be explained by the attack of the radical on the least sterically hindered carbon atom. It is, however, difficult on steric grounds alone to account for the specificity of attack on 1,1-difluoroethylene^{128,129} (XL1) and 2-fluorobut-2-ene¹²⁸ (XL11) (position of attack is shown by arrow), since fluorine is only slightly larger than hydrogen (Van der Waal radii : H = 1.2 Å, F = 1.35 Å). Trifluoromethyl radical attack on 1,1-difluoropropene¹³⁰ (XL111) is exclusively on the more hindered carbon atom of the double bond.



Steric factors are thus not important in determining orientation, except in cases where the two possible intermediate radicals formed, from radical addition to an olefin, are of comparable stability, and the accessibility of a site for attack influences the orientation of addition. For example, the bistrifluoromethylamino radical⁹¹, a large radical, adds only to the less sterically hindered end of perfluoropropene (equation 12), an olefin where bidirectional addition would be expected, but gives two-way addition with trifluoroethylene (equation 13) where

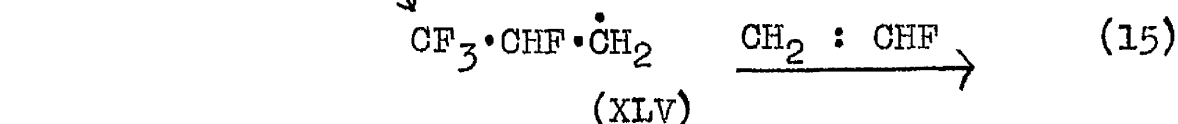
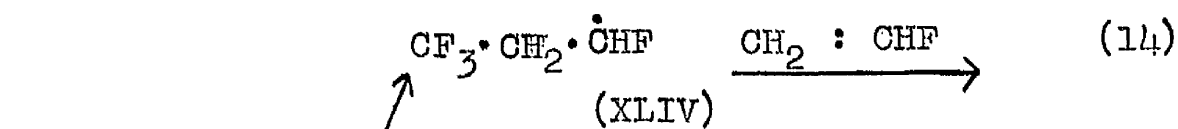
both ends of the double bond are sterically similar.



iv) Nature of attacking radical. An examination of the results given in Table 5 (Page 28) shows that there is a large variation in isomeric distribution depending upon the radical employed.

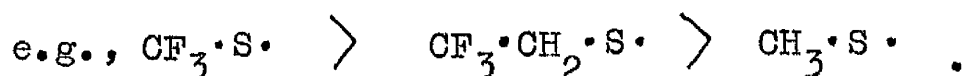
The fact that most free radicals vary in electrophilicity (the Me· radical¹²⁸ and alkylcarboxy radicals are nucleophilic in character) can account for the varying ratios of 1:1 adducts with different radicals. The more electrophilic radicals will seek out the electron-rich site, whereas the less electrophilic radicals will give a lower yield of the product derived from this attack.

In the reaction of trifluoroiodomethane with vinyl fluoride¹³² to form telomers (equations 14 and 15), the rate of attack of the very electrophilic trifluoromethyl radical at the more negative end of the double bond is almost six times as great as the less electrophilic secondary radicals (XLIV) and (XIV) .



	δ^- CH_2	:	δ^+ CHF
$\text{CF}_3\cdot$	11	:	1
$\text{CF}_3\cdot\text{CH}_2\cdot\dot{\text{C}}\text{HF}$	2	:	1
$\text{CF}_3\cdot\text{CHF}\cdot\dot{\text{C}}\text{H}_2$	2	:	1

In the addition of thiols to hexafluoropropene¹²⁰ the increasing rate of attack at the more negative end of the olefin, i.e., the $\text{CF}_3\cdot\text{CF}$ group corresponds to the inductive forces in the radical making it more electrophilic,



Similarly the expected order of decreasing nucleophilicity of the silyl radicals¹²² is one which corresponds to the order of increasing attack at the $\text{CF}_3\cdot\text{CF}$ group in hexafluoropropene.



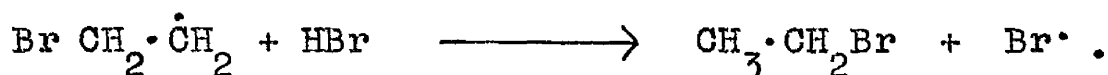
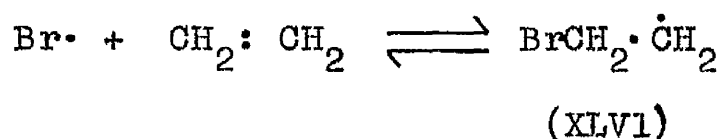
It is to be remembered that the nature of the attacking radical, together with the polarisation of the double bond, only has significance when the stabilities of the two possible intermediate radicals are comparable.

D I S C U S S I O N
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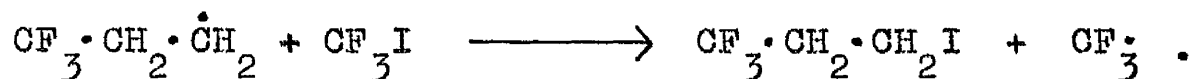
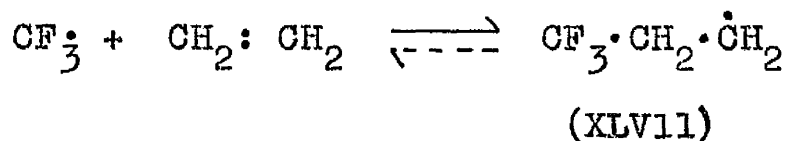
DISCUSSION.

The additions of trifluoriodomethane and hydrogen bromide across the double bonds of olefins under the conditions used in this work are thought to proceed by free-radical chain mechanisms. The general theory of such reactions has already been discussed in the introduction.

It has been shown^{35,47,99} that, in the additions of hydrogen bromide to olefins, the bromine atom is the initial attacking radical, and for the addition to ethylene^{24,133,134} the simple mechanism is considered to be:



In the additions of trifluoriodomethane to olefins, the initial attacking radical is considered to be the trifluoromethyl radical and the mechanism for the addition to ethylene may be represented as:



These simple mechanisms assume that all radicals are in thermal equilibrium with the surrounding gas molecules, and though this is not the case since intermediate radicals (XLVI) and (XLVII) are in a vibrationally excited state, the general mechanisms adequately account for the experimental results.

In the above reaction schemes, the additions of a bromine atom and a trifluoromethyl radical to ethylene are shown as being reversible. The reversibility of bromine atom additions to olefins has been generally accepted¹³³, but no evidence for the reversibility of addition of the trifluoromethyl radical has been reported.

The trifluoromethyl radical is regarded as being extremely electrophilic^{95,135}, and Abell⁹⁹ has reported that the bromine atom is even more electrophilic. This was shown by a comparison of the rates of addition of these two radicals to a series of olefins (Table 2, Page 21) in which electron density was increasingly concentrated in the π -bond of the olefin. The rates for bromine atom addition increased far greater along the series, than did the rates for trifluoromethyl addition, which indicates that the bromine atom is the more electrophilic. Though

bridged structures have been suggested for free-radical intermediates formed by initial bromine atom additions to certain olefins (see Page 14), the electrophilic character of a radical is reflected in its response to the effect on the π -electron density of electron-donating or withdrawing substituents present in the olefin. Such a response is observed whether the addition leads to a classical or a bridged free-radical intermediate.

It is to be expected that this difference in electrophilicity between the bromine atom and the trifluoromethyl radical will be shown by variations in their orientation of addition to highly polarised olefins capable of bidirectional addition. Thus, other things being equal, the bromine atom, ^{if} it is more electrophilic, will give a higher proportion of products derived from attack at the more negatively polarised carbon atom of the double bond.

The orientation of these two radicals to the olefins trifluoroethylene and hexafluoropropene have been previously determined and the results are shown in Table 6.

Table 6.

Orientation of attack of the Br·Atom and
the CF₃· Radical.

Attacking Radical	δ^- δ^+ CHF = CF ₂	δ^- δ^+ CF ₃ ·CF = CF ₂	Ref.
CF ₃ ·	80 20	20 80	116,117
Br·	58 42	38 62	116,118

The results obtained with hexafluoropropene support the suggestion that the bromine atom is the more electrophilic, but the results with trifluoroethylene do not. Clearly, at the moment, there is conflicting evidence as to the relative electrophilicities of these two radicals. Also, the importance of the role their electrophilic character plays in the orientation of their additions to polarised olefins is not fully understood.

Several bidirectional addition reactions to unsymmetrical olefins (see Pages 28 and 31) have been observed, and these have been rationalised on the basis that the two possible free-radical intermediates have similar stabilities. This stability theory is used throughout this present work since it is the generally

accepted theory, although recently it has been proposed that the orientation of addition is due to the relative strengths of the bonds formed (See Page 27).

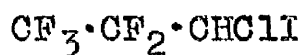
A. CHLORO-1,1-DIFLUOROETHYLENE.

I. Free-Radical Addition of Trifluoroiodomethane.

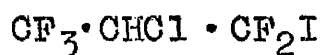
The addition of trifluoroiodomethane to fluoro-olefins to give polyfluoroiodoalkanes may be brought about thermally, photochemically, or by the use of added peroxides, and is considered to proceed by the general free-radical mechanism previously proposed (Page 8).

The total stabilising power of a hydrogen and chlorine atom at the radical centre might not be excessively greater than the total stabilising power of two fluorine atoms (see Page 26), and thus the olefin, chloro-1,1-difluoroethylene, might undergo two-way addition with certain radicals.

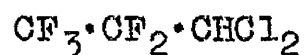
It had been reported¹¹⁴ that the u.v. initiated addition of trifluoroiodomethane to chloro-1,1-difluoroethylene (reaction ratio 2:1) carried out for 6 days in silica gave only one 1 : 1 adduct (XLV111) (72%); the other possible 1 : 1 adduct (XLIX) was not detected.



(XLV111)

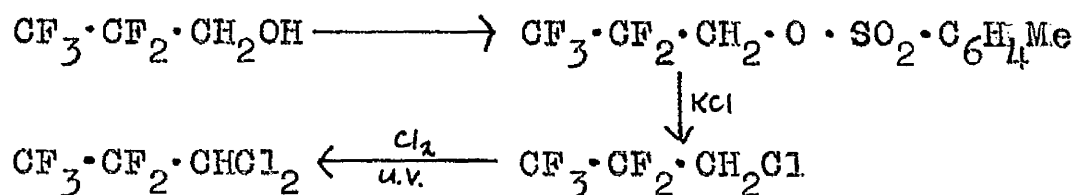


(XLIX)



(L)

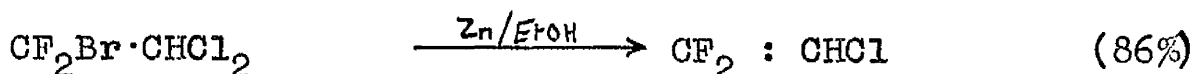
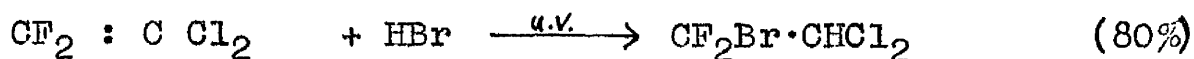
The structure of adduct (XLVII) was established by its reaction with chlorine to give compound (I) which had an identical i.r. spectrum to that of an authentic sample prepared by the unambiguous route:



Since the work described above was undertaken before the potential of g.l.c. as an analytical tool had been realised, it was felt that the presence of 5-10% of the isomeric 1 : 1 adduct (XLIX) in the reaction products could have remained undetected. In order to recheck this early work, to obtain more precise data, and to examine the effect of varying conditions on the reaction, the addition of trifluoriodomethane to chloro-1,1-difluoroethylene was investigated.

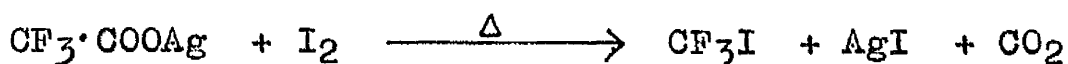
The materials used in this work were prepared by standard procedures operative in these laboratories. Chloro-1,1-difluoroethylene was prepared, in an overall yield of 70%, by the photochemically initiated addition of hydrogen bromide to dichloro-1,1-difluoroethylene followed by dechlorobromination of the resulting

1:1 adduct with zinc and refluxing ethanol¹¹⁴.



The olefin was shown by i.r. and n.m.r. spectroscopy, and by a g.l.c. examination, to be pure.

Trifluoroiodomethane was made by the Hunsdiecker reaction in which dry silver trifluoroacetate, prepared by the neutralisation of trifluoroacetic acid with silver carbonate, was intimately mixed with iodine and the resulting mixture pyrolysed.



The addition of trifluoroiodomethane to chloro-1,1-difluoroethylene to give high yields of the 1:1 adducts and negligible telomer formation is best achieved by the use of an excess of addend to olefin, and in these experiments a ratio of 2:1 was employed in order to be consistent with the published results.

The determination of the isomer ratios in the present work was achieved by a direct comparison of their g.l.c. peak areas, since equivalent molar quantities of individual isomers were shown by experiment

to give identical peak areas under identical operating conditions.

A preliminary addition gave two major products 1 and 2 in the ratio 90:10. These were considered to be the 1 : 1 adducts and thorough structural determinations were carried out.

Identification of the two major products.

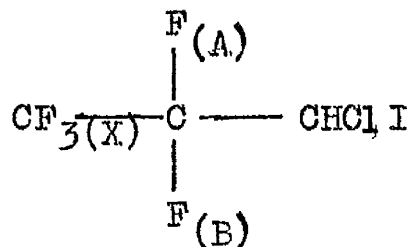
a) Product 1.

From the previous work on the $\text{CF}_2\text{:CHCl/CF}_3\text{I}$ reaction it was expected that the major product would be 1 : 1 adduct (XLVIII), and this premise was shown to be correct.

Chemical analysis and a molecular weight determination showed that this product was a 1 : 1 adduct.

i) ^{19}F and ^1H n.m.r. spectra.

^{19}F spectrum. External reference $\text{CF}_3\cdot\text{COOH}$. No solvent.



Band	Intensity	Chemical Shift (ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	+0.7	singlet	-	F _(X)
2	1	+24.6	doublet of doublets	A-B=265 4.6	F _(A)
3	1	+37.0	doublet of doublets	B-A=265 18	F _(B)

¹H spectrum. Internal reference Me₄Si. No solvent.

Band	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	4.04	doublet of doublets	18.0 4.6	H

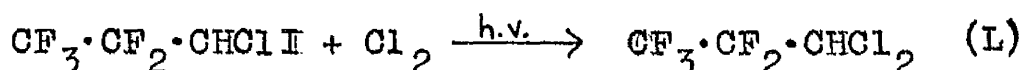
The spectrum is of the ABPX₃-type and the two non-equivalent fluorine nuclei (F_(A) and F_(B)) form the AB portion of the spectrum. Since the spectrum is not first order the \underline{J} values observed do not represent actual coupling constants but a complex association (except \underline{J}_{A-B} which is the true coupling constant). Since this and many other spectra recorded in this work are complex and would require analysis beyond the scope of the author,

only first order interpretations are given and these are considered sufficient for structural determination.

The absence of observed coupling between $F(X)$ and $F(A)$, or $F(B)$ is in accord with previous reports^{136,137} on similar compounds with $CF_3 \cdot CF_2$ substituents. Also, the absence of $HF(X)$ coupling shows that the CF_3 group is not attached to the same atom as the hydrogen atom. The chemical shifts and the coupling of the nuclei are in excellent agreement with the proposed structure, and with similar compounds reported in the literature^{136,138}.

ii) Reaction with chlorine.

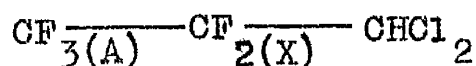
In the original work¹¹⁴, structure (XLVIII) was assigned to the adduct on the basis of its chemical reaction with chlorine to give the dichloride (L).



The photochemical reaction with chlorine was repeated in the present work. The i.r. spectrum of the dichloride (L) was not identical with that reported¹¹⁴; the major difference was that the reported strong band at 10.06μ was absent.

¹⁹F and ¹H n.m.r. spectra of $\text{CF}_3\text{-CF}_2\text{-CHCl}_2$.

¹⁹F spectrum. External reference $\text{CF}_3\text{-COOH}$. No solvent.



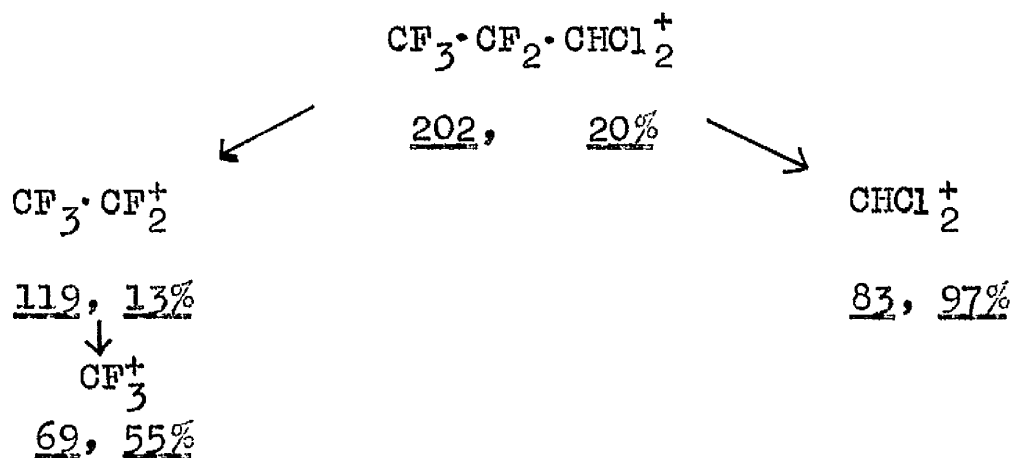
Band	Intensity	Chemical Shift (p.p.m.)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	+3.0	singlet (broad)	-	F(A)
2	2	+44.0	doublet of quartets	X-H=8.8 X-A=0.4	F(X)

¹H spectrum. Internal reference Me_4Si . No Solvent.

Band	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	4.12	triplet	H-X=8.8	H

A first order spectrum is obtained in which there is a small coupling constant (0.4 c/s) between F(A) and F(X). The chemical shifts and the splittings of the nuclei are in excellent agreement with the proposed structure.

Mass spectrum of $\text{CF}_3 \cdot \text{CF}_2 \cdot \text{CHCl}_2$.



The strong peaks at m/e 83 (97%), 85 (100%), and 87 (26%), corresponding to the ion CHCl_2^+ , are strong evidence for the presence of this group in the parent molecule. The peaks at m/e 85 and 87 are stronger than expected due to the presence of the rearranged ion CF_2Cl^+ . The complete spectrum is summarised in Table 26 (Page 196).

This evidence presents conclusive proof that product 1 has the structure $\text{CF}_3 \cdot \text{CF}_2 \cdot \text{CHClI}$.

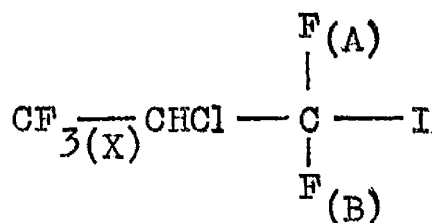
The absence of reaction of product 1 with powdered potassium hydroxide (20 min., in vacuo) is consistent with the hydrogen and iodine atoms not being attached to adjacent carbon atoms.

b) Product 2.

This was shown by chemical analysis and a molecular weight determination to be a 1 : 1 adduct.

i) ^{19}F and ^1H n.m.r. spectra.

^{19}F spectrum. External reference $\text{CF}_3\cdot\text{COOH}$. Solvent CCl_4 .



Band	Intensity	Chemical shift (p.p.m.)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	-14.0	triplet of doublets	11.3 7.05	$\text{F}(\text{X})$
2	1	-27.6	quartet of doublets	11.6 8.2	$\text{F}(\text{A})$
3	1	-28.4	quartet of doublets	11.0 8.5	$\text{F}(\text{B})$

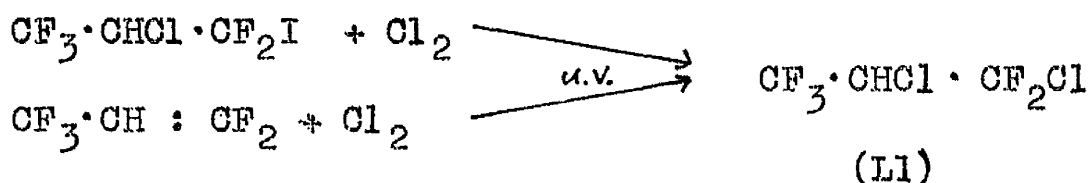
^1H spectrum. Internal reference Me_4Si . Solvent CCl_4 .

Band	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	5.12	sextet	7.4	H

The spectrum is of the ABPX₃-type and the above treatment is only approximate. The reasonably large splitting of the hydrogen nuclei into a sextet infers that is surrounded by five fluorine nuclei on adjacent carbon atoms. The reasonably large splitting between F(A) and F(X) (ca. 11.5 c/s) shows that the group CF₃·CF₂ is absent. The chemical shifts are consistent with the proposed structure.

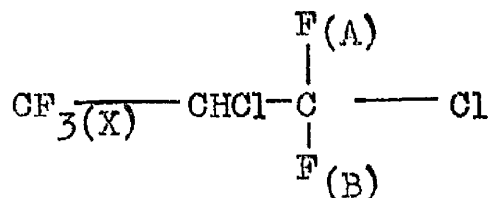
ii) Reaction with chlorine.

The photochemical reaction with chlorine gave a dichloro compound which had an identical i.r. spectrum to an authentic sample of the dichloride (LI) prepared by the photochemical addition of chlorine to 1,1,3,3,3-pentafluoropropene. The i.r. spectrum was also identical to that reported¹¹⁴.



¹⁹F and ¹H n.m.r. spectra of CF₃·CHCl·CF₂Cl.

¹⁹F spectrum. External reference CF₃·COOH. No solvent.



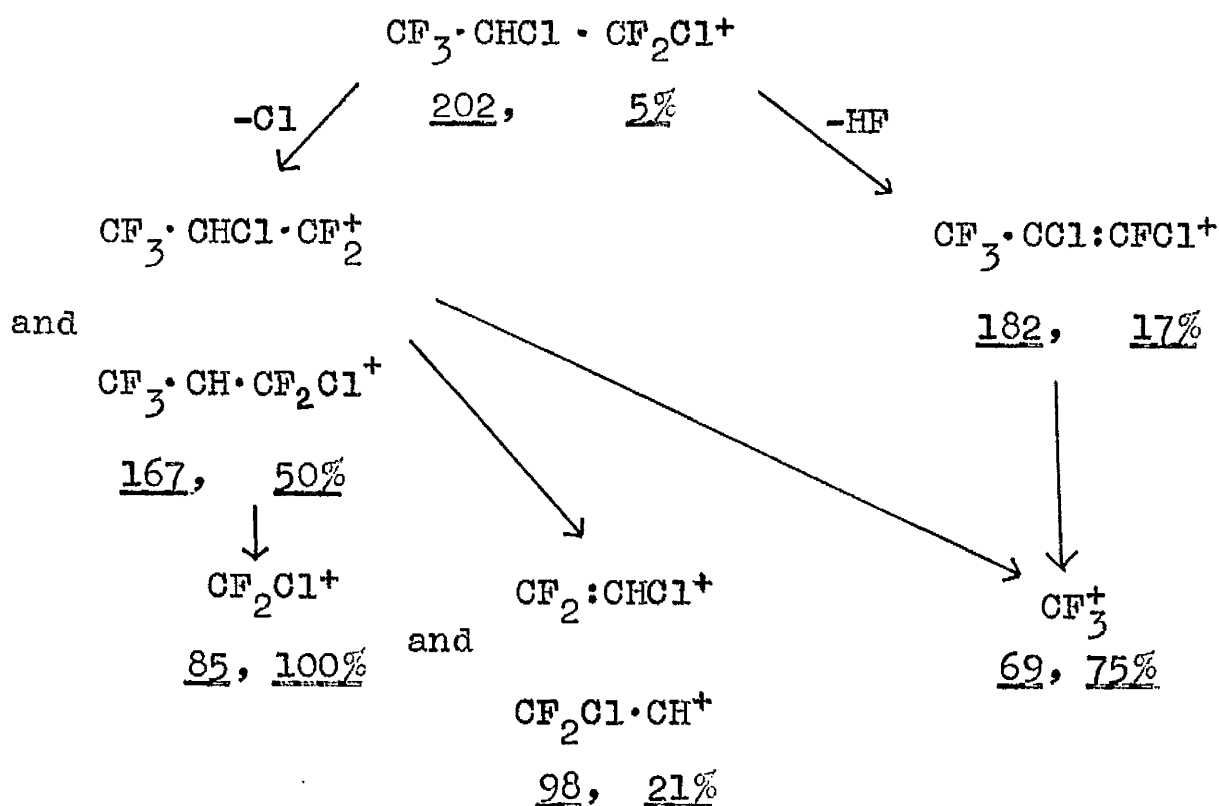
Band	Intensity	Chemical Shift (p.p.m.)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	-7.6	triplet of doublet	11.1 5.7	F(X)
2	1	-19.8	quartet of doublets	11.3 7.6	F(A)
3	1	-20.4	quartet of doublets	11.4 6.3	F(B)

^1H spectrum. Internal reference Me_4Si . No solvent.

Band	Chemical Shift (γ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	5.48	doublet of quintets	7.5 5.7	H

This spectrum is of the ABPX_3 -type and very similar to the parent iodo-compound (XLIX).

i) Mass spectrum of $\text{CF}_3 \cdot \text{CHCl} \cdot \text{CF}_2\text{Cl}$.

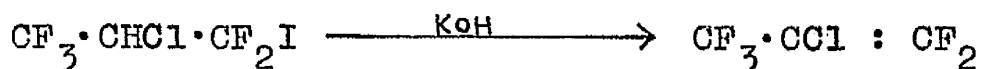


The strong peaks corresponding to the ion CF_2Cl^+ are strong evidence for the presence of this group in the parent molecule.

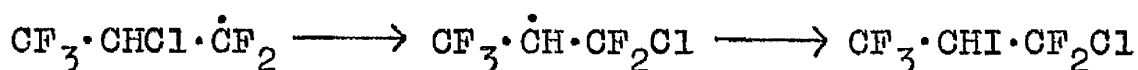
iii)

Reaction with powdered potassium hydroxide.

Reaction of product 2 with powdered potassium hydroxide, under similar conditions as used with product 1, gave 2-chloropentafluoropropene (91 %) identified by a comparison of its ^{19}F n.m.r. spectrum with that reported¹³⁹ in the literature; they were identical.



The formation of this olefin from product 2 rules out the possibility that this adduct is 3-chloro-1,1,1,3,3-pentafluoro-2-iodopropane formed via a 1,2-chlorine shift in the free-radical intermediate derived from "wrong-way round" addition of the CF_3 radical, i.e., attack on the CHCl group.



The above evidence presents conclusive proof that the product 2 has the structure $\text{CF}_3 \cdot \text{CHCl} \cdot \text{CF}_2\text{I}$.

Varying conditions used in the $\text{CF}_3\text{I}/\text{CF}_2:\text{CHCl}$ reaction.

The following reactions were carried out.

i) A short u.v. initiated reaction in silica with a low olefin conversion to determine accurately the 1 : 1 adduct ratio; the short irradiation period diminishes the possibility of further reactions of the primary products.

ii) A long u.v. initiated reaction in silica to give complete olefin conversion in order to directly compare

the results with those reported, and to determine whether the 1 : 1 adduct ratio was the same as in i).

iii) A thermal reaction to determine the difference, if any, in the 1 : 1 adduct ratio.

i) For a low olefin conversion.

The results of these reactions are summarised in Table 7, and agree with the result of the preliminary experiment that trifluoroiodomethane adds bidirectionally to chloro-1,1-difluoroethylene. The average ratio of the 1 : 1 adducts (XLVlll) : (XLlX) was found to be 90:10.

Although little or no telomer formation was detected it was apparent, from the yields (65-76%) of the 1 : 1 adducts isolated, that the reaction was not a clean one, and various other components, most of which were unidentified, were present in small amounts.

The major side-product was identified as 1,1-difluoroiodoethylene.

Table 7. The Addition of Trifluoroiodomethane to Chloro-1,1-difluoroethylene

for a Low Olefin Conversion Varying the Distance from the

Irradiation Source.

Distance From Lamp (cm.)	Irradiation Period (hr.)	% Olefin Conversion	% 1:1 adducts	1 : 1 adduct ratio		% CF ₂ :CHI	% Telomers
				(XLVII)	(XLIX)		
50	4	7	71	91	9	10	0
10	8	28	65	90	10	11	trace
50	8	14	71	90	10	6	0
100	16	10	76	87	13	8	0

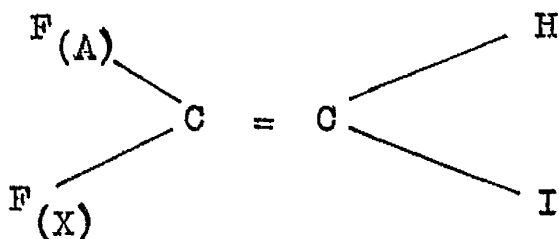
Determination of the structure of 1,1-difluoroiodoethylene.

Chemical analysis and a molecular weight determination established the empirical formula as C_2HF_2I .

i) The i.r. spectrum showed the same major bands as those reported¹⁴⁰ in the literature for the spectrum of 1,1-difluoroiodoethylene.

ii) ^{19}F and 1H n.m.r. spectra.

^{19}F spectrum. External reference $CF_3 \cdot COOH$. Solvent CCl_4 .



Band	Intensity	Chemical Shift (p.p.m)	Multiplet Structure	Coupling J (c/s)	Assignment
1	1	-1.7	doublet of doublets	X-A=27.3 X-H=23.1	$F(X)$
2	1	-6.0	doublet of doublets	A-X=27.3 A-H=2.1	$F(A)$

^1H spectrum. Internal reference Me_4Si . Solvent CCl_4 .

Band	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	5.27	doublet of doublets	$\text{H-X}=23.1$ $\text{H-A}=2.1$	H

Trans H-F coupling has been shown^{141,142} to be larger than cis H-F coupling in olefins, and the above assignment has been based on this fact.

The isomer CHF : CFI can be ruled out as the coupling constant between H and F on the same carbon atom would be much larger than that obtained, and, in fact, the spectrum is very similar to that of chloro-1,1-difluoroethylene (see Page 181).

This evidence presents conclusive proof that the major side-product had the structure $\text{CF}_2\text{:CHI}$.

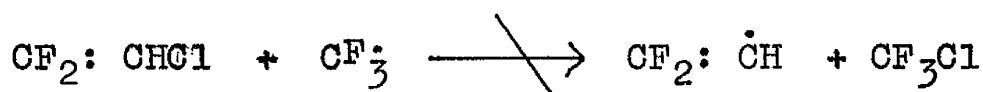
Further Discussion.

The distance of the reaction vessel from the irradiation source appeared to have little or no effect on the 1 : 1 adduct ratio; the largest effect was with the reaction carried out at a distance of 100 cm. which

gave a ratio (XLVlll) : (XLlX) of 87:13, and even this variation from a 90:10 ratio is not considered significant. Similarly, varying the irradiation period appeared to have no significant effect on the adduct ratio.

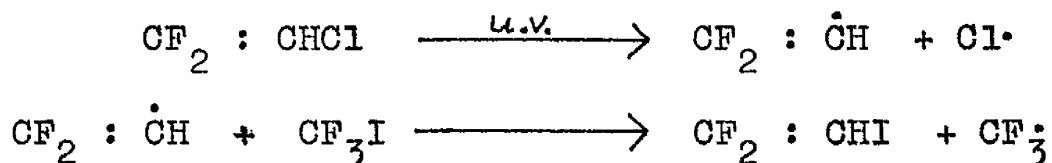
The reaction involving a 24hr. irradiation period (Table 8) can well be mentioned here. For this experiment a very etched silica tube was used in order to diminish the intensity of the u.v. radiation. This resulted in a drastic reduction in the yields of products resulting from side-reactions and the yield of the 1 : 1 adducts (93%) was almost quantitative; such a reaction is considered to give a true 1 : 1 adduct ratio, (XLVlll) : (XLlX) of 92:8, for irradiation conditions.

The formation of 1,1-difluoroiodoethylene (6-11%) was a surprising feature of these experiments. Its formation was not accompanied by the production of chlorotrifluoromethane, since none, or only a trace, of this compound was detected. The absence of chloro - trifluoromethane infers that the abstraction of chlorine from the olefin by a CF_3 radical either does not occur,



or that chlorotrifluoromethane reacts further; this last possibility seems unlikely.

Iodine was present in such small amounts that its participation in the reactions leading to the iodo-olefin is thought to be very unlikely. A possible mechanism for the formation of the iodo-olefin is shown below.



The chlorine atom and the $\text{CF}_3\cdot$ radical will not, of course, combine but attack the olefin or any other suitable electron-rich species; such an attack by the chlorine atom would cause side-products.

ii) For complete olefin conversion and further irradiation.

From an examination of Table 8, it is apparent that increasing the irradiation period after complete olefin conversion results in:

- i) a lower yield of 1:1 adducts,
- ii) increased formation of non-volatile products,
- iii) an increasing (XLIX) : (XLVIII) adduct ratio, and
- iv) a lower yield of 1,1-difluoroiodoethylene, probably due to further reaction of this olefin.

Since short irradiation periods produce little or no telomer, the increasing amounts of non-volatile

Table 8. The Addition of Trifluoroiodomethane to Chloro-11-difluoroethylene

for Complete or Almost Complete Conversion and Further Irradiation.

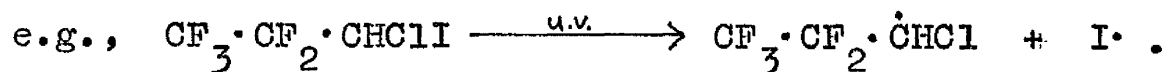
Irradiation Period (hr.)	% Olefin Conversion	% 1:1 adducts	1:1 adduct ratio		% CF ₂ :CHI	% Telomers [†]
			(XLVII)	(XLIX)		
24 [#]	34	93	92	8	4	0
72	100	75	89	11	1-2	*
96	100	60	83	17	1-2	*
150	100	34	72	28	1	16
192	100	37	51	49	1	21
330	100	23	35	65	0	33

[†] Calculated for a 2:1 adduct, which is not necessarily the case.

[#] In a very etched silica tube.

* Not determined.

products observed with increasing irradiation periods indicate that they are formed from the decomposition of the initially formed 1:1 adducts, probably by the cleavage of the relatively weak C — I bonds,



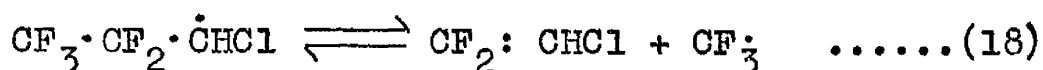
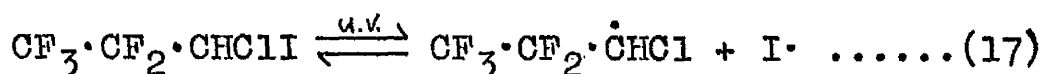
The intermediate radicals so formed could react further,



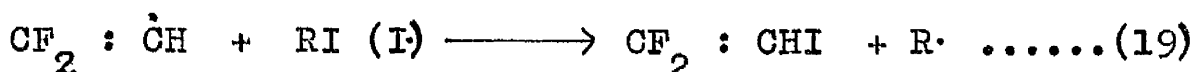
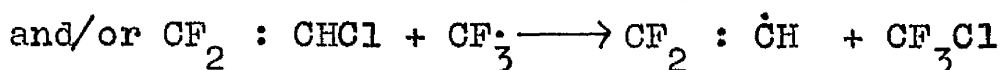
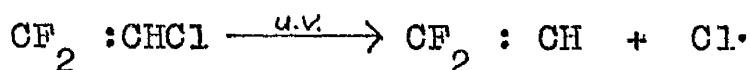
Not only does the adduct ratio (XLIX) : (XLVlll) increase but the actual amount of isomer (XLIX) increases with further irradiation from a 7% yield in the 24 hr. reaction to a 15% yield in the 330 hr. reaction. This observation indicates the participation of some reaction, or reactions, after complete olefin conversion to give isomer (XLIX). To determine whether or not isomer (XLVlll) rearranged to give isomer (XLIX) the following experiments were carried out.

a) Irradiation of isomer (XLVlll). No rearrangement was detected when the vapour phase irradiation (24 hr.) of isomer (XLVlll) contaminated with isomer (XLIX) (9%) was carried out (see Table 9). The major products were

1,1-difluoroiodoethylene (44%), trifluoroiodomethane (31%), and chlorotrifluoromethane (63%). A mechanism involving the formation of chloro-1,1-difluoroethylene (observed in the products) as an intermediate is proposed.



The formation of the products can then be accounted for by the following reaction scheme.



Chlorotrifluoromethane is the major product presumably because of all the products identified it is the least likely to break~~down~~ under u.v. irradiation. The proposed mechanism depends on whether the equilibrium depicted in equation (18) can proceed to the right.

b) Irradiation of isomer (XLVlll) with an excess of
trifluoroiodomethane.

The results of this investigation, Table 10, show that out of four experiments only one resulted in any observed rearrangement of isomer(XLlX) (24%), which was identified

Table 9. The Vapour Phase Irradiation of Isomer (XLVII) Contaminated with

Isomer (XLIX) (9%).

% Conversion	% CF_3Cl	% CF_3I	% $\text{CF}_2:\text{CHCl}$	% $\text{CF}_2:\text{CHI}$	% (XLIX)	% Non-volatiles
23	63	31	trace	44	0	trace

Table 10. The Vapour Phase Irradiation of Isomer (XLVII) with an Excess of

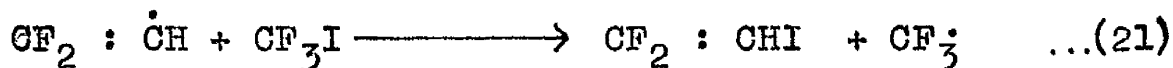
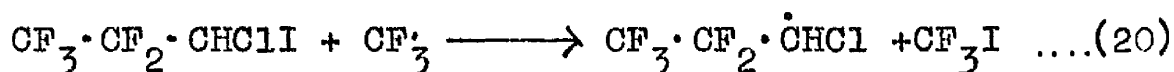
Trifluoroiodomethane.

	% Conversion	% CF_3Cl	% recovered CF_3I	% $\text{CF}_2:\text{CHI}$	% Unknown Product	% (XLIX)	% Non-volatiles
1	83	60	99	40	25	24	trace
2	9	ca. 80	100	80	trace	0	0

Two further reactions (60-90% conversion) gave no isomer (XLIX).

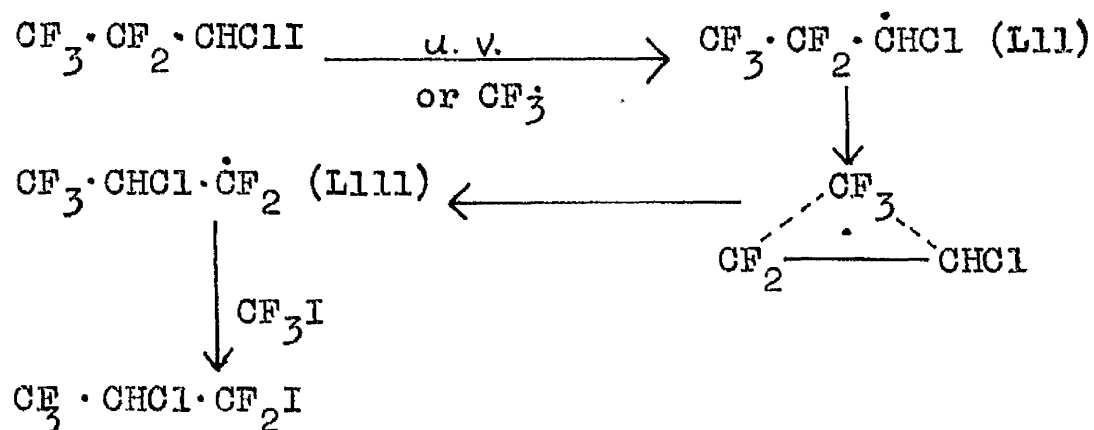
by its g.l.c. retention time. Again the major products were 1,1-difluoroiodoethylene and chlorotrifluoromethane together with an unknown product which had a g.l.c. retention time between that of 1,1-difluoroiodoethylene and the 1:1 adducts. Only a trace of this unknown product was isolated and the weak i.r. spectrum obtained indicated a saturated compound containing fluorine.

A similar mechanism to that proposed for the formation of the identified compounds from isomer (XLVlll) alone is proposed here. The only difference will be due to the expected greater participation of the $\text{CF}_3\cdot$ radical derived from the breakdown of trifluoroiodomethane, and so reactions (17) and (19) will, in this experiment, probably be superseded by reactions (20) and (21) respectively.

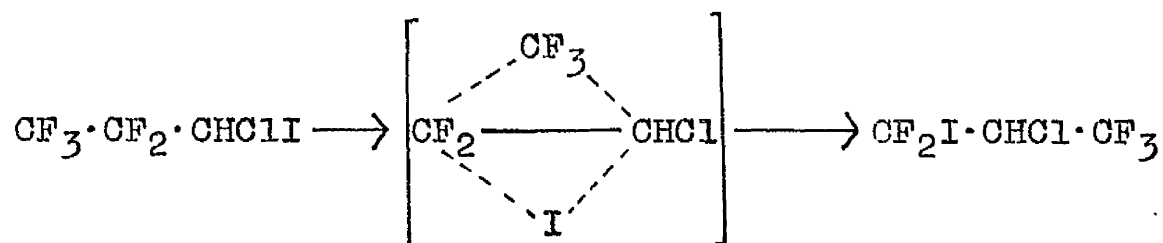


It seems, therefore, unlikely that a direct rearrangement of the 1:1 adduct (XLVlll) takes place, but that the rearrangement proceeds by a devious route probably involving one or more of the unidentified side-products. Reported rearrangements of radicals¹⁴³ always produce a more stable radical from a less stable one, and since it

has been shown by the addition reaction that radical (L11) is more stable than radical (L111), it seems improbable that isomer (XLV111) will rearrange to isomer (XL1X) according to the following direct mechanism.



A four-centre rearrangement, under the influence of u.v. radiation, involving simultaneous 1,2 shifts of the iodine atom and the trifluoromethyl group seems just as improbable.



Although such four-centre mechanisms are often proposed for the reactions of organo-metallic compounds¹⁴⁴ and have recently been postulated for reactions involving organo-silicon¹⁴⁵ and boron compounds¹⁴⁶, such mechanisms have not been proposed for halocarbon rearrangements.

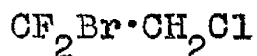
iii) Thermally.

A mixture of trifluoroiodomethane and chloro-1,1-difluoroethylene was heated (225°, 20 hr.) to give a 48% olefin conversion and the 1:1 adducts (ratio (XLV111) : (XLIX) of 98:2) in a 13% yield; the major product was a black tar. The reactants were recovered unchanged after being heated at 195° (100 hr.).

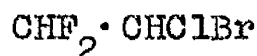
At the reaction temperature employed the 1:1 adducts expected to be formed are probably decomposed. If this is the case, then it seems reasonable that such instability of the adducts would make it difficult to obtain an accurate 1:1 adduct ratio in a thermal reaction, and so no further investigation was undertaken.

II Free-Radical Addition of Hydrogen Bromide.

The u.v. initiated reaction between hydrogen bromide and chloro-1,1-difluoroethylene was reported¹¹⁴ to give only one 1:1 adduct (LIV); the isomeric 1:1 adduct (LV) was not detected.



(LIV)



(LV)

In view of the discovery that two-way addition of trifluoroiodomethane to this olefin does occur, and the

inference from Table 6 that the Br•atom is less specific than the CF₃ radical in its additions to olefins, it was considered very likely that the radical addition of hydrogen bromide would give the two 1:1 adducts resulting from bidirectional addition, and the addition reaction was accordingly re-investigated.

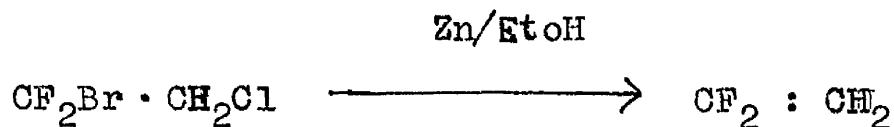
No reaction occurred when hydrogen bromide and chloro-1,1-difluoroethylene, in a reaction ratio of 2:1, were left in the dark for 3 weeks; the addition of a trace of bromine to the reaction mixture gave no reaction after a further 8 weeks. Since these reactions were unsuccessful, it is probable that ionic addition of hydrogen bromide does not occur under the conditions used for free-radical addition.

When a u.v. initiated reaction was carried out in silica, immediate reaction was seen to occur and after 20 min. complete conversion of the olefin was achieved. Only one product (97%) was formed and this was shown to be adduct (LLV); no trace of the other adduct (LV) was detected by g.l.c. or n.m.r. techniques.

Identification of the product.

The structure of the 1:1 adduct was proved earlier¹¹⁴ by dechlorobromination with zinc and refluxing ethanol to give 1,1-difluoroethylene (95%); an olefin which

could only be derived from isomer (LIV).

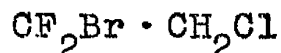


The i.r. spectrum of the product obtained in this present work was identical to that reported for adduct (LIV).

Chemical analysis and a molecular weight determination showed that this product was indeed a 1:1 adduct.

^{19}F and ^1H n.m.r. spectra.

^{19}F spectrum. External reference $\text{CF}_3\cdot\text{COOH}$. No solvent.



Band	Chemical Shift	Multiplet Structure	Coupling J (c/s)	Assignment
1	-24.8	triplet (broad)	12.0	F

^1H spectrum. Internal reference Me_4Si . No solvent.

Band	Chemical Shift	Multiplet Structure	Coupling J (c/s)	Assignment
1	5.92	triplet	12.0	H

Since further weak splitting was apparent in the ^1H spectrum, the first order treatment above is only an approximate treatment and the system is of the AA^1XX^1 -type. The deceptively simple spectrum requires the two hydrogen atoms and the two fluorine atoms to be on different carbon atoms.

This evidence presents conclusive proof that the product is the 1:1 adduct of structure $\text{CF}_2\text{Br}\cdot\text{CH}_2\text{Cl}$.

Summary.

The addition of trifluoroiodomethane to chloro-1,1-difluoroethylene was bidirectional, but the addition of hydrogen bromide, which might have been expected to give a ratio of adducts closer to 1:1 than obtained with trifluoroiodomethane, gave only one adduct. Since the olefin is polarised in the direction $\overset{\delta+}{\text{CF}_2} : \overset{\delta-}{\text{CHCl}}$ for ionic additions, the orientation of addition would suggest that a $\text{CF}_3\cdot$ radical is more electrophilic than a $\text{Br}\cdot$ atom, although the observed rate of hydrogen bromide addition was much faster.

The previous work on this olefin has, thus, been shown by the present work to be correct for hydrogen bromide addition, but in need of minor revision for the addition of trifluoroiodomethane.

B. 1,1,3,3,3-Pentafluoropropene.

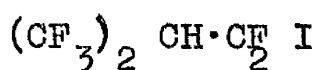
I. The Free-Radical Addition of Trifluoriodomethane.

It was considered that the olefin, 1,1,3,3,3-pentafluoropropene, was even more likely to exhibit bidirectional addition than chloro-1,1-difluoroiodoethylene. The observed two-way additions of both trifluoriodomethane and hydrogen bromide to hexafluoropropene and trifluoroethylene (Table 6) indicate that the stabilising powers of a CF_2 group, a CHF group, and a $\text{CF}_3\cdot\text{CF}$ group towards a lone electron are of comparable magnitude, and it was considered that a $\text{CF}_3\cdot\text{CH}$ group might stabilise to a comparable extent, and hence bidirectional addition to 1,1,3,3,3-pentafluoropropene might be observed with certain radicals.

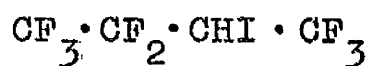
It had been reported ¹⁴⁷ that the CF_3 radical and the $\text{Br}\cdot$ atom added, as far as could be determined, exclusively to the $\text{CF}_3\cdot\text{CH}$ and CF_2 groups of the olefin $\text{CF}_3\cdot\text{CH} : \text{CF}_2$ respectively. The unusual nature of this report, noted by the earlier authors, provided a second incentive to repeat the earlier additions to this olefin, and to obtain more precise data than previously obtained.

The addition of trifluoriodomethane was reported to give probably exclusively (or $> 90\%$) isomer (LV1), and the

isomeric 1:1 adduct (LV11) was not detected.

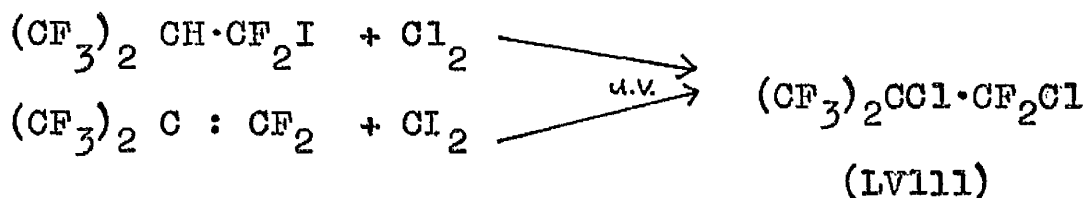


(LV1)

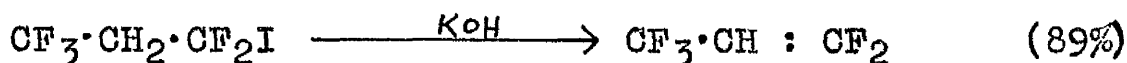
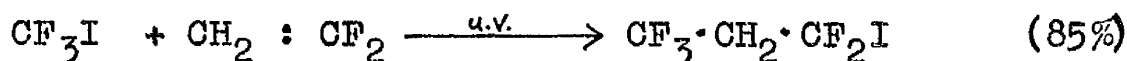


(LV11)

The structure of the 1:1 adduct (LV1) obtained was proved chemically by the photochemical reaction with chlorine to give the dichloride (LV111) which had an identical i.r. spectrum to that of a sample of the same dichloride prepared by the addition of chlorine to perfluoroisobutene.



In the present work 1,1,3,3,3-pentafluoropropene was prepared¹⁴⁷, in an overall yield of 75%, by the photochemically initiated addition of trifluoriodomethane to 1,1-difluoroethylene, followed by dehydroiodination of the resulting 1:1 adduct with powdered potassium hydroxide.



The addition of trifluoriodomethane to 1,1,3,3,3-pentafluoropropene was investigated under both

photochemical and thermal conditions.

A preliminary photochemically initiated experiment gave two major products 1 and 2 in the ratio 55:45. These were considered to be the 1:1 adducts and a thorough investigation to determine their structures was carried out.

Identification of the two major products.

a) Product 1.

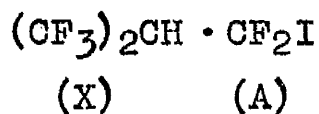
Chemical analysis and a molecular weight determination showed that this product was a 1:1 adduct.

i) Reaction with powdered potassium hydroxide.

Dehydroiodination gave only one product (55%) which had an identical i.r. spectrum to that reported¹⁴⁸ in the literature for perfluoroisobutene. This olefin can only be formed from the 1:1 adduct (LV1).

ii) ^{19}F and ^1H n.m.r. spectra.

^{19}F spectrum. External reference $\text{CF}_3\cdot\text{COOH}$. No solvent.



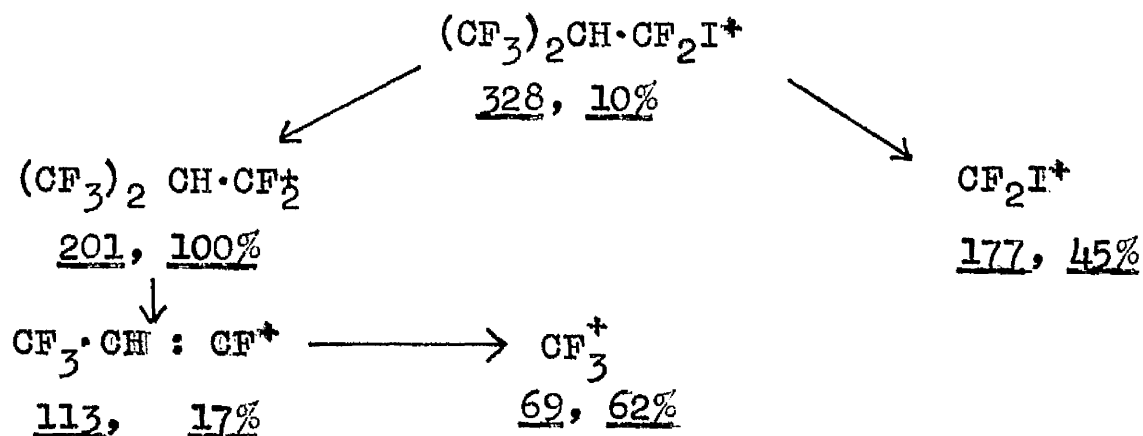
Band	Intensity	Chemical Shift (ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	6	-15.2	triplet of doublets	X-A=10.9 X-H=7.3	F(X)
2	2	-37.4	septet of doublets	A-X=10.9 A-H=10.0	F(A)

^1H spectrum. Internal reference Me_4Si . No solvent.

Band	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	6.24	triplet of septets	H-A=10.0 H-X=7.3	H

This simple spectrum is of the A_2PX_6 -type. The two CF_3 groups, because of their equivalence, are inferred to be on the same carbon atom. The chemical shift observed for the two equivalent fluorine atoms $\text{F}(\text{A})$ is typical for fluorine nuclei present in the CF_2I group (see Page 192).

iii) Mass spectrum.



The strong peak, corresponding to the ion CF_2I^+ , is strong evidence for the proposed structure.

This evidence presents conclusive proof that product 1 has the structure $(\text{CF}_3)_2\text{CH}\cdot\text{CF}_2\text{I}$.

b) Product 2.

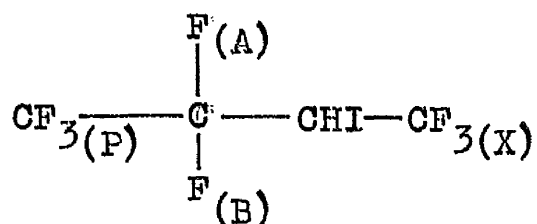
Chemical analysis and a molecular weight determination showed that this product was also a 1:1 adduct.

i) Reaction with powdered potassium hydroxide.

No reaction was observed with product 2 under approximately the same conditions as employed for product 1. This infers that the hydrogen and iodine substituents are not on adjacent carbon atoms.

ii) ^{19}F and ^1H n.m.r. spectra.

^{19}F spectrum. External reference $\text{CF}_3\cdot\text{COOH}$. No solvent.



Band	Intensity	Chemical Shift (ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	-14.6	doublet of doublets of doublets of quartets	12.7 8.3 X-H=6.9 X-P=5.4	$\text{F}(\text{X})$
2	3	+3.6	quartet	P-X=5.4	$\text{F}(\text{P})$
3	1	+25.0	doublet of doublets of quartets	A-B=277 11.2 8.3	$\text{F}(\text{A})$
4	1	+36.0	doublet of quintets	B-A=277 12.7	$\text{F}(\text{B})$

^1H Spectrum. Internal reference Me_4Si . No solvent.

Band	Chemical shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	5.32	triplet of quartets	12.6 H-X=6.9	H

The spectrum is of the $ABLP_3X_3$ -type, and the above treatment is only approximate. The two fluorine atoms $F_{(A)}$ and $F_{(B)}$ must be non-equivalent geminal fluorine atoms, since they have a very large coupling constant ($J_{A-B} = 277$). The absence of coupling between $F_{(P)}$ and $F_{(A)}$, or $F_{(B)}$ is typical of the $CF_3 \cdot CF_2$ group. As hydrogen substituents on one carbon atom are not generally split by fluorine atoms other than those on the same or adjacent carbon atoms, the observed hydrogen spectrum suggests that the grouping $CF_3 \cdot CHX \cdot CF_2$ is present.

iii) Mass spectrum.

The spectrum was of little help as far as structure determination is concerned. A parent ion peak at m/e 328 (100%), and a peak at m/e 127 (34%), corresponding to the ion I^+ , were obtained.

This evidence presents conclusive proof that product 2 has the structure $CF_3 \cdot CF_2 \cdot CHI \cdot CF_3$.

Results and Discussion.

1) Photochemically.

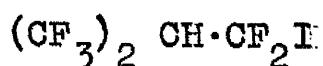
The results of a series of u.v. initiated additions of trifluoriodomethane to 1,1,3,3,3-pentafluoropropene are summarised in Table 11. The two 1:1 adducts

Table 11.

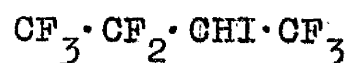
The Photochemically Initiated Addition of Trifluoroiodomethane to
1,1,3,3,3-Pentafluoropropene.

Irradiation Time (hr.)	Lamp (W.)	Distance (cm.)	Temp. (°)	% Olefin Conversion	% 1:1 adducts	Ratio of 1:1 adducts	
						(LV1)	(LV11)
265	500	8	30	20	85	55	45
192	500	2	60	30	76	58	42
216	500	8	100	44	78	63	37
144	250	2	60	17	80	60	40

were shown to be present in the average ratio (LV1):(LV11) of 60:40.



(LV1)



(LV11)

This ratio infers that the two possible intermediate radicals are of very similar stability; the preponderance of isomer (LV1) can be accounted for either by,

i) the greater stability of the intermediate tertiary radical $(\text{CF}_3)_2 \text{CH} \cdot \dot{\text{C}}\text{F}_2$ as compared with the secondary radical $\text{CF}_3 \cdot \text{CF}_2 \cdot \dot{\text{C}}\text{H} \cdot \text{CF}_3$, or by

ii) the polarisation of the olefin in the sense $\text{CF}_3 \cdot \overset{\delta-}{\text{CH}} : \overset{\delta+}{\text{CF}_2}$, and the preferred CF_3 radical attack at the more negative carbon atom.

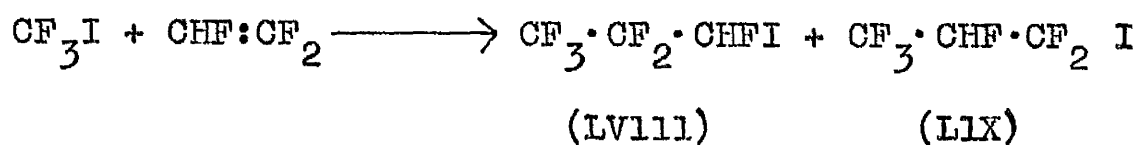
More forcing conditions were required for the addition of trifluoriodomethane to this olefin than were required for the corresponding addition to chloro-1,1-difluoroethylene. Thus, after the preliminary experiment, the reactions were carried out at a distance of 2cm. from the lamp, or with the reaction tube heated to 100° in a furnace during irradiation. The difference in reactivity of the two olefins can be accounted for in terms of the π -electron densities of the double bonds of the olefins

and the electrophilicity of the CF_3 radical. The CF_3 group has been shown to have a stronger $-I$ effect than the chlorine atom¹⁴⁹, and the replacement of a chlorine atom by a CF_3 group in an olefin will decrease the π -electron density of the double bond, and hence decrease the rate of attack by the electrophilic CF_3 radical.

Increasing the reaction temperature resulted in an increase in the ratio (LV1):(LV11) from 55:45 at 30° to 63:37 at 100° , which can be explained in terms of greater selectivity of attack by the CF_3 radical at higher temperatures, but such small variations may not be significant.

However, the observation that a radical shows greater selectivity of attack at higher temperatures is contrary to the generally accepted view that selectivity decreases with an increase in temperature, e.g., chlorine atoms¹⁵⁰ show a decreasing selectivity as the temperature is raised in the vapour phase radical chlorination of saturated hydrocarbons. In general, the greater the energy a radical possesses the more numerous is the choice of reaction paths for that radical.

Higginbottom¹⁵¹ has studied the effect of temperature on the selectivity of CF_3 radical attack on the olefin trifluoroethylene.



Although the ratio (LIX):(LV111) varied from 76:24 at -55° to 67:33 at 140° , it was considered that this variation in the adduct ratio was too small to be significant and that, in any case, the variation could be accounted for by preferential telomer formation from one isomer at the higher temperature.

The present results are clearly at variance with the earlier work, and in an attempt to resolve this discrepancy, a 250W. lamp was used so that the conditions¹⁵² used previously could be reproduced as closely as possible. Table 11 shows that no difference in the isomer ratio was observed when such a lamp was used.

ii) Thermally.

A thermal reaction (212° , 70 hr.) between trifluoriodomethane and 1,1,3,3,3-pentafluoropropene gave a 63% olefin conversion. The major products were identified as the 1:1 adducts (36%), present in the ratio (LV1):(LV11) of 17:83, and the decomposition product perfluoroisobutene (ca. 22-23%).

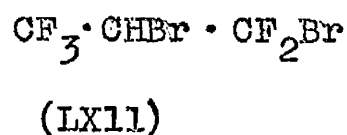
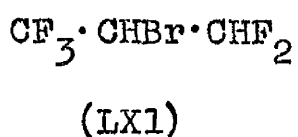
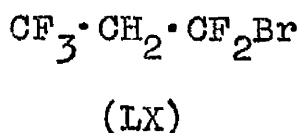
It would appear at first sight that the orientation of addition is reversed, but this apparent reversal is best explained by the decomposition of isomer (LV1) at the temperature employed, whilst isomer (LV11) is stable.

Since perfluoroisobutene can only be formed from the decomposition of isomer (LV1), and since the actual yield of isomer (LV1) was 6%, then the yield of isomer (LV1) would, if it had been stable, have been ca. 28-29% . This would have given a 1:1 adduct ratio (LV1):(LV11) of ca. 48:52. Even this derived ratio is probably very inaccurate, since many other unidentified products (42%) were present in small amounts, and these minor products may have also been derived from the decomposition of isomer (LV1), and indeed, of isomer (LV11).

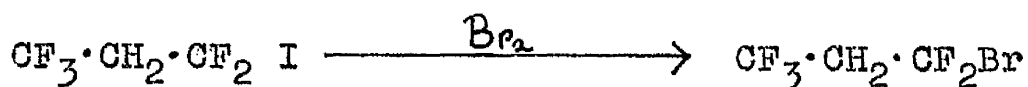
It is, therefore, apparent that no reliable 1:1 adduct ratio can be obtained from such a thermal reaction. If the breakdown products are derived only from isomer (LV1), then a similar 1:1 adduct ratio to that for the irradiation additions would have been obtained if the adduct had been stable.

II Free-Radical Addition of Hydrogen Bromide.

As mentioned previously the addition of hydrogen bromide to 1,1,3,3,3-pentafluoropropene was reported¹⁴⁷ to give only one 1:1 adduct (LX) (40%) and the dibromide (LXI) (50%); the isomeric 1:1 adduct (LXI) was not detected.



The structure of the 1:1 adduct isolated was proved to be isomer (LX) by its having an identical i.r. spectrum to that of an authentic sample prepared from the reaction of bromine with 1,1,1,3,3-pentafluoro-3-iodopropane in the dark.



The work was repeated because again it was considered that two-way addition should occur.

A preliminary photochemically initiated experiment gave three major products, two of which 1 and 2, present in the ratio 72:28, were thought to be 1:1 adducts, and the third product 3, with a longer g.l.c. retention time, was considered to be the olefin dibromide.

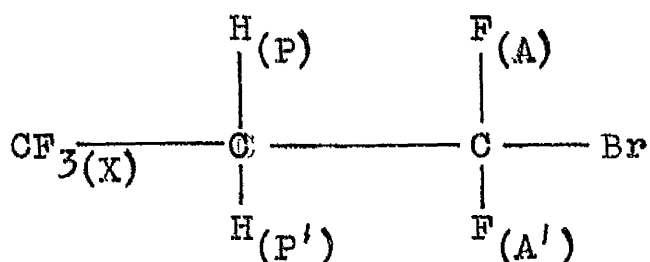
Identification of the Major Products.

a) Product 1.

Chemical analysis and a molecular weight determination confirmed that this product was a 1:1 adduct.

i) ^{19}F and ^1H n.m.r. spectra.

^{19}F spectrum. External reference $\text{CF}_3\cdot\text{COOH}$. No solvent.



Band	Intensity	Chemical Shift (ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	-13.5	triplet (broad)	8.6	F(X)
2	2	-30.5	triplet (broad)	13.0	F(A)

^1H spectrum. Internal reference Me_4Si . No solvent.

Band	Chemical shift (τ)	Multiplet Structure	Coupling J(c/s)	Assignment
1	6.78	triplet of quartets	13.0 8.6	H(P)

The spectrum represents an $AA^1PP^1X_3$ -system and the above approximate treatment is deceptively simple.

The two hydrogen and the two fluorine nuclei $F(A)$ are both shown to be almost identical. This indicates that the two hydrogen atoms are attached to the same carbon atom, and the two fluorine atoms $F(A)$ are similarly attached to one carbon atom. The splittings in the spectrum indicate the presence of the grouping $CF_3 \cdot CH_2 \cdot CF_2-$, with negligible coupling between $F(A)$ and $F(X)$.

ii) Mass spectrum.

Strong peaks at m/e 129 (26%) and 131 (26%), corresponding to the ion CF_2Br^+ , were given by this product, whilst corresponding peaks in the spectrum of product 2 were only weak (6%).

This evidence is conclusive proof that product 1 has the structure $CF_3 \cdot CH_2 \cdot CF_2Br$.

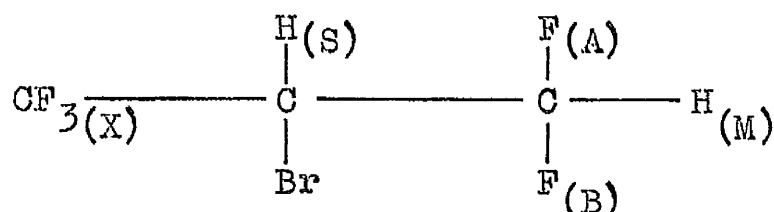
b) Product 2.

Chemical analysis and a molecular weight determination showed that this product was also a 1:1 adduct.

i) ^{19}F and ^1H n.m.r. spectra.

^{19}F spectrum.

External reference $\text{CF}_3\cdot\text{COOH}$. No solvent.



Band	Intensity	Chemical Shift (ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	2.9	-7.7	doublet of triplets (broad)	8.7 7.7	$\text{F}(\text{X})$
2	1	+43.6	doublet of quintets	55.0 8.4	$\text{F}(\text{A})$
3	1	+44.4	doublet of doublets of quartets	55.0 11.8 7.9	$\text{F}(\text{B})$

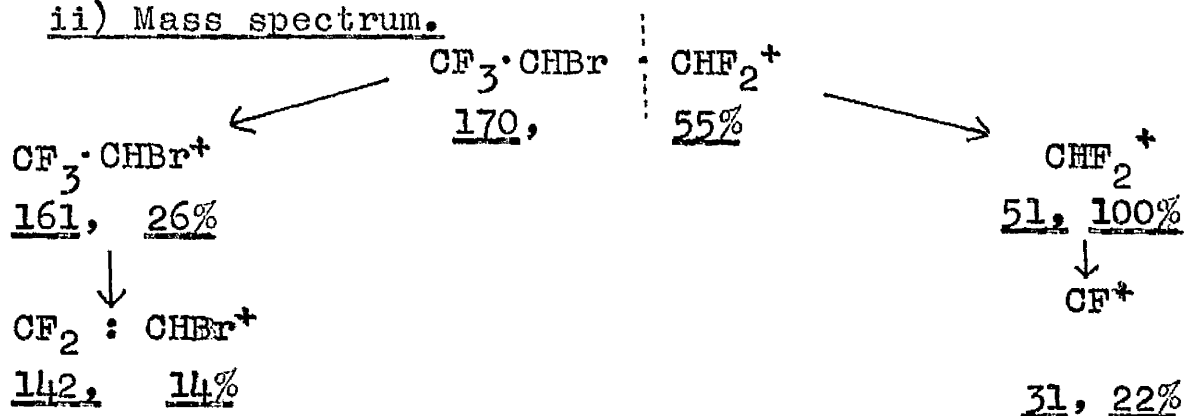
^1H spectrum.

Internal reference Me_4Si . No solvent.

Band	Intensity	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	1	4.03	triplet of doublets	55.0 $\text{M}-\text{S}=3.4$	$\text{H}(\text{M})$
2	1	5.68	doublet of doublets of quartets of doublets	11.8 9.0 $\text{S}-\text{X}=7.0$ $\text{S}-\text{M}=3.4$	$\text{H}(\text{S})$

The spectrum is of the ABMSX₃-type, but only a first order interpretation was attempted. The different shifts of the two hydrogen nuclei show that they are probably not attached to the same carbon atom, and the large splitting (55.0 c/s) between F_(A) and F_(B), and H_(M) indicates the presence of a CHF₂ group since only geminal H-F couplings give such large values. The shifts of nuclei agree with the shifts observed in similar compounds (see Page 192).

ii) Mass spectrum.



The presence of these major peaks is good evidence for the proposed structure.

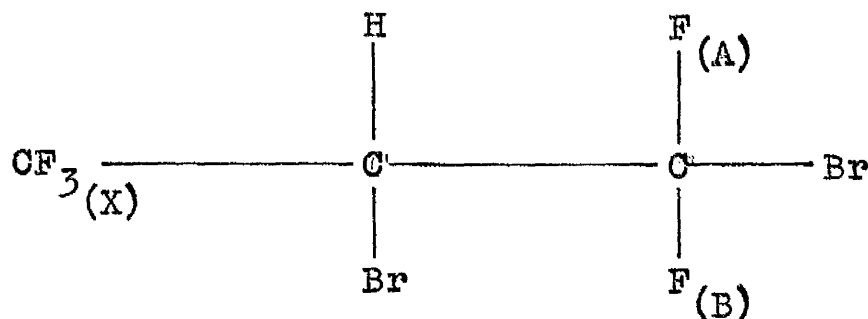
This evidence presents conclusive proof that product 2 is the 1:1 adduct of structure $\text{CF}_3 \cdot \text{CHBr} \cdot \text{CHF}_2$.

c) Product 3.

Chemical analysis and a molecular weight determination confirmed that this was the olefin dibromide.

i) ^{19}F and ^1H n.m.r. spectra.

^{19}F spectrum. External reference $\text{CF}_3\cdot\text{COOH}$. No solvent.



Band	Intensity	Chemical Shift (ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	-10.0	triplet of doublets	11.0 6.0	$\text{F}_{(\text{X})}$
2	2	-27.8	quartet of doublets	11.0 8.7	$\text{F}_{(\text{A})}\text{F}_{(\text{B})}$

^1H spectrum. Internal reference Me_4Si . No solvent.

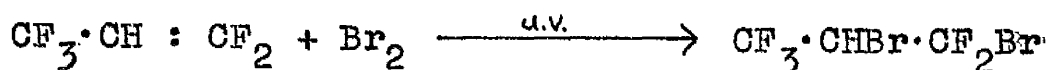
Band	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	5.38	triplet of quartets	8.4 6.0	H

The spectrum represents an ABPX_3 -system in which $\text{F}_{(\text{A})}$ and $\text{F}_{(\text{B})}$ are very similar. The above interpretation is only approximate. The chemical shifts agree with those

reported for similar compounds (see Page 192).

ii) Bromination of 1,1,3,3,3-pentafluoropropene.

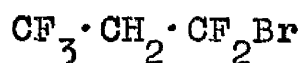
The photochemical addition of bromine to 1,1,3,3,3-pentafluoropropene gave a dibromide which had an identical i.r. spectrum to product 3.



This evidence provides conclusive proof that product 3 has the structure $\text{CF}_3 \cdot \text{CHBr} \cdot \text{CF}_2 \text{Br}$.

Results and Discussion.

The results of this present investigation into the addition of hydrogen bromide to 1,1,3,3,3-pentafluoropropene are summarised in Table 12. Bidirectional addition was observed and the most accurate ratio (LX):(LX1) obtained is considered to be 37:63.



(LX)



(LX1)

The large bromine atom thus appears to have a similar preferential attack on the $\text{CF}_3 \cdot \text{CH}$ group of the

Table 12. The Photochemical Addition of Hydrogen Bromide to

1,1,3,3,3-Pentafluoropropene.

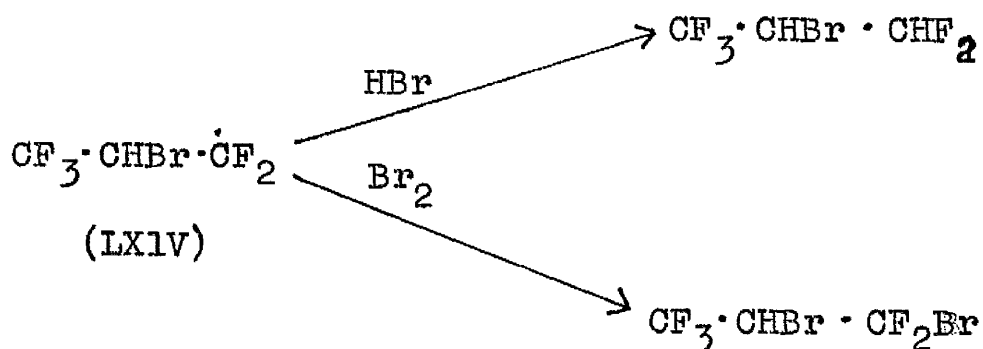
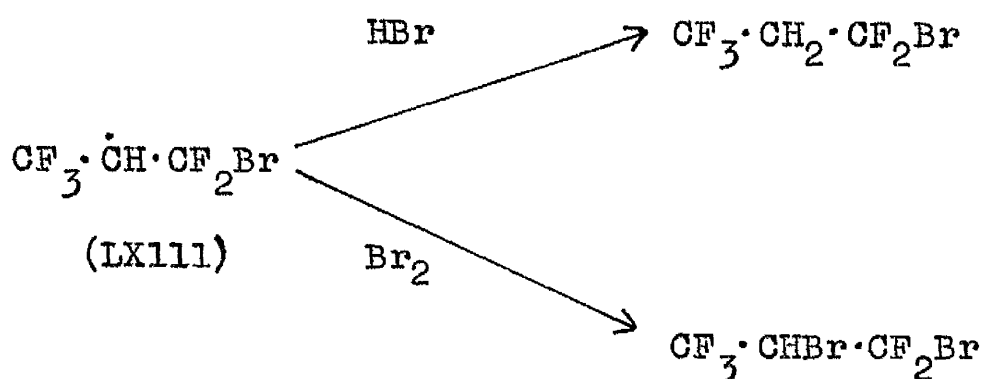
	Irradiation Period (hr)	% Olefin Conversion	% 1:1 adducts	Ratio of 1:1 Adducts		% Dibromide
				(LX)	(LXL)	
1	48	67	33	72	28	48
2 [*]	12	2	59	37	63	40
3 [†]	140	100	<u>ca.</u> 32	36	64	<u>ca.</u> 60

* In the presence of silver powder.

† No stringent mass balance was kept.

olefin to the $\text{CF}_3\cdot$ radical, even though this is the more sterically hindered site of the olefin. With hexafluoropropene (Table 6, Page 36), the bromine atom has been shown to give a higher proportion of attack on the more hindered $\text{CF}_3\cdot\text{CF}$ group than does the $\text{CF}_3\cdot$ radical.

Since the addition was slow, bromine molecules were formed by the combination of bromine atoms, and these took part in the chain-transfer reaction to yield the olefin dibromide. The formation of the dibromide causes the 1:1 adduct ratio to lose much of its significance since either, or both, intermediates (LXIII) and (LXIV) may lead to the dibromide.

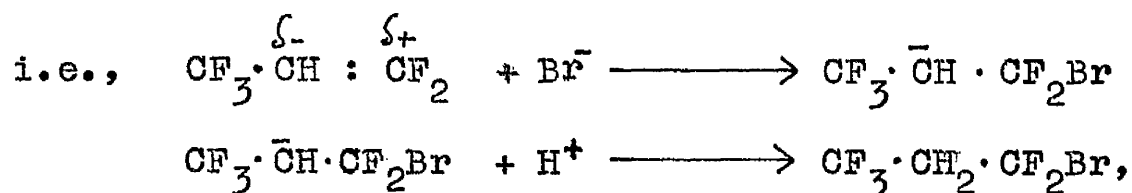


It was considered that a reaction carried out in the presence of a small amount of silver powder might reduce the concentration of the bromine molecules by reaction to give silver bromide. This would diminish the formation of the dibromide and a more accurate 1:1 adduct ratio should be obtained. Unfortunately, the silver powder also apparently removed bromine atoms from the reaction mixture and the only reaction observed was the production of hydrogen and silver bromide. When all the silver powder was converted to the bromide, then the reaction proceeded normally.

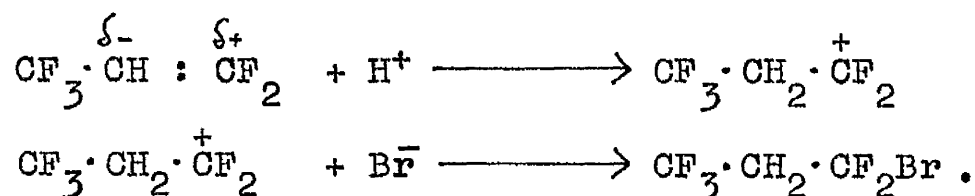
Out of the three experiments recorded in Table 12, two gave an almost identical 1:1 adduct ratio showing a preponderance of isomer (LX1). This would be expected to be the major adduct in keeping with the direction of addition shown by trifluoroiodomethane to this olefin.

Reaction 1 gave isomer (LX) as the major 1:1 adduct and in this respect it is completely different from the other two reactions. It is difficult to explain such a variation unless the preponderance of isomer (LX) in reaction 1 results from an ionic addition of hydrogen bromide, which did not occur in the other two reactions. Such an ionic addition may involve either initial

electrophilic or nucleophilic attack. Initial electrophilic attack is the general mode of ionic hydrogen bromide addition, but nucleophilic addition must be considered because such additions have been shown¹⁵³ to be facile in reactions with olefins containing strong electron-withdrawing groups, e.g., fluoro-olefins, since such groups reduce the π -electron density in the double bond,



or more probably,



Although an ionic additon can explain the discrepancy, it does not explain why such an addition should occur in one reaction only, although it must be remembered that the earlier workers obtained unidirectional addition. An ionic addition could have been caused by the presence of some impurity in reaction 1, which could induce hydrogen bromide to ionise. Although these proposals are tentative, it is difficult to explain such variations in addition by any other means.

Summary.

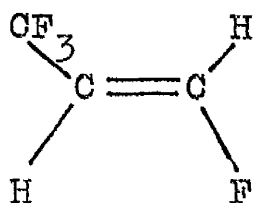
The ratio obtained for bidirectional addition of trifluoroiodomethane to 1,1,3,3,3-pentafluoropropene is considered to be accurate for photochemical conditions, but the addition of hydrogen bromide was not sufficiently precise to enable firm conclusions to be drawn.

C. 1,3,3,3-TETRAFLUOROPROPENE.

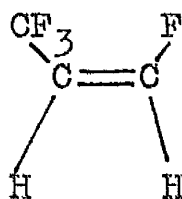
I Preparation.

At this stage, it was decided to investigate additions to olefins not previously studied, and 1,3,3,3-tetrafluoropropene was considered to be a suitable olefin for investigation, since it was structurally very similar to 1,1,3,3,3-pentafluoropropene, and should exhibit bidirectional addition.

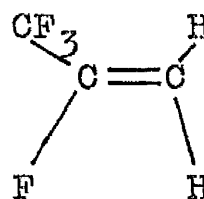
The olefin was prepared by the following sequence of reactions. The photochemical addition of trifluoroiodomethane to vinyl fluoride (reactant ratio of 2:1) gave a product fraction (90%) boiling at 85-88°. Dehydroiodination of this fraction with powdered potassium hydroxide produced a mixture of three olefins (75%) in the ratio 57:39:4, which were identified as trans-1,3,3,3-tetrafluoropropene (43%) (LXV), cis-1,3,3,3-tetrafluoropropene (29%) (LXVI), and 2,3,3,3-tetrafluoropropene (3%) (LXVII)^{respectively}.



(LXV)



(LXVI)



(LXVII)

The mixture of olefins was shown by chemical analysis and by a molecular weight determination to have

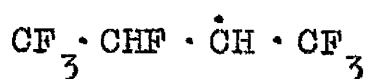
the empirical formula $C_3H_2F_4$. The olefins were separated, and olefin (LXVII) was identified by its i.r. spectrum which was identical to that of an authentic sample¹⁵⁴. Olefins (LXV) and (LXVI) were distinguished by the vicinal H-F and H-H coupling constants in their n.m.r. spectra, since trans H-F and H-H coupling constants have been shown to be larger than the corresponding cis coupling constants^{141,142}. Thus, the trans-olefin showed a relatively small vicinal H-F ($J=14.8\text{c/s}$) and a large H-H coupling constant ($J=11.4\text{c/s}$), whilst the cis-olefin showed a relatively large H-F ($J=36.7\text{c/s}$) and a small H-H coupling constant ($J=5.6\text{c/s}$). The complete spectra are tabulated elsewhere (Page 183-4).

This olefin mixture was generally used for the addition reactions, although pure trans- and cis-olefins were separated, and used for small-scale addition reactions with trifluoroiodomethane. The presence of isomer (LXVII) in the olefin reactant mixture was considered not to effect the additions under consideration.

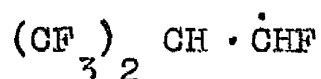
It is to be noted that the formation of olefin (LXVII) showed that bidirectional addition of trifluoroiodomethane to vinyl fluoride occurred, and indicated that the ratio of 1:1 adducts $CF_3 \cdot CH_2 \cdot CHF I : CF_3 \cdot CHF \cdot CH_2 I$ was of the order of 96:4; this is in agreement with previous investigations with this system^{132,154}.

II The Free-Radical Addition of Trifluoroiodomethane.

A complicating stereochemical factor must be considered in the addition of trifluoroiodomethane to 1,3,3,3-tetrafluoropropene. There are two possible intermediate radicals, (LXVlll) and (LXlX), formed by the initial addition of CF_3 radicals to the olefin.

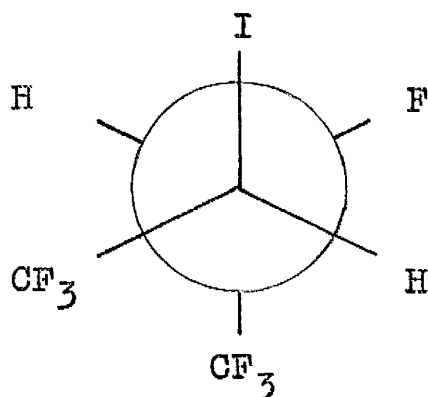


(LXVlll)

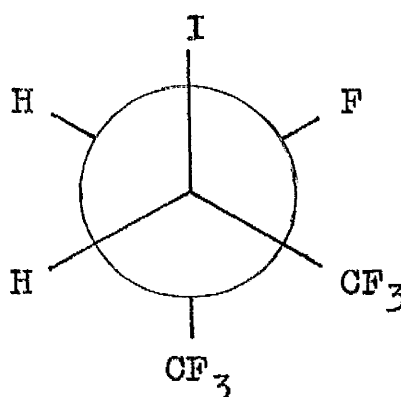


(LXlX)

The abstraction of an iodine atom by the intermediate (LXVlll) in the chain-transfer reaction then produces a compound containing two asymmetric carbon atoms; this compound is, therefore, capable of existing in two forms, threo (LXX) and erythro (LXXl), which would possess different properties.



(LXX)



(LXXl)

Intermediate (LXlX) leads only to one compound (LXXll).



A preliminary photochemically initiated experiment gave four major products 1,2,3, and 4 in the ratio 27:32:17:16 respectively. These were considered to be the expected 1:1 adducts, and so thorough structural determinations were carried out.

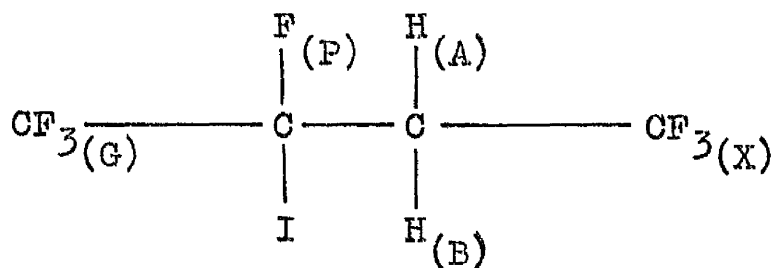
Identification of the products.

a) Product 1.

Chemical analysis and a molecular weight determination showed that this product was a 1:1 adduct.

i) ^{19}F and ^1H n.m.r. spectra.

^{19}F spectrum. External reference $\text{CF}_3 \cdot \text{COOH}$. Solvent Me_4Si .

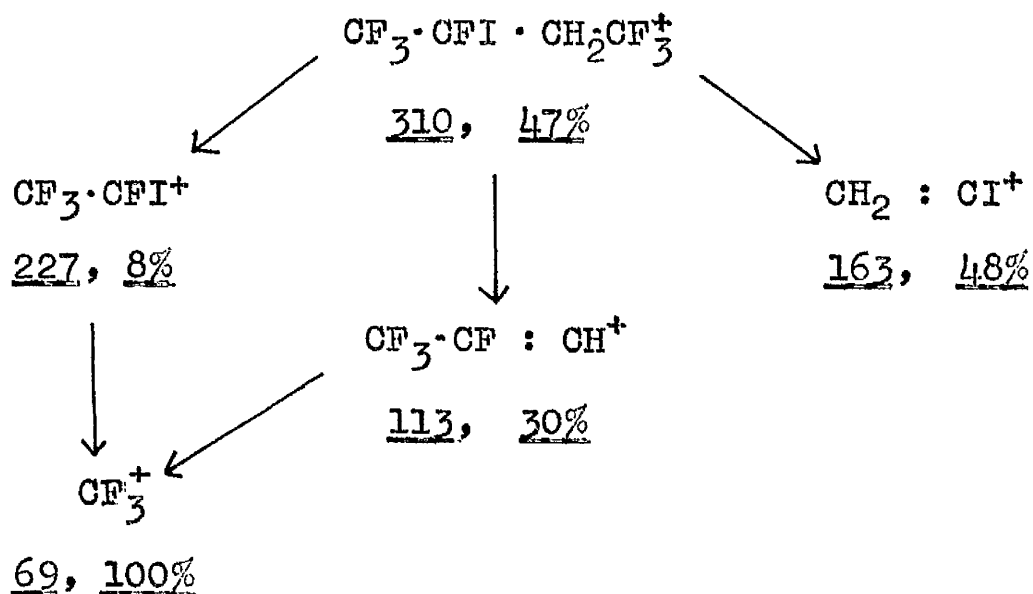


Band	Intensity	Chemical Shift(ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	-16.2	doublet of triplets of quartets	10.9 9.0 X-G=2.1	F _(X)
2	3	+3.0	doublet of quartets	G-P=11.4 G-X=2.1	F _(G)
3	1	+55.0	doublet of octets	15.8 11.3	F _(P)

The ^1H spectrum consists of a complex band system centred at ca. 7.00 τ which is interpreted as the AB portion of an ABPX₃-type spectrum (no coupling to F_(G) observed); $\underline{J}_{\text{A-B}}$ ca. 16c/s is as expected for a geminal H-H coupling constant, but outside the range for vicinal coupling constants ($\underline{J} < 9\text{c/s}$).

The ^{19}F spectrum is of the ABG₃PX₃-type, and shows the presence of two non-equivalent CF₃ groups and a F atom. The shifts of the nuclei are consistent with the proposed structure.

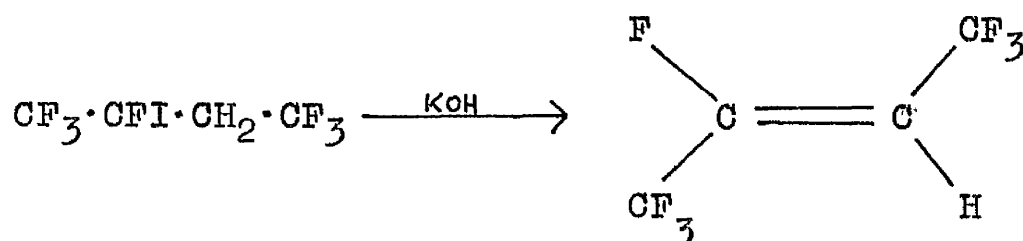
ii) Mass spectrum.



The peak corresponding to the ion $\text{CF}_3 \cdot \text{CFI}^+$ was not present in the spectra of the other three products. The complete spectrum is summarised in Table 34 (Page 203).

iii) Reaction with powdered potassium hydroxide.

Dehydroiodination gave trans-1,1,1,2,4,4,4-heptafluorobut-2-ene (84%) and an unknown product (2%). [The olefin was identified by its n.m.r. spectrum (Page 185); the H-F coupling constant (29.8 c/s) is in the expected region for a trans H-F coupling constant.]



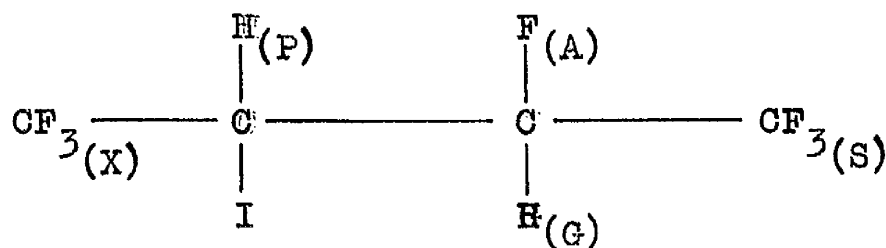
This evidence presents conclusive proof that product 1 has the structure $\text{CF}_3 \cdot \text{CFI} \cdot \text{CH}_2 \cdot \text{CF}_3$.

b) Product 2.

Chemical analysis and a molecular weight determination showed that this compound was also a 1:1 adduct.

i) ^{19}F and ^1H n.m.r. spectra.

^{19}F spectrum. External reference $\text{CF}_3 \cdot \text{COOH}$. No solvent.



Band	Intensity	Chemical Shift (ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	-9.6	doublet of doublets of quartets	X-P=8.2 X-A=6.4 X-S=0.9	$\text{F}(\text{X})$
2	3	-0.6	doublet of doublets of quartets	S-A=11.9 S-G=5.8 S-X=0.9	$\text{F}(\text{S})$
3	1	+115.6	doublet of doublets of quartets of quartets	A-G=47.5 A-P=24.4 A-S=11.9 A-X=6.4	$\text{F}(\text{A})$

¹H spectrum. Internal reference CF₃·COOH. No solvent.

Band	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	5.35	doublet of quartets of doublets	G-A=47.5 G-S=5.8 G-P=1.8	H _(G)
2	5.48	doublet of quartets of doublets	P-A=24.4 P-X=8.2 P-G=1.8	H _(P)

No coupling is observed between F_(X) and H_(G), and F_(S) and H_(P). The coupling constants and chemical shifts can fit only the proposed structure, and the n.m.r. spectrum is further discussed later (Page 109).

ii) Mass Spectrum.

The only peak helpful for structural determination was at m/e 209 (6%), corresponding to the ion CF₃·CHI⁺. The complete spectrum is summarised in Table 32 (Page 201).

iii) Reaction with powdered potassium hydroxide.

Dehydroiodination was accompanied by dehydrofluorination, and in a typical experiment

the products were hexafluorobut-2-yne (29%) and trans -1,1,1,2,4,4,4-heptafluorobut-2-ene (69%).



This reaction shows that the two CF_3 groups are situated on different carbon atoms, but no evidence as to whether this is the erythro- or threo-isomer is obtained from this reaction, which is discussed later (Page 114).

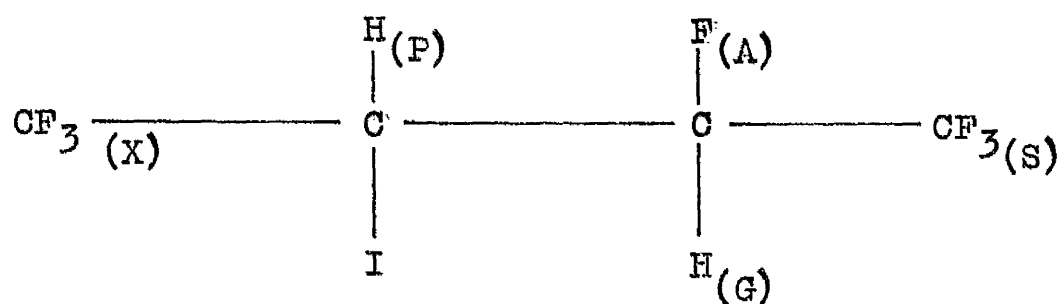
The above evidence presents conclusive proof that product 2 is one of the isomers of structure $\text{CF}_3 \cdot \text{CHF} \cdot \text{CHI} \cdot \text{CF}_3$, and this isomer is labelled isomer A in the following discussion (in the experimental section it is labelled isomer I).

c) Product 3.

Chemical analysis and a molecular weight determination showed that this product was a third 1:1 adduct.

i) ^{19}F and ^1H n.m.r. spectra.

¹⁹F spectrum. External reference CF₃·COOH. No Solvent.



Band	Intensity	Chemical Shift(p.p.m.)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	-12.6	doublet of doublets of quartets	X-A=15.0 X-P=7.6 X-S=2.8	F(X)
2	3	-2.2	doublet of doublets of quartets	S-A=8.4 S-G=5.4 S-X=2.8	F(S)
3	1	+111.6	doublet of quartets of doublets of quartets	A-G=44.3 A-X =15.0 A-P=11.3 A-S=8.4	F(A)

^1H spectrum. Internal reference Me_4Si . No solvent.

Band	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	5.04	doublet of doublets of quartets	G-A=44.3 G-P=7.7 G-S=5.4	$\text{H}_{(\text{G})}$
2	5.44	doublet of doublets of quartets	P-A=11.3 P-G=7.7 P-X=7.6	$\text{H}_{(\text{P})}$

No coupling is observed between $\text{F}_{(\text{X})}$ and $\text{H}_{(\text{G})}$, and $\text{F}_{(\text{S})}$ and $\text{H}_{(\text{P})}$. The large $J_{\text{A-X}}$ is a surprising feature of the spectrum, but the general coupling constants can only fit the proposed structure; this is discussed later (Page 109).

ii) Mass spectrum.

The only peak helpful for structural determination was at m/e 209 (6%), corresponding to the ion $\text{CF}_3\cdot\text{CHI}^+$ (see Table 32, Page 201).

iii) Reaction with powdered potassium hydroxide.

Dehydroiodination was accompanied by dehydrofluorination and the products, hexafluorobut-2-yne (56%) and trans-1,1,1,2,4,4,4-heptafluorobut-2-ene (7%),

formed in a typical experiment, were the same as those obtained from Product 2.

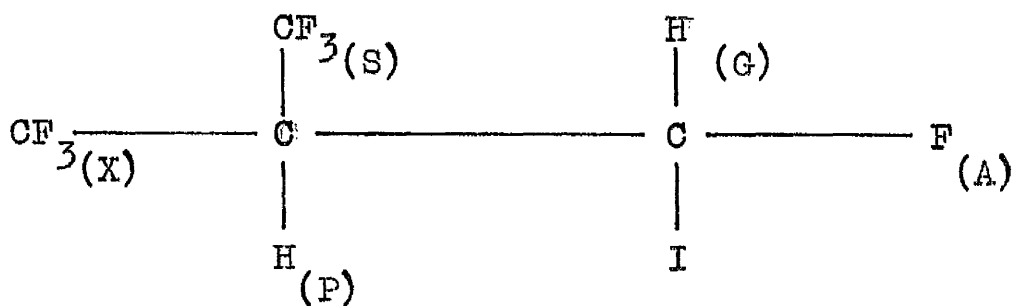
The above evidence presents conclusive proof that this product is the second isomer of structure $\text{CF}_3 \cdot \text{CHF} \cdot \text{CHI} \cdot \text{CF}_3$, and in the following discussion it is labelled isomer B (in the experimental section it is labelled isomer II).

d) Product 4.

Chemical analysis and a molecular weight determination showed that this product was the fourth 1:1 adduct.

i) ^{19}F and ^1H n.m.r. spectra.

^{19}F spectrum. External reference $\text{CF}_3 \cdot \text{COOH}$. No solvent.



Band	Intensity	Chemical Shift (ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	-12.2	doublet of quartets of doublets of doublets	X-A=11.4 X-S=9.4 X-P=7.5 X-G=0.9	F _(X)
2	3	-11.0	quartet of doublets of doublets	S-X=9.4 S-P=7.7 S-A=6.8	F _(S)
3	1	+80.6	doublet of doublets of quartets of quartets	A-G=46.6 A-P=20.0 A-X=11.4 A-S=6.8	F _(A)

¹H Spectrum. Internal reference Me₄Si. No solvent.

Band	Intensity	Chemical Shift (τ)	Multiplet Structure	Coupling J(c/s)	Assignment
1	1	2.82	doublet of doublets of quartets	G-A=46.6 G-P=1.8 G-X=0.9	H _(G)
2	1	6.40	doublet of heptets of doublets	P-A=20.0 P-SX=7.2 P-G=1.8	H _(P)

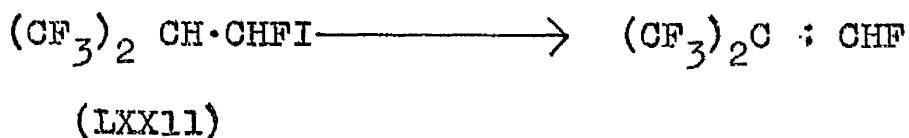
The two CF_3 groups are shown to be equivalent towards $\text{H}_{(\text{P})}$, and the reasonably large splitting suggests the grouping $(\text{CF}_3)_2\text{CH}-$; $\underline{J}_{\text{G-P}} = 1.8 \text{ c/s}$ is within the range for vicinal hydrogen atoms.

ii) Mass spectrum.

A strong band at m/e 159 (59%), corresponding to the ion CHF_2^+ , was obtained, which was not present in the mass spectra of the other three products (see Table 33, Page 202).

iii) Reaction with powdered potassium hydroxide.

Dehydroiodination gave 1,3,3,3-tetrafluoro-2-trifluoromethylpropene (95%), which could only be derived from isomer (LXX11).

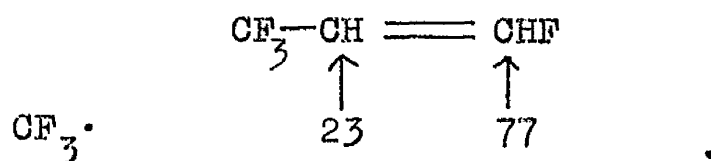


The olefin was identified by n.m.r. spectroscopy ($\underline{J}_{\text{H-F}} = 72.0 \text{ c/s}$ is in the expected region for a geminal H-F coupling constant) (see Page 187), and by a comparison of its b.p. with that reported in the literature¹⁵⁵; they were identical.

The above evidence is conclusive proof that this product has the structure $(\text{CF}_3)_2\text{CH}\cdot\text{CHF}\cdot\text{I}$.

Results and discussion.

The results of this investigation are summarised in Table 13. The addition is shown to proceed through both possible intermediates (LXVIII) and (LXIX), and the average ratio of attack at the two ends of the double bond in the olefin was found to be:-



At first sight, the addition of the $\text{CF}_3\cdot$ radical to the cis-, or the trans-olefin, appears to be reversible, since a mixture of both olefins was formed in both cases. However, the irradiation of the trans-olefin alone gave the cis-olefin (11%), which shows that cis-trans isomerisation, a well known phenomenon¹⁵⁶, occurs with this olefin alone. In view of this observed isomerisation, it is not possible to say whether reversible addition of the $\text{CF}_3\cdot$ radical to the olefin does, in fact, occur.

The olefin mixture in reactions 1 and 2 (Table 13) contained 2,3,3,3-tetrafluoropropene (4%).

Table 13. The Photochemical Addition of Trifluoroiodomethane to

Cis- and Trans-1,3,3,3-tetrafluoropropene.

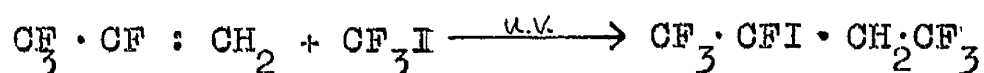
	Olefin ratio		Irradiation Time (hr.)	% Total Olefin Conversion	% Olefin recovered		% 1:1 adducts	Ratio of 1:1 adducts		
	Trans	Cis			Trans	Cis		A	B	(LXXII)
1*	59	41	30	5	96	93	100	49	26	25
2*	59	41	140	21	90	64	82	51	28	21
3	67	33	150	-	-	-	-	45	27	28
4	100	0	140	43	57	†	49	55	23	22
5	0	100	148	42	‡	58	32	61	24	15

* Olefin mixture contained 2,3,3,3-tetrafluoropropene (4%).

† The other major product was cis-1,3,3,3-tetrafluoropropene (51%).

‡ The other major product was trans-1,3,3,3-tetrafluoropropene (33%).

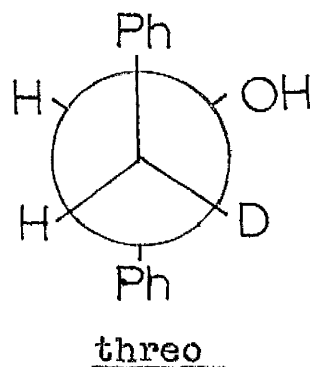
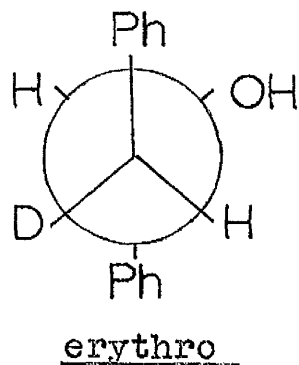
This olefin was consumed to an extent of 52% and 100% in reactions 1 and 2 respectively compared to 5% and 20% conversion of the 1,3,3,3-tetrafluoropropene; the yield of the 1:1 adduct was quantitative in both cases. Thus, this olefin is shown to react faster than the isomeric 1,3,3,3-tetrafluoropropenes.



An interesting feature of these experiments was the formation of both the erythro and threo forms of 1,1,1,2,4,4,4-heptafluoro-3-iodobutane. Unfortunately, it was not possible to determine definitely which isomer was the threo form and which the erythro form. The diastereomer produced in larger yield will be referred to as isomer A, and isomer B will be the minor diastereomer.

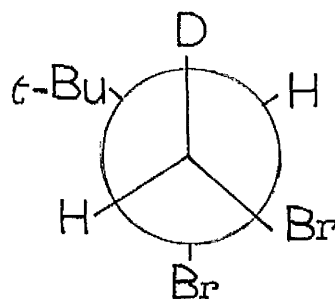
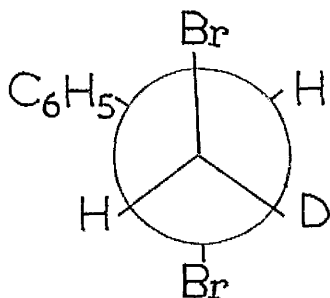
Although, it was not found possible to determine the absolute structures of the two diastereomers from their n.m.r. spectra, it is interesting to consider these spectra. In the n.m.r. studies^{157,158} on 2-deutero-1,2-diphenylethan-1-ol, the predominant conformation was shown to be that with the two bulky phenyl groups trans. The erythro and threo forms were distinguished by the large H-H coupling constant ($J=8.4$, trans) in the former as compared with the smaller coupling constant ($J=4.9$, gauche)

in the latter.



However, since the largest groups prefer a trans orientation, the replacement of the hydroxyl group by a bulky group may cause the preferred conformation to be with this new group trans to phenyl¹⁵⁸.

The preferred conformations of erythro- $\text{C}_6\text{H}_5\text{CHBr}\cdot\text{-CHDBr}$ and threo-(CH_3)₃C·CHBr·CHDBr are shown below.



In the latter compound, the two bulky groups are in a preferred trans conformation, but in the former this is not the case presumably because electrostatic (dipole - dipole) repulsions between gauche bromines are greater than are steric repulsions between gauche bromine-phenyl¹⁵⁹. It appears, therefore, that both electrostatic and steric factors are important in deciding the preferred conformation.

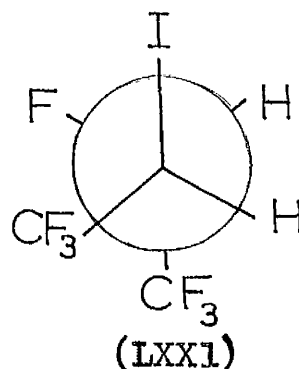
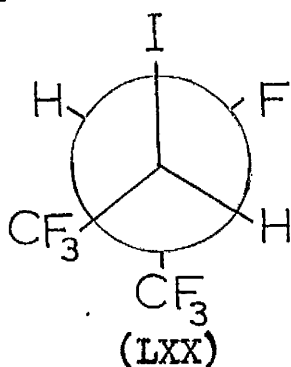
In the present work, there are two preferred conformations, on steric grounds, which isomers A and B can adopt. These are with the CF_3 group on C_1 either trans to the CF_3 group, or trans to the iodine atom on C_2 . It is not possible on the evidence available to predict which would give the preferred conformer on steric and electrostatic grounds. The observed relevant coupling constants for the two diastereomers are summarised in Table 14.

Table 14. Coupling Constant Assignment.

<div><div><div><div><div><div>CF₃</div><div></div><div></div><div></div><div></div></div><div><div></div><div>H(A)</div><div></div><div>C</div><div></div><div>F(C)</div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><div></div><div></div><div></div><div></div><div></div></div><div><d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The CF_3 group and the fluorine atom in isomer A must be gauche since the fluorine atom is shown, by the large coupling constant, to be trans to the hydrogen atom. In isomer B, the coupling constant between CF_3 group and the fluorine atom is shown to be over twice as large as that for the gauche coupling in isomer A, which would suggest that the two groups are stereochemically different in isomer B, i.e., trans. This is, of course, an assumption since no work on such systems has been done before.

Therefore, the only configuration of isomer B which then fits the n.m.r. spectrum is conformer (LXX), the threo form.



Isomer A must then be the erythro form of conformation (LXXI), and the CF_3 group is trans to the iodine atom rather than trans to the other CF_3 group.

The results given in Table 13 show that the two diastereomers are formed in the ratio A:B of approx. 2:1, independent of whether the cis- or trans-olefin is used.

Several similar observations have been reported in the literature. Fredericks and Tedder¹⁶⁰ reported that the chlorination of 2-chlorobutane gave meso- and dl-2,3-dichlorobutane in a ratio of 2.5:1. The mechanism proceeded by way of hydrogen abstraction, followed by the reaction of the chlorobutyl radical with molecular chlorine.

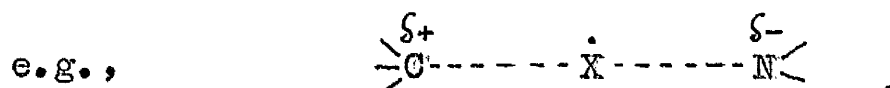


The peroxide initiated reaction of N-bromosuccinimide with bibenzyl or α -bromobibenzyl in carbon tetrachloride¹⁶¹ afforded meso- and dl- α, α' -dibromosuccinimide in a ratio of 11:1. The additions of thiolacetic acid and hydrogen bromide to cis- or trans-2-chlorobut-2-ene at -20° ¹⁶² were shown to give the same ratios of diastereomers; thiolacetic acid addition gave a ratio threo: erythro of 9:1, whilst hydrogen bromide addition gave a ratio of 2.3:1.

The addition of hydrogen bromide to cis- and trans-2-bromobut-2-ene³⁵ at 25° gave, in both cases, dl- and meso-2,3-dibromobutane in a ratio of 3:1 respectively; a similar ratio of the diastereomers was

obtained with deuterium bromide. However, at low temperatures (-78°), the last two additions were shown to be stereospecifically trans (See Page 12). Similar observations of stereospecificity have been made for cyclic systems^{163,164}.

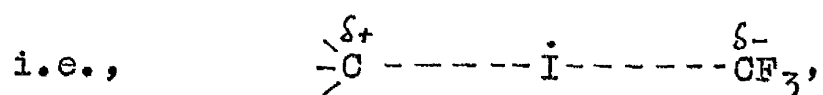
These additions, in which one diastereomer is formed in preference to the other, have been explained in terms of dipole-dipole and steric effects in the transition state of the chain-transfer reaction. Greene, Remers, and Wilson¹⁶¹ have pointed out that the negative ρ -values, observed in radical reactions at the benzyl positions of *p*-substituted toluenes, indicate considerable ionic character in the transition state, in which the negative end of the dipole is directed away from the site of attack,



Consider the transition state in the chain transfer reaction



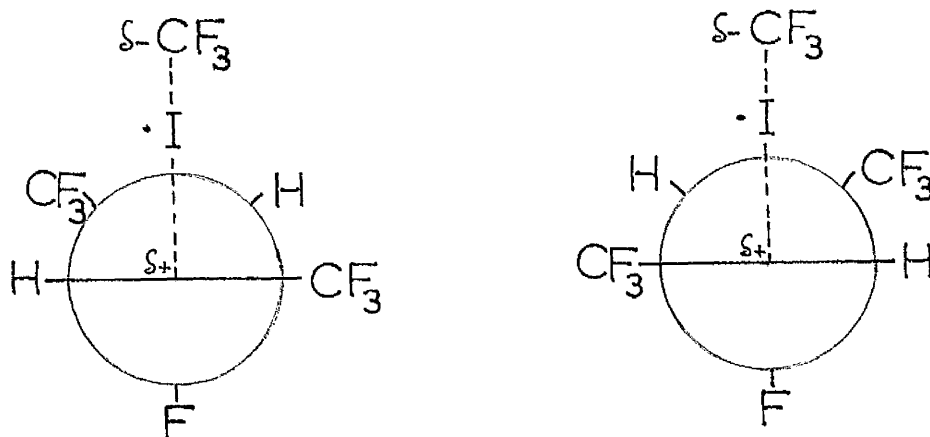
If such a dipole is occurring, it should be with the negative pole on the CF_3 group of the trifluoriodomethane,



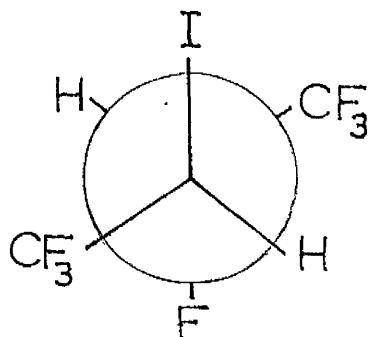
and should be preferentially oriented away from the largest permanent negative dipole of the saturated carbon atom.

This can be realised only if the trifluoriodomethane preferentially approaches the radical centre trans to the most negative group on the saturated carbon atom, i.e., the fluorine atom.

At the same time, steric interactions should be minimised. The larger group on the radical carbon atom, i.e., the CF_3 group, should be positioned in the larger remaining steric "hole" afforded by groups on the saturated carbon, i.e., between the hydrogen and fluorine atoms.



These transition states would lead to a preferred erythro diastereomer.



The argument outlined above suggests that the major isomer A is the erythro form and isomer B is the threo form, which is in agreement with the results obtained from the n.m.r. studies previously discussed.

Elimination Reactions of the Two Diastereomers.

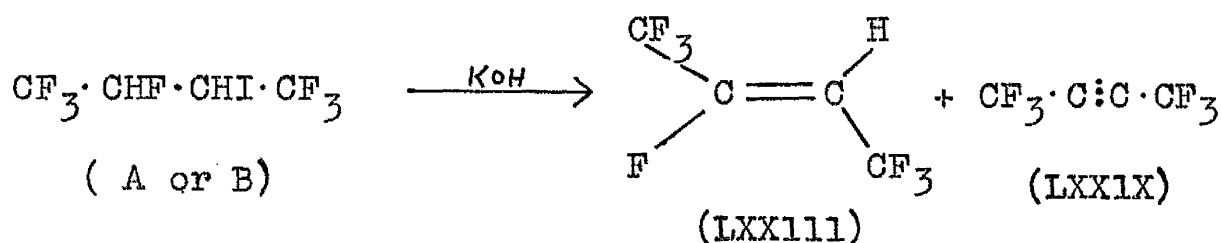
Results of the elimination reactions carried out with powdered potassium hydroxide are summarised in Table 15, and have been mentioned in the section devoted to the identification of the 1:1 adducts.

Table 15. Reaction of the Two Diastereomers A and B
with Potassium Hydroxide in vacuo.

		% $\text{CF}_3 \cdot \text{C} \equiv \text{C} \cdot \text{CF}_3$	% $\text{CF}_3 \cdot \text{CH} : \text{CF} \cdot \text{CF}_3$ (<u>trans</u>)	% $\text{CF}_3 \cdot \text{CH} : \text{CF} \cdot \text{CF}_3$ (<u>cis</u>)
isomer A	1	29	69	-
	2	28	70	-
	3	83	13	-
	* 4	63	4	4
isomer B	1	56	7	-
	2	74	8	2

* Aqueous KOH solution (3M) used.

Both the diastereomers A and B yield the trans-olefin (LXX111) derived from dehydroiodination and the alkyne (LXX1X) produced by a further dehydrofluorination.

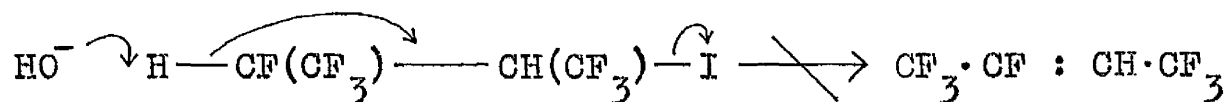


There are four possible mechanisms by which such eliminations can occur, the E1, E2, E1cB, and E2cB mechanisms. The E1 mechanism, involving an intermediate

carbonium ion, is considered to be very unlikely under the conditions used.

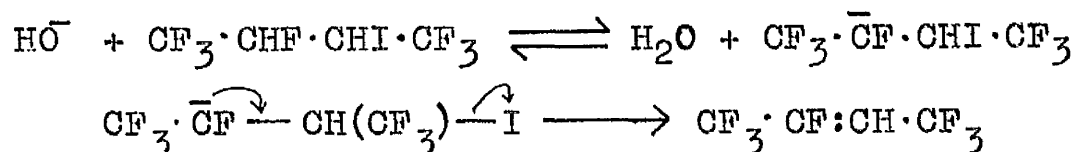
E2 mechanism.¹⁶⁵

With the E2 mechanism, the two diastereomers would be expected to give different olefins, since a trans stereospecificity is observed in the E2 mechanism^{166,167}. However, the cis-olefin is not formed as a major product from either of the diastereomers, and so the E2 mechanism is not occurring.

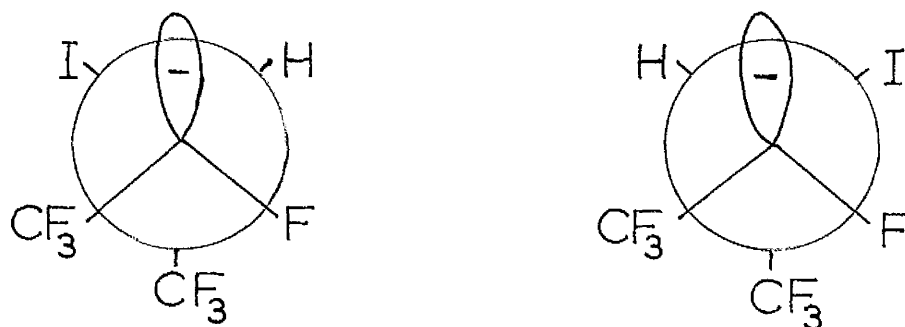


ElcB and E2cB mechanisms.¹⁶⁸

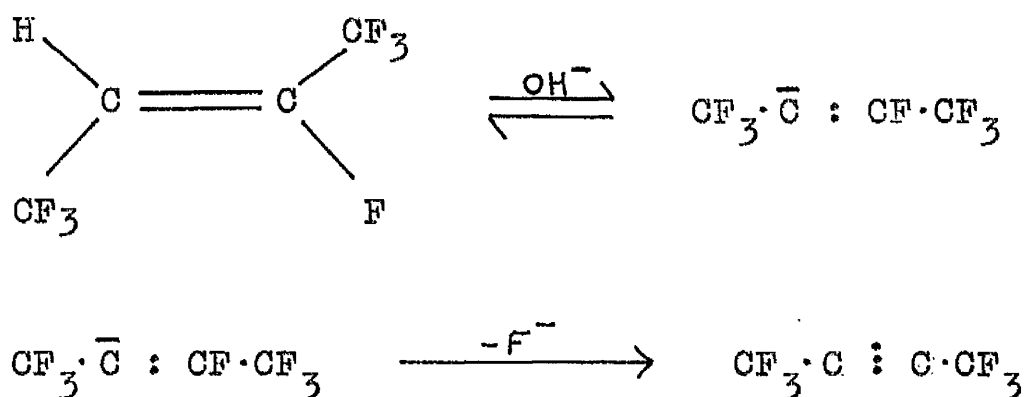
~~ElcB and E2cB mechanisms.~~ Since only one major olefin is formed from both diastereomers, the mechanistic path leading to the olefin must involve the finite existence of an intermediate carbanion which would allow rotation to occur about the carbon-carbon bond. Such a scheme can be accounted for by either the ElcB or the E2cB mechanisms (where the molecularity refers to the mode of decomposition of the conjugated base). The ElcB mechanism is depicted below.



The preferred formation of the trans-olefin can then be accounted for by the loss of iodine from the intermediates to give presumably the thermodynamically more stable olefin.

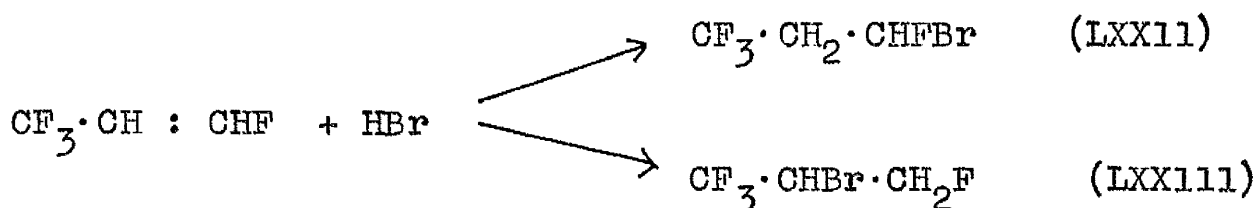


Dehydrofluorination of the trans-olefin would be expected to go by a E1cB mechanism, since such a mechanism is generally accepted^{169,170} in eliminations leading to alkynes, although recently a synchronous process has also been proposed.¹⁷¹



III Free-Radical Addition of Hydrogen Bromide.

The results obtained from the addition of trifluoroiodomethane to 1,3,3,3-tetrafluoropropene indicate that bidirectional addition of hydrogen bromide to this olefin should also occur, and a preponderance of compound (LXX11) is to be expected.



No reaction occurred when the reactants were left in the dark (200 hr.); this showed that the possibility of ionic addition occurring in the photochemical reactions was small.

A preliminary photochemical addition gave four major products 1,2,3, and 4 in the ratio 31:19:27:10 respectively. Products 1 and 2 were considered to be the 1:1 adducts, and products 3 and 4, with longer g.l.c. retention times, were considered to be the two diastereomeric dibromides.

Identification of the four major products.

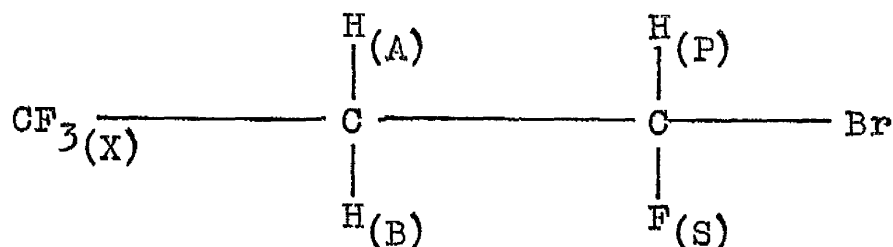
a) Product 1.

Chemical analysis and a molecular weight

determination showed that this product was a 1:1 adduct.

i) N.m.r. Spectra.

^{19}F spectrum. External reference $\text{CF}_3\cdot\text{COOH}$. No solvent.



Band	Intensity	Chemical Shift (p.p.m.)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	-12.6	triplet of doublets	9.8 X-S=7.5	$\text{F}(\text{X})$
2	1	+59.6	doublet of doublets of doublets of quartets	S-P=50.5 25.0 15.1 S-X=7.5	$\text{F}(\text{S})$

^1H spectrum. Internal reference Me_4Si . No solvent.

Band	Intensity	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	1	3.38	doublet of doublets of doublets	P-S=50.5 7.2 4.0	$\text{H}(\text{P})$
2	2	7.08	complex	-	$\text{H}(\text{A}) \quad \text{H}(\text{B})$

The spectrum is of the ABPSX₃-type, and the treatment shown above is only approximate. The large coupling constant between F(S) and H(P) suggests that they are geminal in the grouping -CHFX (where X is not H or F). The relatively large splitting (9.8 c/s) between F(X) and the non-equivalent H(A) and H(B) suggests the grouping CF₃·CH₂⁻. The general form of the spectrum is that expected for the proposed structure.

ii) Mass Spectrum.

The spectrum contained a parent peak at m/e 194 (8%), a peak at m/e 115 (100%) which corresponds to the loss of bromine from the parent ion, and a peak at m/e 51 (56%) assigned to the rearranged ion CHF₂⁺; these were of no help in elucidating the structure.

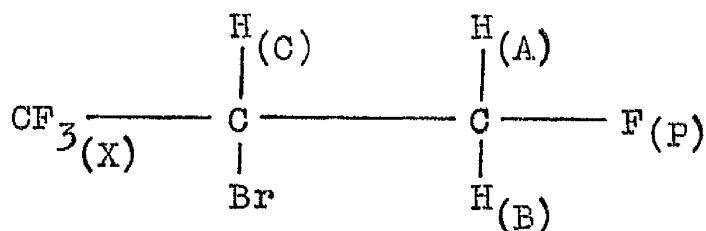
The n.m.r. evidence above can leave no doubt that product 1 is a 1:1 adduct of structure CF₃·CH₂·CHFBr.

b) Product 2.

Chemical analysis and a molecular weight determination showed that this product was also a 1:1 adduct.

i) ¹⁹F and ¹H n.m.r. spectra.

^{19}F spectrum. External reference $\text{CF}_3\cdot\text{COOH}$. No solvent.

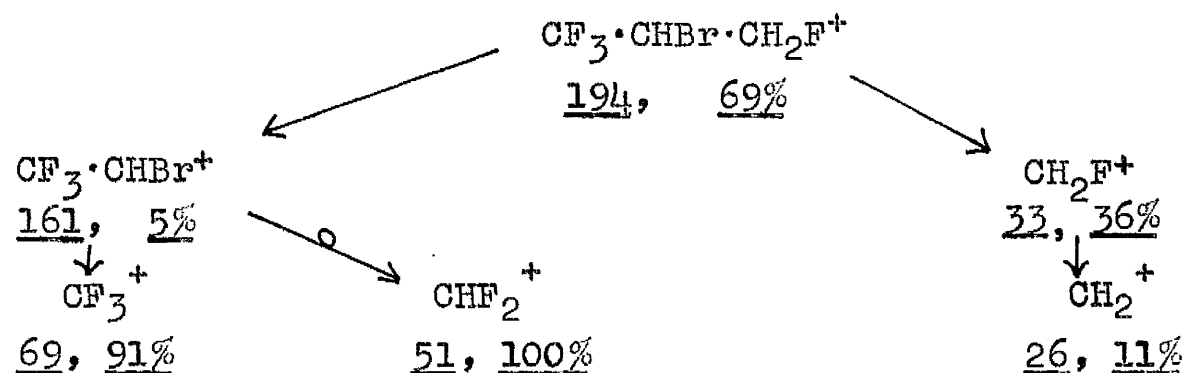


Band	Intensity	Chemical Shift (p.p.m.)	Multiplet Splitting	Coupling J (c/s)	Assignment
1	3	-6.8	triplet (broad)	7.6	F(X)
2	1	+142.0	triplet (complex)	48.0	F(P)

The ^1H spectrum showed a complex region between 4.96 and 6.12 τ .

The spectrum fits an ABCPX_3 -system, and the treatment above is only approximate. However, the large splitting (48 c/s) of F(P) into a triplet shows that the group CH_2F is present.

ii) Mass spectrum.



The breakdown pattern shown above is consistent with the proposed structure. The major peak, corresponding to the ion CHF_2^+ , is caused by rearrangement, as in the spectrum of product 1.

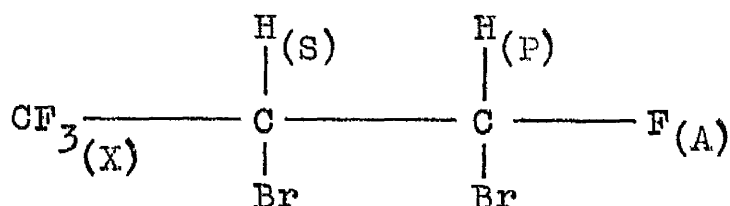
This evidence presents conclusive proof that product 2 is a 1:1 adduct of structure $\text{CF}_3 \cdot \text{CHBr} \cdot \text{CH}_2\text{F}$.

c) Product 3.

Chemical analysis and a molecular weight determination showed that this product was an olefin dibromide.

i) ^{19}F and ^1H n.m.r. spectra.

^{19}F spectrum. External reference $\text{CF}_3 \cdot \text{COOH}$. No solvent.



Band	Intensity	Chemical Shift (ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	-10.0	doublet of doublets	X-A=11.3 X-S=6.9	F(X)
2	1	+60.2	doublet of quartets of doublets	A-P=48.5 A-X=11.3 A-S=7.9	F(A)

^1H spectrum. Internal reference Me_4Si . No solvent.

Band	Intensity	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	1	3.47	doublet of doublets	P-A=48.5 P-S=5.5	$\text{H}(\text{P})$
2	1	5.50	doublet of quartets of doublets	S-A=7.9 S-X=6.9 S-P=5.5	$\text{H}(\text{S})$

The chemical shifts and the coupling constants can only fit the proposed structure.

ii) Mass spectrum.

A weak parent peak at m/e 272 (4%), and a strong peak at m/e 193 (100%), which corresponds to the loss of bromine from the parent ion, were the only helpful indications for structural determination. A peak at m/e 51 (59%), corresponding to the ion CHF_2^+ , was also present.

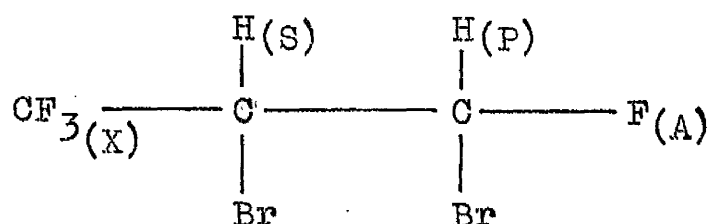
The above evidence, especially the n.m.r. spectra, presents conclusive proof that product 3 is one of the isomers of structure $\text{CF}_3 \cdot \text{CHBr} \cdot \text{CHFBr}$. The isomer is labelled isomer E in the following discussion (in the experimental section, it is labelled isomer I).

d) Product 4.

Chemical analysis and a molecular weight determination showed that this product was also an olefin dibromide.

i) ^{19}F and ^1H n.m.r. spectra.

^{19}F spectrum. External reference $\text{CF}_3\cdot\text{COOH}$. Solvent Me_4Si .



Band	Intensity	Chemical Shift (ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	-9.2	doublet of doublets	X-A=7.9 X-S=6.8	$\text{F}(\text{X})$
2	1	+65.6	doublet of doublets of quartets	A-P=49.4 A-S=19.8 A-X=7.9	$\text{F}(\text{A})$

¹H spectrum. Internal reference and solvent Me₄Si.

Band	Intensity	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	1	3.35	doublet of doublets	P-A=49.4 P-S=2.8	H _(P)
2	1	5.62	doublet of quartets of doublets	S-A=19.8 S-X=6.8 S-P=2.8	H _(S)

The chemical shifts and coupling constants can only fit the proposed structure.

ii) Mass spectrum.

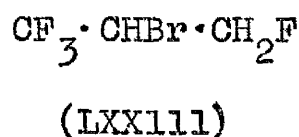
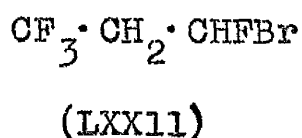
It was almost identical to that obtained for product 3.

The above evidence presents conclusive proof that product 4 is the other isomer of structure CF₃·CHBr·CHFBr. This isomer is labelled isomer F in the following discussion (in the experimental section, it is labelled isomer II).

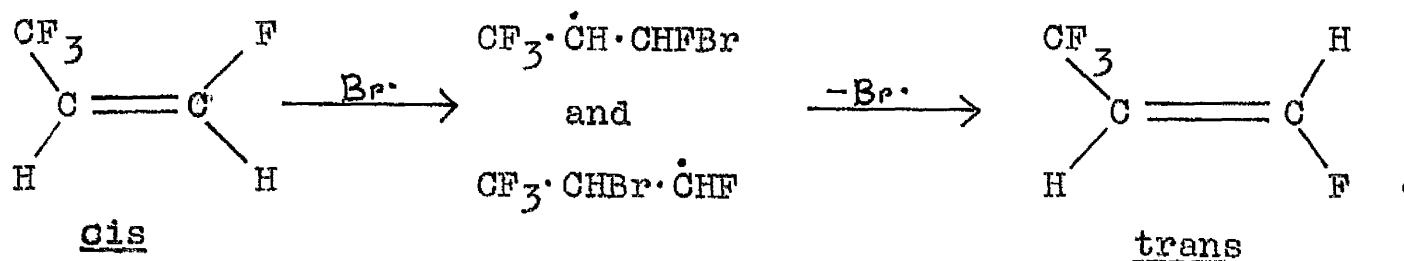
Results and Discussion.

The results of the photochemical investigation are summarised in Table 16.

The ratios of the 1:1 adducts obtained are unsatisfactory as they vary from a ratio (LXX11):(LXX111) of 62:38 to 42:58. The average ratio for the four experiments investigated is 52:48.



The reversibility of bromine atom addition is illustrated in these reactions. The isomeric 1,3,3,3-tetrafluoropropenes were present in an initial reactant ratio trans:cis of 57:41. The recovered olefins from reactions 1 and 4, involving only a 4% conversion, were shown to have a trans:cis ratio of 88:12. The cis-olefin is rapidly converted to the trans-olefin, probably by the following mechanism:



Although cis-trans isomerisation of the olefins on irradiation alone does occur, this is not as rapid

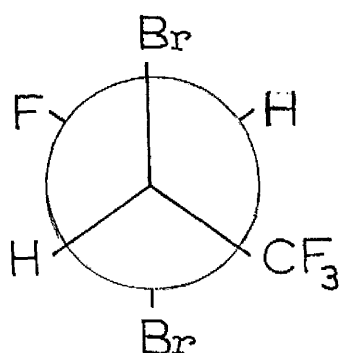
Table 16. The photochemical addition of Hydrogen Bromide to a Mixture of
Mixture of Cis- and Trans-1,3,3,3-tetrafluoropropene.

	Irradiation Period (hr.)	% Olefin Conversion	% 1:1 Adducts	Ratio of 1:1 Adducts		% Olefin dibromides	Ratio of Dibromides	
				(LXXII)	(LXXIII)		E	F
1	7	4	49	62	38	38	73	27
2	26	37	54	50	50	35	-	-
3	72	100	26	54	46	62	63	37
⁺ 4	16	4	44	42	58	11	86	14

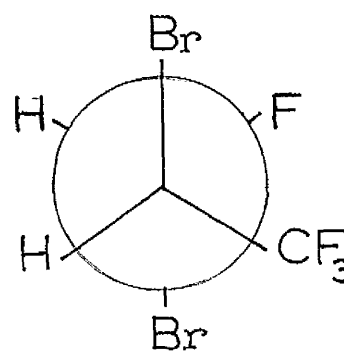
⁺ In the presence of silver powder.

as the isomerisation observed under similar irradiation conditions with hydrogen bromide present.

The addition reaction appears to be slow, and so molecules of bromine have time to form and these can take part in the chain-transfer step. This would lead to the production of the two diastereomers **E** and **F**.

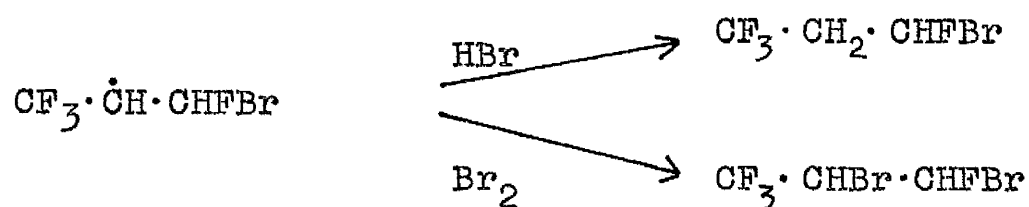


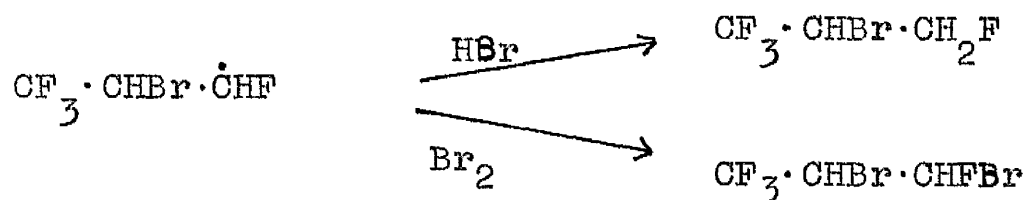
erythro
(**E** or **F**)



threo
(**F** or **E**)

The production of these dibromides causes the 1:1 adduct ratio to lose much of its significance, since both the 1:1 adducts and the dibromides are formed via the same intermediates.





The addition of silver powder, in an attempt to diminish the concentration of bromine molecules formed during the reaction, in order to obtain a more accurate 1:1 adduct ratio, met with but partial success. Not only did the silver powder abstract bromine molecules, but it stopped the addition reaction because it also reacted with bromine atoms. The yield of the olefin dibromides compared to the yield of the 1:1 adducts was, however, greatly reduced (reaction 4, Table 16.).

The ratio of the two dibromides formed from these additions also varies considerably but the average ratio E:F is approximately 3:1. It was expected that the free-radical addition of bromine to the same cis/trans mixture of olefins would give a similar ratio of the two diastereomers. In fact, the u.v. initiated addition (110 hr.) of bromine gave a ratio E:F of 1:2, contrary to that expected.

The possibility of ionic addition occurring together with radical addition must also be considered, as briefly mentioned earlier. If some ionic addition is occurring in the addition of bromine then

the different diastereomer ratio can be accounted for. Since the ionic addition of bromine is considered to be trans, and since the trans-olefin is the major component of the reaction mixture, then the major diastereomer F might be expected to be the erythro form, if ionic addition does occur.

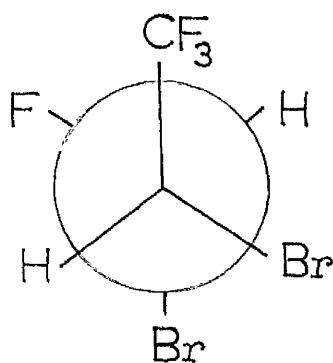
The relevant coupling constants in the n.m.r. spectra of the two diastereomers are listed in Table 17.

Table 17. Coupling Constant Assignment.

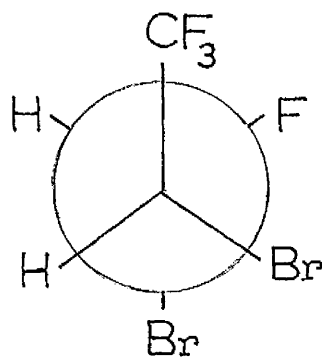
$ \begin{array}{c} \text{H(C)} \qquad \qquad \text{H(B)} \\ \qquad \qquad \quad \\ \text{CF}_3\text{(D)} - \text{C} - \text{C} - \text{F(A)} \\ \qquad \qquad \quad \\ \text{Br} \qquad \qquad \quad \text{Br} \end{array} $				
Coupling J (c/s)	Isomer E		Isomer F	
	Value	Inference	Value	Inference.
C - B	5.5	trans	2.8	gauche
A - C	7.9	gauche	19.8	trans
A - D	11.3	-	7.9	gauche

The CF_3 group and the fluorine atom in isomer F must be gauche, since the fluorine atom is shown, by the large coupling constant, to be trans to the hydrogen atom. In isomer E, the coupling constant between the CF_3 group

and the fluorine atom is shown to be 1.4 times as large as that for the gauche coupling in isomer F; this difference is only small and suggests that the two groups are stereochemically similar in isomer E, i.e., gauche; this is, of course, an assumption. If the CF_3 group and the fluorine atom are, in fact, gauche in isomer E, then this isomer is the threo configuration, and isomer F will be the erythro configuration.



threo
(isomer E)

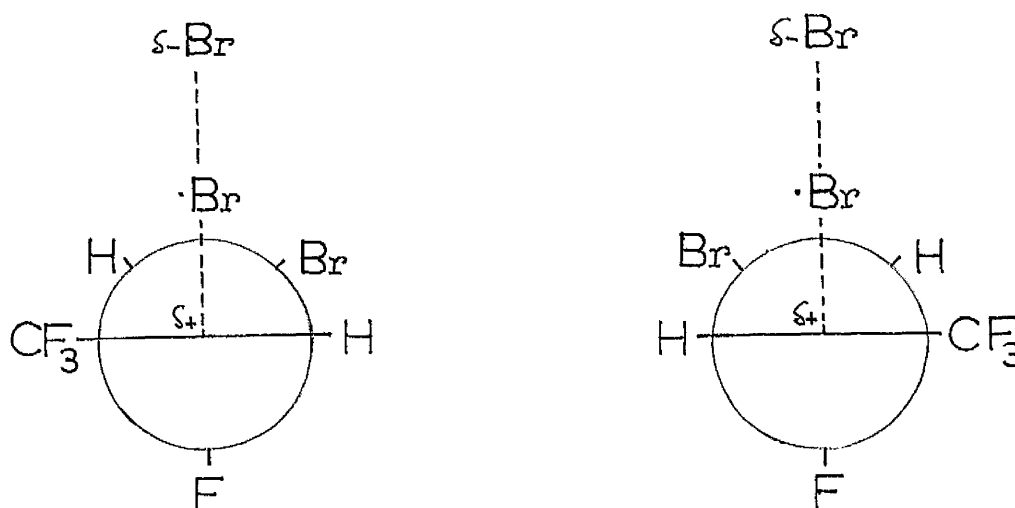


erythro
(isomer F)

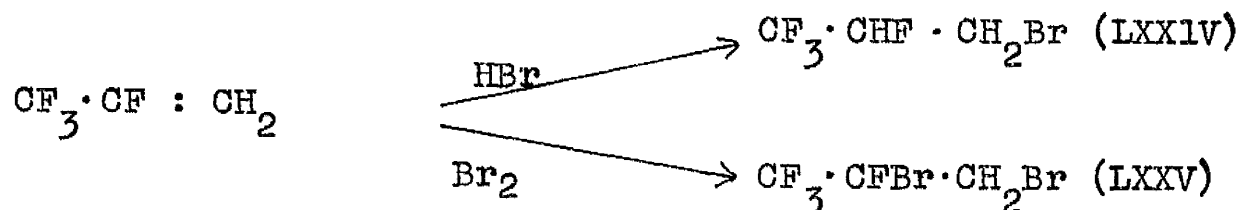
If isomer F is the erythro form, then it seems probable that ionic addition is the main reaction which occurred in the attempted free-radical addition of bromine to this olefin.

The preferred free-radical formation of isomer E (if it is the threo form) can be explained in the same terms of dipole-dipole and steric effects as those

employed to explain the preferred erythro configuration in the trifluoroiodomethane addition. The preferred conformation of the transition state of the chain-transfer reaction (shown below) will lead to the threo configuration.



In the reactions reported in Table 16, the olefins used were contaminated with 2,3,3,3-tetrafluoropropene (4%). This olefin would be expected to give the products (LXXIV) and (LXXV) in a similar manner to the 1,3,3,3-tetrafluoropropenes.



In reactions 1 and 4, where only a 4% conversion of the

1,3,3,3-tetrafluoropropene was obtained, 2,3,3,3-tetrafluoropropene was consumed to an extent of about 50%. The products obtained from these two reactions would be expected to contain about 30% of compounds (LXXIV) and (LXXV). However, a g.l.c. examination of these products gave only peaks which could be accounted for as products from 1,3,3,3-tetrafluoropropene except that the g.l.c. peak corresponding to the 1:1 adduct (LXXIII), from reaction 4, had a shoulder on it (representing ca. 3% of the liquid fraction). This extra peak may be derived from compound (LXXIV). Though no impurities were observed in the n.m.r. spectra of the identified products separated from reactions 2 and 3, it seems probable that the products in reactions 1 and 4, identified by a g.l.c. examination, may not be pure, and this could account for the varying ratios of 1:1 adducts in reactions 1 and 4. For example, the higher yield of the diastereomer E in reaction 4 may be caused by the presence of the dibromide (LXXV), with a similar g.l.c. retention time.

Summary.

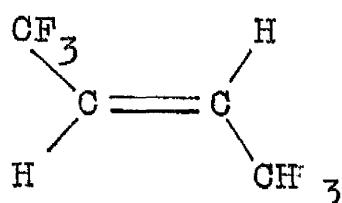
The ratio for bidirectional addition of trifluoriodomethane to 1,3,3,3-tetrafluoropropene is considered to be accurate for photochemical conditions, but the u.v. initiated addition of hydrogen bromide was

not sufficiently precise, due to the formation of
olefin dibromide, to enable firm conclusions to be drawn.

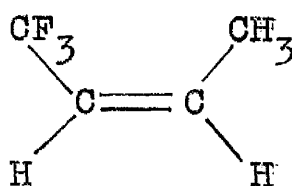
D. 1,1,1-TRIFLUOROBUT-2-ENE.

Another suitable olefin to exhibit bidirectional addition was considered to be 1,1,1-trifluorobut-2-ene, since it was thought that the methyl and the trifluoromethyl groups might have comparable radical stabilising abilities.

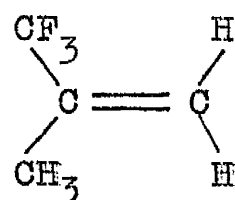
The cis/trans olefin mixture was prepared by the ultraviolet initiated addition of trifluoroiodomethane to propene to give a mixture of 1:1 adducts (91%)¹⁵⁴, which was dehydroiodinated with potassium hydroxide to a mixture of three olefins (91%), in the ratio 79:17:4, identified as trans-1,1,1-trifluorobut-2-ene (LXXVI), cis-1,1,1-trifluorobut-2-ene (LXXVII), and 2-trifluoromethylpropene (LXXVIII) respectively.



(LXXVI)



(LXXVII)

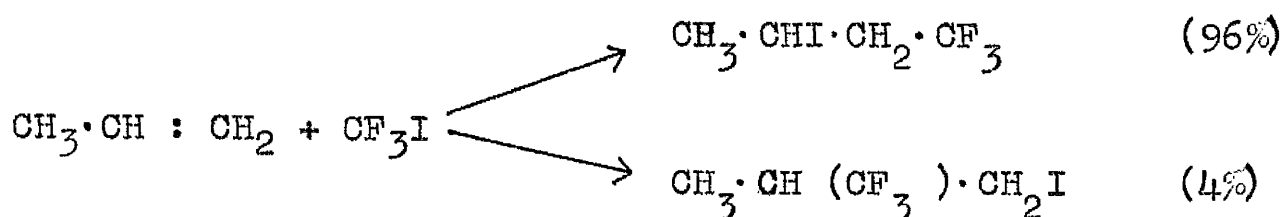


(LXXVIII)

The trans-olefin was distinguished from the cis-olefin by n.m.r. spectroscopy. The large H-H coupling constant (15.8 c/s) in the trans-olefin is outside the reported range¹⁷² (< 14 c/s) for cis H-H coupling constants. 2-Trifluoromethylpropene was identified by a comparison of its i.r. spectrum with that of an authentic

sample; they were identical.

The formation of 2-trifluoromethylpropene (4%) shows that the addition of trifluoroiodomethane to propene was bidirectional as expected, and would suggest a 1:1 adduct ratio of 96:4.

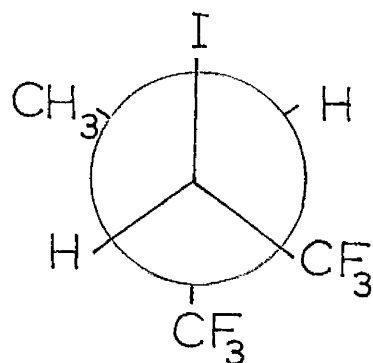


This ratio is in agreement with previous results¹⁵⁴ obtained with this system.

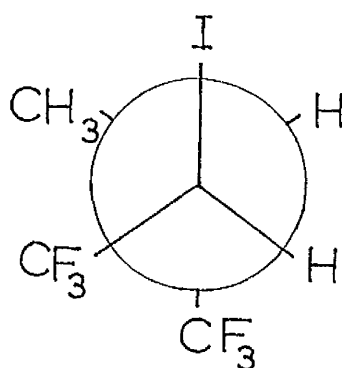
The following addition reactions were carried out on the olefin mixture described above unless stated otherwise.

I Free-Radical Addition of Trifluoroiodomethane.

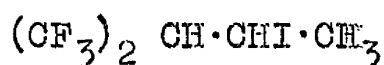
As with 1,3,3,3-tetrafluoropropene, three 1:1 adducts are to be expected from the bidirectional addition of trifluoroiodomethane; the two diastereomers (LXXIX) and (LXXX) derived from $\text{CF}_3\dot{\text{C}}$ radical attack on the $\text{CH} \cdot \text{CH}_3$ group of the olefin, and the adduct (LXXXI) derived from attack on the $\text{CF}_3 \cdot \text{CH}$ group.



Threo
(LXXIX)



Erythro
(LXXX)



(LXXXI)

A preliminary photochemically initiated addition gave four major products 1,2,3, and 4 in the ratio 40:8:22:25 respectively. They were all considered to be 1:1 adducts and thorough structure determinations were carried out.

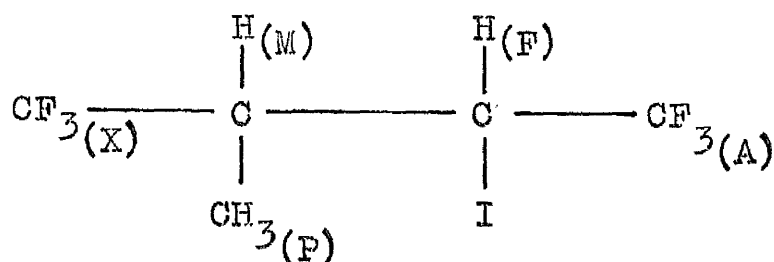
Identification of the major products.

a) Product 1.

Chemical analysis and a molecular weight determination showed that this product was a 1:1 adduct.

i) ^{19}F and ^1H n.m.r. spectra.

^{19}F spectrum. External reference $\text{CF}_3\cdot\text{COOH}$. No solvent.



Band	Intensity	Chemical Shift(ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	-10.4	doublet	8.4	$\text{F}_{(\text{A})}$ or $\text{F}_{(\text{X})}$
2	3	-5.8	doublet	8.4	$\text{F}_{(\text{X})}$ or $\text{F}_{(\text{A})}$

^1H Spectrum. Internal reference Me_4Si . No solvent.

Band	Intensity	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	1	5.40	quartet	$\text{F-A}=8.4$	$\text{H}_{(\text{F})}$
2	1	7.64	heptet	$\text{M-PX}=8.0$	$\text{H}_{(\text{M})}$
3	3	8.70	doublet	$\text{P-M}=7.5$	$\text{H}_{(\text{P})}$

It was not possible to differentiate between the two CF_3 groups because the coupling constants between $\text{F}_{(\text{X})}$ and $\text{H}_{(\text{M})}$, and $\text{F}_{(\text{A})}$ and $\text{H}_{(\text{F})}$ were identical.

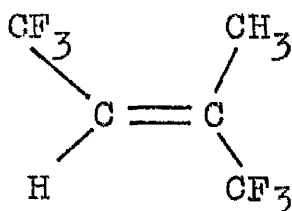
The spectrum obtained can only fit the proposed structure.

ii) Mass spectrum.

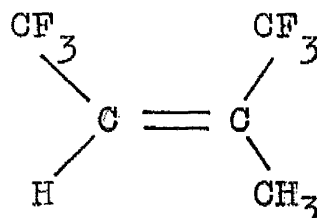
The only peak helpful in the structure determination was at m/e 209 (3%), which corresponds to the ion $CF_3 \cdot CHI^+$.

iii) Reaction with powdered potassium hydroxide.

Dehydroiodination occurred and gave trans-1,1,1-trifluoro-3-trifluoromethylbut-2-ene (LXXX11) (70%), an olefin which was considered to be cis-1,1,1-trifluoro-3-trifluoromethylbut-2-ene (LXXX111) (10%), and an unknown product (2%).



(LXXX11)



(LXXX111)

The trans-olefin was identified by its n.m.r. spectrum (Page 190). This olefin was assigned the trans rather than the cis configuration because of the small coupling observed ($J=1.9$ c/s) between the two CF_3 groups. If the two groups had been cis, then a larger coupling would have been expected, as was observed with cis-1,1,1,2,4,4,4-heptafluorobutene, but not with trans-1,1,1,2,4,4,4-hepta -

fluorobut-2-ene (Page 185-6).

The olefin thought to be the cis-isomer (LXXX111) was not positively identified as such. It had a similar g.l.c. retention time and i.r. spectrum to those of the trans-olefin, and it is difficult to envisage this olefin having any other structure.

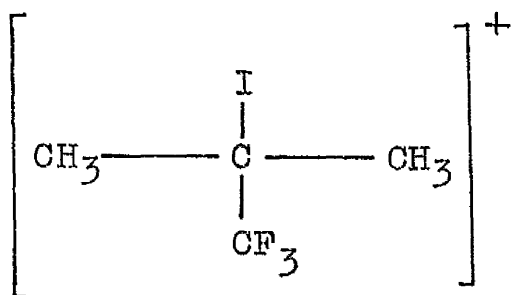
This evidence presents conclusive proof that product 1 is one of the isomers of structure $\text{CF}_3 \cdot \text{CH}(\text{CH}_3) \cdot \text{CHI} \cdot \text{CF}_3$. This 1:1 adduct is labelled isomer C in the following discussion (in the experimental section, it is labelled isomer I).

b) Product 2.

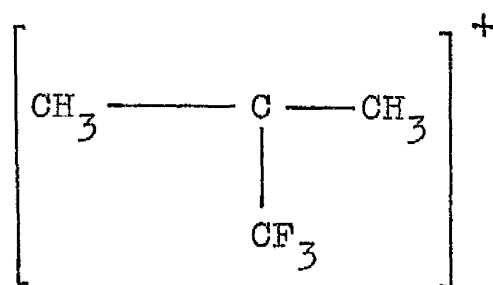
Chemical analysis and a molecular weight determination showed that this was a second 1:1 adduct.

i) Mass spectrum.

The spectrum (Table 39, Page 208) showed a 1:1 adduct parent peak at m/e 306 (38%), and a general breakdown pattern consistent with a 1:1 adduct, but additional peaks at m/e 238 (57%) and 111 (100%), corresponding to the ions (LXXXIV) and (LXXXV) respectively, may be due to rearrangement, or have been caused by the presence of an impurity in the original sample.



(LXXXIV)



(LXXXV)

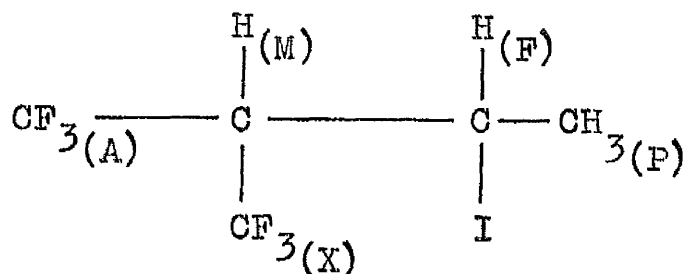
Since this product was shown to be a 1:1 adduct, and only appeared in the product mixture when the reactant olefins were contaminated with 2-trifluoromethylpropene, it suggests that product 2 has the structure $\text{CF}_3 \cdot \text{CH}_2 \cdot \text{Cl}(\text{CF}_3) \cdot \text{CH}_3$.

c) Product 3.

Chemical analysis and a molecular weight determination showed that this product was a third 1:1 adduct.

i) ^{19}F and ^1H n.m.r. spectra.

^{19}F spectrum. External reference $\text{CF}_3 \cdot \text{COOH}$. Solvent Me_4Si .



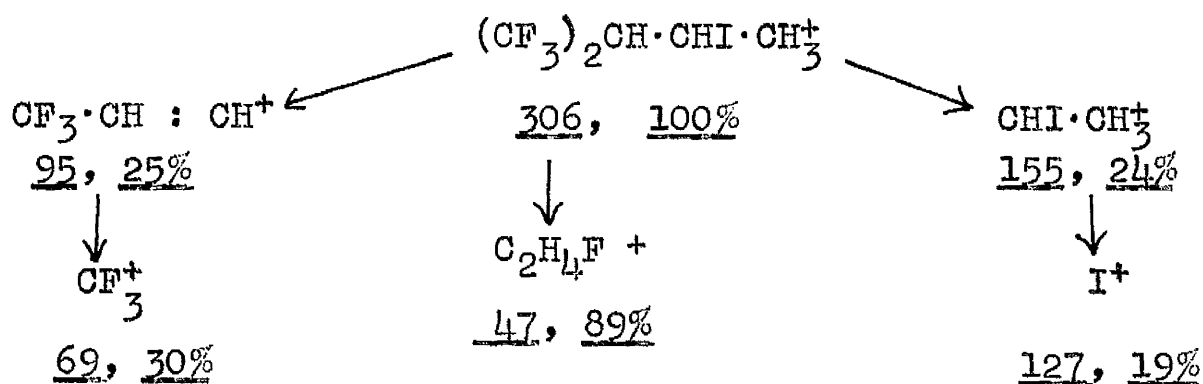
Band	Intensity	Chemical Shift (ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	-15.6	quintet	A-MX=9.0	F(A)
2	3	-12.6	quintet	X-AM=9.0	F(X)

^1H spectrum. Internal reference and solvent Me_4Si .

Band	Intensity	Chemical Shift (ν)	Multiplet Structure	Coupling J (c/s)	Assignment
1	1	5.45	quartet of doublets	F-P=8.0 F-M=3.0	H(F)
2	1	6.62	heptet of doublets	M-AX=9.0 M-F=3.0	H(M)
3	3	7.96	doublet	P-F=8.0	H(P)

The chemical shift of the CH_3 group is well downfield, and is in the region expected for such a group in the grouping $\text{CH}_3\cdot\text{CHI}-$. Thus, the spectrum can only fit the proposed structure.

ii) Mass spectrum.



The presence of the peak at m/e 155 (24%), corresponding to the ion $\text{CHI}\cdot\text{CH}_3^+$, is strong evidence for the presence of this grouping in the parent molecule.

iii) Reaction with powdered potassium hydroxide.

Dehydroiodination occurred and gave only 1,1,1-trifluoro-2-trifluoromethylbut-2-ene (97%).

The olefin was identified by its n.m.r. spectrum (page 191), where the reasonably large coupling constant (7.6 c/s) between the H atom and CH_3 group shows that they are attached to the same carbon atom.

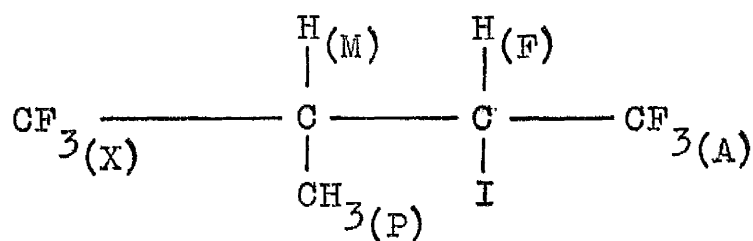
The above evidence presents conclusive proof that product 3 has the structure $(\text{CF}_3)_2\text{CH}\cdot\text{CHI}\cdot\text{CH}_3$.

d) Product 4.

Chemical analysis and a molecular weight determination showed that this product was a fourth 1:1 adduct.

i) ^{19}F and ^1H n.m.r. spectra.

^{19}F spectrum. External reference $\text{CF}_3\cdot\text{COOH}$. Solvent Me_4Si .



Band	Intensity	Chemical Shift (ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	-14.3	quintet	8.2	F(A) or F(X)
2	3	-8.2	quintet	8.2	F(X) or F(A)

^1H spectrum. Internal reference and solvent Me_4Si .

Band	Intensity	Chemical Shift (v)	Multiplet Structure	Coupling J (c/s)	Assignment
1	1	5.54	quartet of doublets	F-A=8.2 F-M=3.0	H(F)
2	1	7.34	heptet of doublets	M-PX=8.2 M-F=3.0	H(M)
3	3	8.75	doublet	P-M=8.1	H(P)

The coupling constants are very similar to those observed in the spectrum of product 3, but the chemical shifts are different, e.g., the CH_3 group is at 7.96 v in product 3, but at 8.75 v in product 4.

ii) Mass spectrum. The spectrum was almost identical to that of product 1.

iii) Reaction with powdered potassium hydroxide.

Dehydroiodination occurred and gave trans-1,1,1-trifluoro-3-trifluoromethylbut-2-ene (25%), the olefin which was considered to be cis-1,1,1-trifluoro-3-trifluoromethylbut-2-ene (40%), and an unknown product (8%). The products obtained were the same three as obtained from product 1.

The above evidence presents conclusive proof that product 4 is the other isomer of structure $\text{CF}_3 \cdot \text{CH}(\text{CH}_3) \cdot \text{CHI} \cdot \text{CF}_3$. In the following discussion this product will be called isomer D (in the experimental section, this product is called isomer II).

Results and Discussion.

The results of the photochemical investigation are summarised in Table 18.

The variation of the 1:1 adduct ratio with the composition of the reactant olefin mixture is also summarised (Table 19).

Table 18. The Photochemical Addition of Trifluoriodomethane to
Cis- and Trans-1,1,1-trifluorobut-2-ene.

	Olefin Ratio		Irradiation Period (hr.)	%Total olefin conversion	% Olefin		%	Ratio of 1:1 Adducts		
					Recovered					
	Trans	Cis			Trans	Cis		C	D	LXXXL
1	82	18	96	20	83	53	90	46	29	25
2	87	13	170	60	-	-	95	50	28	22
3	100	0	100	54	46	0	90	57	26	17

Table 19.

Orientation of CF₃ Radical Attack

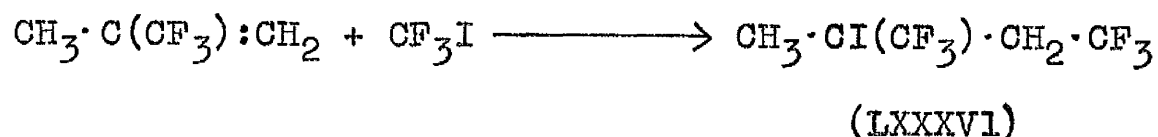
Reaction	Attack on starred Carbon Atom	
	CF ₃ ·CH [*]	CH [*] ·CH ₃
1	25	75
2	22	78
3	17	83

It is apparent from Table 18, that, in the addition to the trans-olefin, no cis-olefin was observed in the reaction mixture, and thus, it seems probable that little or no isomerisation of the olefin occurs. Also, no cis-trans isomerisation of the olefins was observed when the trans-olefin, contaminated with the cis-olefin (4%), was irradiated (70 hr.).

It is also apparent from reaction 1 (Table 18), that the cis-olefin reacts faster towards addition than does the trans-olefin. As one moves from reaction 1 through to reaction 3, there is a higher percentage of trans-olefin in the reactant mixture. This increase in the trans-olefin is accompanied by an increase in attack on the CH₃·CH group of the olefin. Thus, more CF₃ radical attack occurs on the CH₃·CH group of the trans-olefin than on the same group in

the cis-olefin.

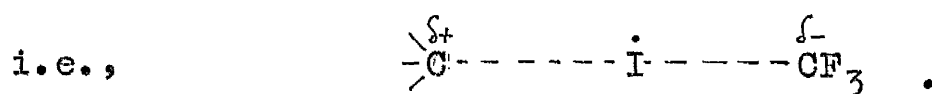
The reactant olefin mixture in reaction 1 (Table 18) contained 2-trifluoromethylpropene (4%), and the reaction products were found to include the corresponding 1:1 adduct (LXXXVI) (8%).



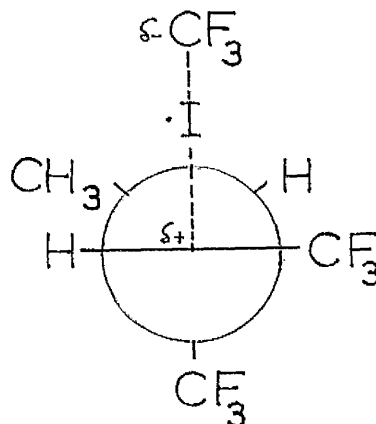
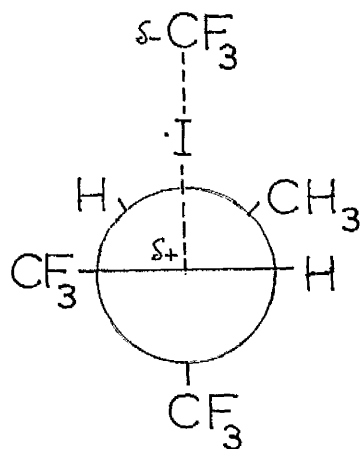
2-Trifluoromethylpropene is thus shown to react faster than the 1,1,1-trifluorobut-2-enes as expected, since terminal double bonds have been shown to react faster than internal double bonds (see Page 22). Only a trace of the 2-trifluoromethylpropene was present in the reactant olefin mixture used in reaction 2, and none in that used in reaction 3.

As with the addition of trifluoriodomethane to 1,3,3,3-tetrafluoropropene, the two diastereomers, C and D, formed are in a ratio of approximately 2:1. Although the coupling constants in their n.m.r. spectra were different, it was not possible to differentiate between isomers C and D by such a study.

A similar explanation, which involves both electrostatic and steric factors, as that proposed for the higher yield of isomer A compared to isomer B in the addition to 1,3,3,3-tetrafluoropropene, is put forward to account for the higher yield of isomer C compared to isomer D. If a similar dipole is forming in the transition state of the transfer reaction, the negative pole will be directed towards the CF_3 group of trifluoriodomethane,



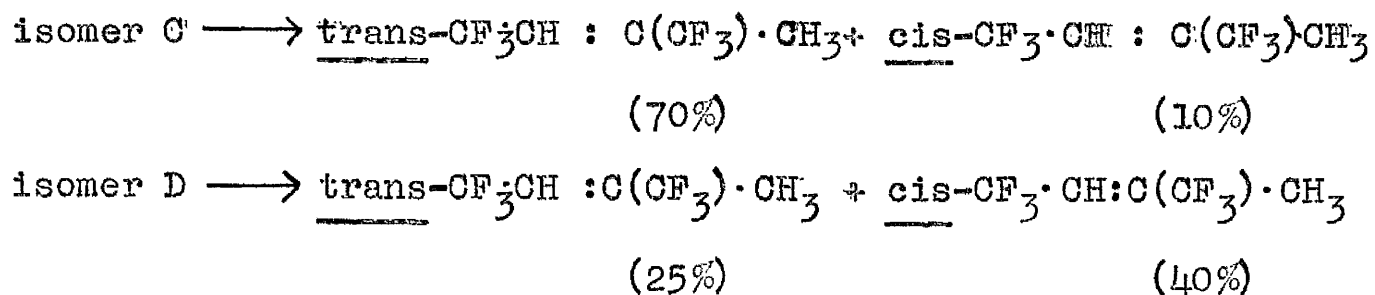
This dipole will be preferentially oriented away from the largest negative dipole of the saturated carbon atom, and this can only be realised if the trifluoriodomethane molecule preferentially approaches the radical centre trans to the most negative dipole on the saturated carbon atom, i.e., the CF_3 group. At the same time steric interactions should be minimised. The larger group on the radical carbon atom will be preferentially placed in the larger remaining steric "hole" afforded by groups on the saturated carbon.



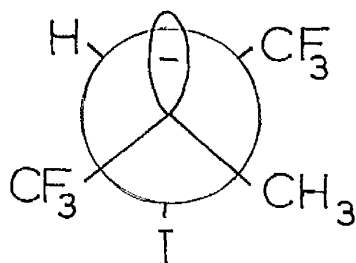
This argument would lead to a preferred threo-isomer, and, if this is correct, isomer C would have the threo configuration and isomer D the erythro configuration.

Elimination reactions of the two diastereomers.

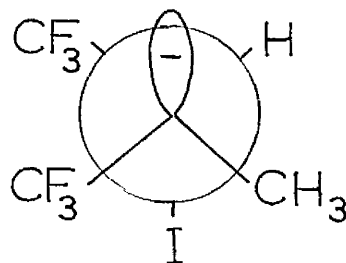
The dehydroiodination with potassium hydroxide of the two diastereomers C and D probably gave both cis- and trans- 1,1,1-trifluoro-3-trifluoromethylbut-2-ene as the major products, although, as previously mentioned, the cis-olefin was not positively identified as such.



The fact that both olefins are formed from both diastereomers must involve the formation of the intermediate carbanions (LXXXVI) and (LXXXVIII), as previously outlined for the elimination reactions of isomers A and B obtained from addition to 1,3,3,3-tetrafluoropropene (Page 114).



(LXXXV11)



(LXXXV111)

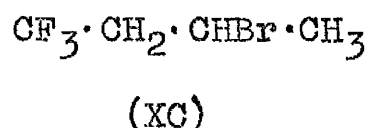
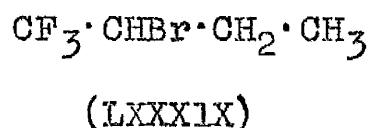
However, since the major olefins formed from the two diastereomers, C and D, are different, it might suggest that an E2 elimination reaction is also occurring. The E2 reaction may arise in this case, since the intermediate carbanion might not be as stable as the carbanion $\text{CF}_3\cdot\text{CHI}\cdot\bar{\text{C}}\text{F}\cdot\text{CF}_3$ (from isomers A and B) because of the electron-releasing methyl group attached to the carbanion site.

If such a trans E2 elimination reaction is occurring, then isomer C, which gives more of the trans-olefin, would have the threo configuration, and isomer D, which gives more of the cis-olefin, would have the erythro configuration.

This conclusion agrees with the prediction, on steric and dipole grounds in the transition state of the chain-transfer reaction, that the major isomer C would have the threo configuration.

II Addition of Hydrogen Bromide to 1,1,1-Trifluorobut- 2-ene.

The results obtained from the photochemical addition of trifluoroiodomethane to this olefin suggest that two-way radical addition of hydrogen bromide should occur, and a preponderance of adduct (XC) is to be expected.



A dark reaction was first carried out to determine if ionic addition of hydrogen bromide to this olefin does occur. A mixture of the two reactants was, therefore, left in the dark (425 hr.), in the presence of aluminium bromide (1 g.) to catalyse any ionic addition; no reaction was observed. This shows that the likelihood that the ionic addition of hydrogen bromide would occur during the u.v. initiated addition was small.

A preliminary u.v. initiated experiment gave three major products 1,2, and 3 in the ratio 35:26:34 respectively. A thorough investigation to determine their structures was carried out.

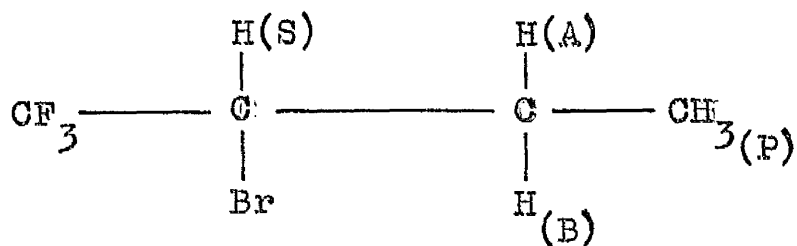
Identification of the three major products.

a) Product 1.

Chemical analysis and a molecular weight determination showed that this product was a 1:1 adduct.

1) ^{19}F and ^1H n.m.r. spectra.

^{19}F spectrum. External reference $\text{CF}_3 \cdot \text{COOH}$. No solvent.



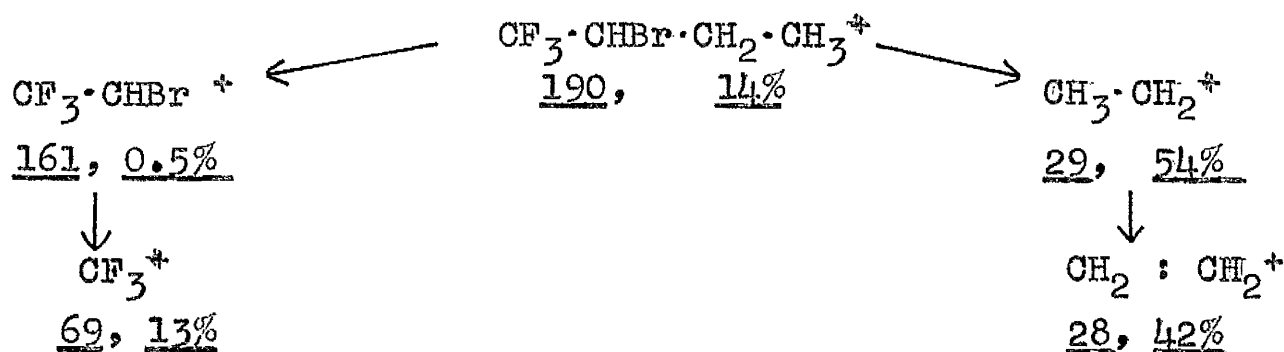
Band	Chemical Shift (p.p.m.)	Multiplet Structure	Coupling J (c/s)	Assignment
1	-4.9	doublet of quartets	F-S=7.2 F-P=0.9	F

¹H spectrum. Internal reference Me₄Si. No solvent.

Band	Intensity	Chemical Shift (τ)	Multiplet Structure	Coupling J(c/s)	Assignment
1	1.0	6.00	doublet of quartets of doublets	9.3 S-F=7.2 4.3	H(S)
2	2.2	7.98	complex		H(A) H(B)
3	3.4	8.88	triplet of quartets (distorted)	7.3 P-F=0.9	H(P)

The spectrum is of the ABP₃SX₃-type, and the above treatment is only approximate. The reasonably large coupling between the fluorine nuclei and only one hydrogen nucleus suggests the grouping CF₃·CHX- (where X is not H or F). The chemical shift of the CH₃ group is in the expected region for a CH₃ group in the grouping CH₃·CH₂-.

ii) Mass spectrum.



Two further major peaks at m/e 111 (76%), which corresponds to the loss of bromine from the parent ion, and a peak at m/e 73 (100%), which corresponds to the ion $C_4H_6F^+$, were present.

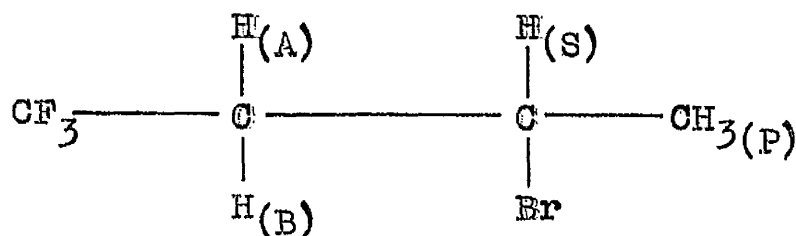
The above evidence can leave no doubt that product 1 has the structure $CF_3 \cdot CHBr \cdot CH_2 \cdot CH_3$.

b) Product 2.

Chemical analysis and a molecular weight determination showed that this product was also a 1:1 adduct.

i) ^{19}F and 1H n.m.r. spectra.

^{19}F spectrum. External reference $CF_3 \cdot COOH$. Solvent Me_4Si .



Band	Chemical Shift (p.p.m.)	Multiplet Structure	Coupling J (c/s)	Assignment
1	-13.0	triplet	10.4	F

An impurity band [doublet ($J=7.9$ c/s)] at -4.7 p.p.m. from the reference was also present.

^1H spectrum. Internal reference and solvent Me_4Si .

Band	Intensity	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	1	5.82	sextet	6.6	$\text{H}(\text{S})$
2	2	7.05	complex		$\text{H}(\text{A})$ $\text{H}(\text{B})$
3	3	8.23	doublet	$\text{P-S} = 6.6$	$\text{H}(\text{P})$

An impurity band [doublet ($J=6.5$ c/s)] at 8.72τ was also present.

The spectrum is of the ABP_3SX_3 -type, and the above treatment is only approximate. The coupling between $\text{H}(\text{P})$ and $\text{H}(\text{S})$ suggests the grouping $\text{CH}_3\text{-CHX-}$ (where X is not H or F), and the general form of the spectrum is consistent with the proposed structure.

ii) Mass Spectrum.

The spectrum showed a parent peak at m/e 190 (14%), and a peak at m/e 111 (93%), due to loss of bromine from the parent ion, and was of little help towards structure determination.

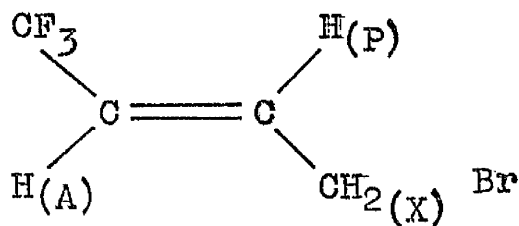
The n.m.r. spectroscopic evidence is proof that this product has the structure $\text{CF}_3\text{-CH}_2\text{-CHBr-CH}_3$.

c) Product 3.

Chemical analysis and a molecular weight determination indicated the empirical formula $C_4H_4BrF_3$, and the i.r. spectrum showed a medium strength band at 5.92μ , probably due to olefinic double bond stretch.

i) ^{19}F and 1H n.m.r. spectra.

^{19}F spectrum. External reference $CF_3 \cdot COOH$. No solvent.



Band	Chemical Shift (pp.m.)	Multiplet Structure	Coupling J (c/s)	Assignment
1	-13.0	doublet of quartets	F-A=6.0 F-PX=2.0	F

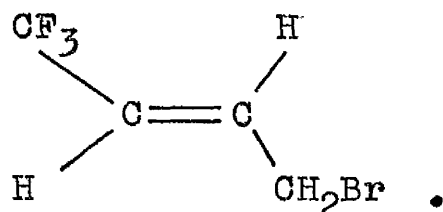
¹H spectrum. Internal reference Me₄Si. No solvent.

Band	Intensity	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	1	3.40	doublet of triplets of quartets	P-A=15.8 P-X=6.8 P-F=2.0	H _(P)
2	1	4.10	doublet of quartets of triplets	A-P=15.8 A-F=6.0 A-X=1.0	H _(A)
3	2	6.04	doublet of quartets of doublets	X-P=6.8 X-F=2.0 X-A=1.0	H _(X)

The two hydrogen atoms H_(A) and H_(P) are shown, by their chemical shifts, to be vinylic in character, and the large coupling constant between the two is in the expected region for trans H-H coupling, but outside the range for cis coupling. Thus, the spectrum can fit only the proposed structure.

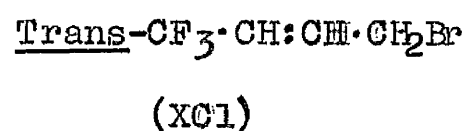
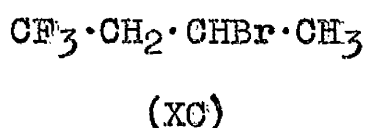
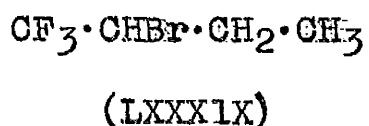
ii) Mass Spectrum. The spectrum showed a parent peak at ^m/_e 188 (16%) and a peak at ^m/_e 109 (100%), which corresponds to loss of bromine from the parent peak, and the remaining peaks, though consistent with the proposed structure, were not helpful for structure determination.

The above evidence, especially the n.m.r. spectra, is proof that product 3 has the structure



Results and Discussion.

The results of the photochemical investigation are summarised in Table 20. The 1:1 adduct ratio obtained in the reactions is unsatisfactory as it varied from a ratio (LXXXIX) : (XC) of 74:26 to 57:43. The third major product (XC1) was presumably formed via allylic hydrogen abstraction.



A third reaction (14% olefin conversion) gave only a 62% total yield of 1:1 adducts (50%), present in the ratio (LXXXIX):(XC) of 44:56, and compound (XC1) (12%). A fourth major product was formed in this third reaction, which is discussed later. This reaction is not considered sufficiently precise for inclusion in Table 20.

The general direction of bromine atom addition shown

Table 20.

Free-Radical Addition of Hydrogen Bromide to

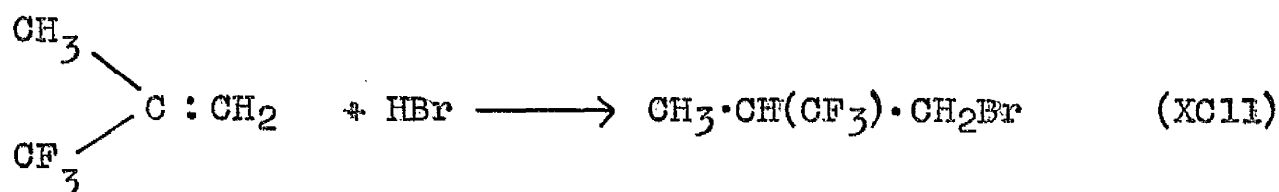
1,1,1-Trifluorobut-2-ene.

	% Reactant Olefin		Irradiation Period (hr.)	% Total Olefin Conversion	% Olefin Recovered		% 1:1 Adducts	Ratio of 1:1 Adducts		% XCl
	Trans	Cis			Trans	Cis		LXXXIX	XC	
1	82	18	6	30	82	17	61	57	43	34
2	96	4	19	95	-	-	62	74	26	38

by these reactions is rather surprising, since it indicates preferred attack at the more sterically hindered $\text{CF}_3\cdot\text{CH}$ group of the olefin; this is opposite to the direction of addition obtained with the CF_3 radical, which showed a preferred attack at the $\text{CH}_3\cdot\text{CH}$ group of the olefin. The participation of ionic addition in the hydrogen bromide addition would lead to isomer (XC), since the olefin is polarised in the direction $\text{CF}_3^{\delta-}\cdot\text{CH} : \text{CH}^{\delta+}\cdot\text{CH}_3$. Thus, the preferred adduct (LXXXIX) is contrary to that expected for ionic addition. This difference in preferred attack by the $\text{Br}\cdot$ and CF_3 radicals was not observed in the additions to the olefins previously discussed in which both radicals showed a preferred attack on the same group of the olefin; this is further discussed later (Page 177).

Isomer (XC), isolated by g.l.c. from the combined product mixtures of reaction 1 and 2, was shown by n.m.r. spectroscopy to contain an unknown impurity, which must have a similar g.l.c. retention time. If the yield of this impurity varied for each reaction investigated, then the observed discrepancies in the 1:1 adduct ratio, calculated from g.l.c. peak areas, might possibly be partly accounted for on this basis.

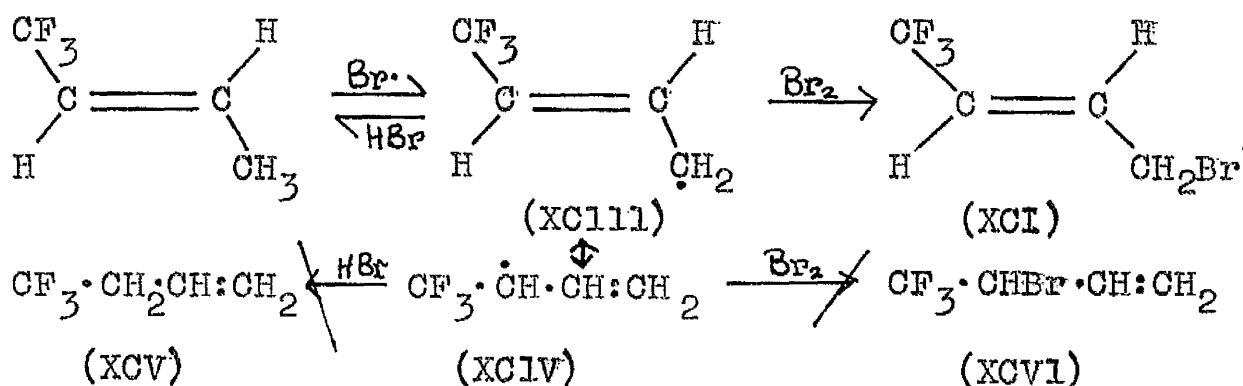
The reactant olefin mixture contained 2-trifluoromethylpropene (4%) in reactions 1 and 3, but only a trace in reaction 2. The formation of a further product, which made up 5, 0, and 32% of the product mixture of reactions 1, 2, and 3 respectively, and had a g.l.c. retention time slightly longer than those of the 1:1 adducts, was considered to be derived from the addition of hydrogen bromide to this olefin, i.e., isomer (XC11).



The mass spectrum (Page 327) of this product considered to be isomer (XC11) showed a parent 1:1 adduct ion peak at m/e 190 (13%), and major peaks at m/e 111 (84%), and 28 (100%), corresponding to loss of bromine from the parent ion and C_2H_4^+ respectively.

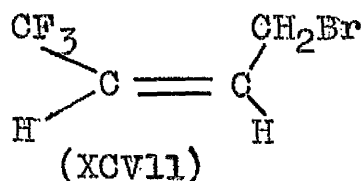
The formation of the olefin dibromides, which occurred in the hydrogen bromide additions to the previous two olefins studied, did not occur in these reactions. However, an abstraction reaction is considered to occur simultaneously with the hydrogen bromide addition reaction, as is shown by the formation of compound (XC1). Thus, the free bromine, which is probably initially formed in appreciable amounts (since hydrogen is also formed in

appreciable amounts in these reactions), is quickly consumed in the fast abstraction reaction of the allylic radical leading to compound (XCl). The following scheme is the probable mechanistic path leading to its formation.



The intermediate allylic radical produced by hydrogen abstraction will be a hybrid of structures (XCIII) and (XCLV). Structure (XCIII) appears to be the reactive form, since the allyl bromide (XCI) formed is derived from this intermediate. Indeed, the identified products, the 1:1 adducts and compound (XCI), correspond to the total amount of consumed olefin, 1,1,1-trifluorobut-2-ene, in reaction 2 (Table 20). Thus, products (XCV) and (XCVI) derived from the abstraction of hydrogen or bromine by the intermediate (XCLV) were not detected.

In view of the formation of trans-4-bromo-1,1,1-trifluorobut-2-ene, the cis isomer (XCVII) was also an expected product.



However, the absence of this product can be partially accounted for by the fast reversible addition of the bromine atom to the original cis-trans mixture of the 1,1,1-trifluorobut-2-ene. In a third reaction (previously mentioned), the trans-cis ratio was shown to be 95:5 after a 3 hr. irradiation period. Thus, the concentration of the cis-olefin is drastically reduced, and the yield of compound (XCV11), compared to that of compound (XCl), would be expected to be small.

Summary.

The 1:1 adduct ratio obtained for the addition of trifluoroiodomethane to this olefin is considered to be accurate for photochemical conditions. However, the u.v. initiated addition of hydrogen bromide proved to be more complicated than originally anticipated, and the 1:1 adduct ratio obtained varied, so that it is unreasonable to draw any firm conclusions apart from those already discussed.

III Addition of Bromine to 1,1,1-Trifluorobut-2-ene.

The original intention of this section of the research was to prepare cis- and trans-4-bromo-1,1,1-trifluorobut-2-ene by the homolytic abstraction reaction observed

in the reaction of hydrogen bromide with this olefin.

When a mixture of cis- and trans-1,1,1-trifluoro - but-2-ene and bromine was allowed to warm from -196° , an immediate reaction occurred in the liquid phase. This spontaneous reaction appeared only to occur in the liquid phase, and gaseous reactants (shown by an examination of the products) remained even after the reaction was allowed to continue (8 hr.) in the dark. Two major products (96%), 1 and 2, were formed in the ratio 80:20 respectively.

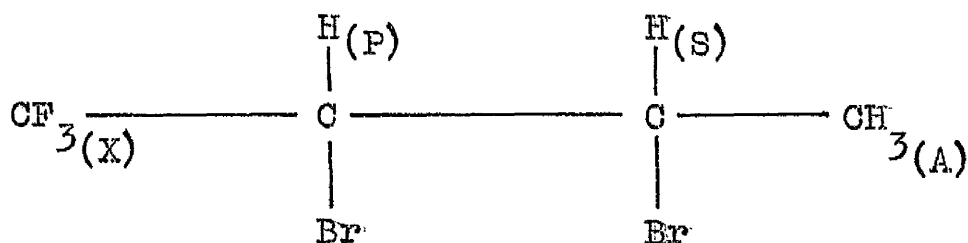
Identification of the two major products.

a) Product 1.

Chemical analysis showed that this product was an olefin dibromide.

^{19}F and ^1H n.m.r. spectra.

^{19}F spectrum. External reference $\text{CF}_3 \cdot \text{COOH}$. No solvent.



Band	Chemical Shift (ppm.)	Multiplet Structure	Coupling J (c/s)	Assignment
1	-9.9	doublet of quartets (distorted)	X-P=7.4 X-A=0.9	F(X)

^1H spectrum. Internal reference Me_4Si . No solvent.

Band	Intensity	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	2	5.45	complex	-	$\text{H}_{(\text{P})}$ $\text{H}_{(\text{S})}$
2	3	8.19	doublet of quartets	A-S=6.5 A-X=0.9	$\text{H}_{(\text{A})}$

The shifts of $\text{H}_{(\text{P})}$ and $\text{H}_{(\text{S})}$ are very similar, and so a complex system is produced. The spectrum, however, is consistent with the proposed structure.

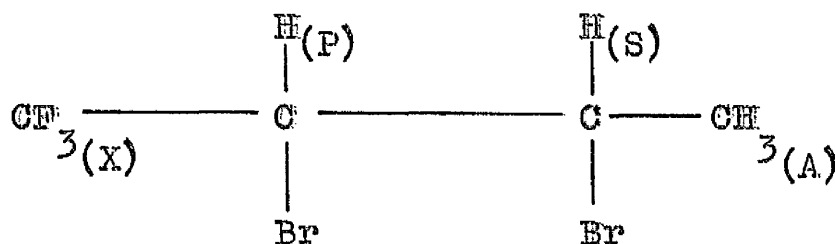
The evidence, thus, shows that product 1 is an olefin dibromide, but there is no indication from the n.m.r. spectrum as to whether this product is the threo or erythro form of $\text{CF}_3 \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{CH}_3$.

Product 2.

Chemical analysis showed that this product was the second olefin dibromide.

^{19}F and ^1H n.m.r. spectra.

^{19}F spectrum. External reference $\text{CF}_3\cdot\text{COOH}$. Solvent Me_4Si .



Band	Chemical Shift (ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	-9.9	doublet of quartets (distorted)	X-P=7.4 X-A=0.7	F(X)

^1H spectrum. Internal reference and solvent Me_4Si .

Band	Intensity	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	2	5.67	complex		H(P) H(S)
2	3	8.22	doublet of quartets	A-S=6.5 A-X=0.7	H(A)

The spectrum is almost identical to that of product 1.

This evidence shows that product 2 is also an olefin dibromide, and again it is not possible to determine whether the product is the threo or erythro form of structure $\text{CF}_3\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CH}_3$.

Discussion.

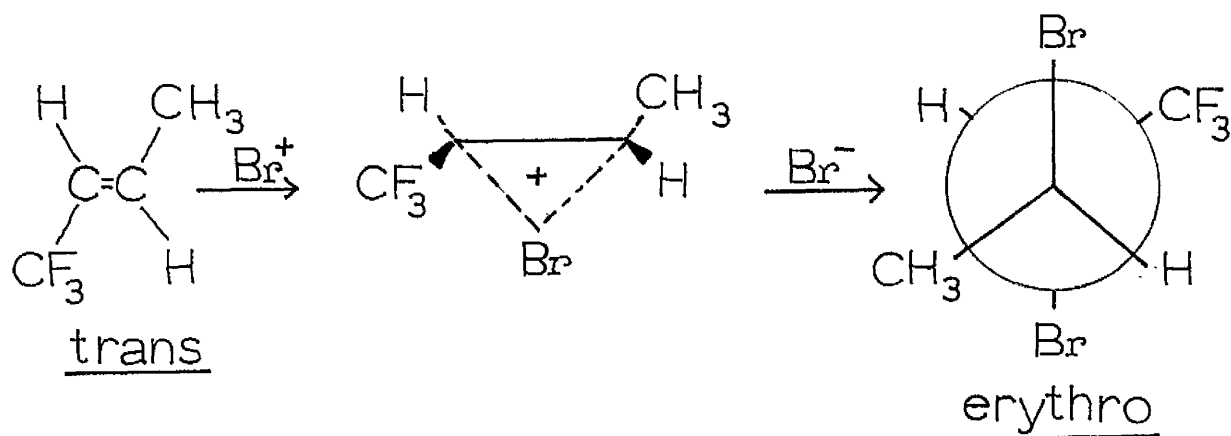
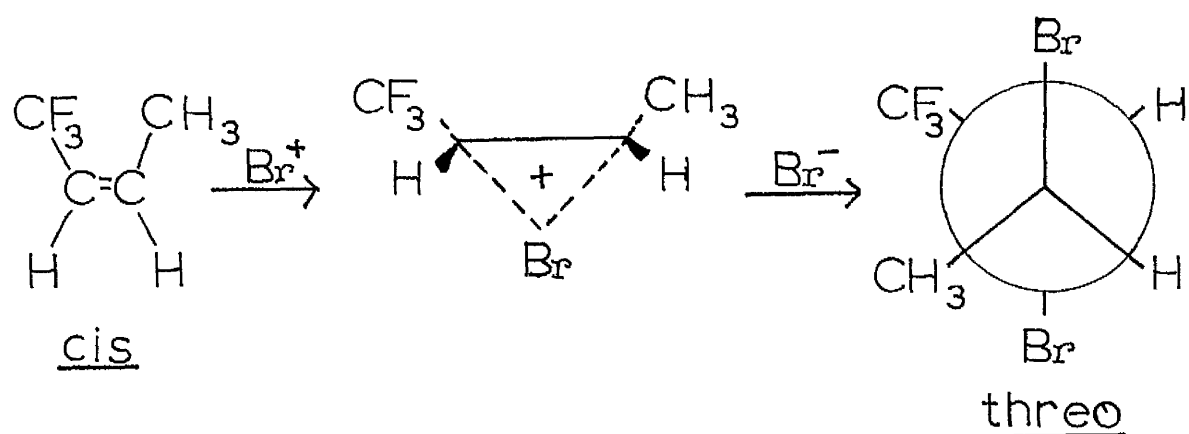
Since the reaction is spontaneous and occurs in the dark, it is almost certainly an ionic addition, which proceeds via an intermediate carbonium ion.

Table 21. Ionic Addition of Bromine to
1,1,1-Trifluorobut-2-ene.

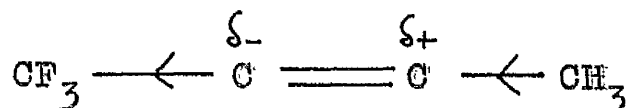
MOLE RATIO OF OLEFINS USED		MOLE RATIO OF DIBROMIDES	
Trans	Cis	1	2
79	21	80	20

It is apparent from Table 21 that the ratio of the two diastereomers formed was identical (within experimental error) with the ratio of the two olefins consumed in the reaction. It is, thus, highly probable that the major diastereomer is the erythro form, derived from trans addition of bromine to the trans-olefin, and the minor diastereomer is the threo form, derived from trans-addition to the cis-olefin.

This specificity can readily be explained in terms of a bromine bridging atom in the intermediate carbonium ion.



This olefin is the only one of the three examined (1,1,3,3,3-pentafluoropropene, page 85, 1,3,3,3-tetrafluoropropene, page 129) to exhibit this spontaneous ionic addition of bromine. This is presumably because it is the most strongly polarised olefin with an electron-releasing CH_3 group at one end of the double bond, and an electron-withdrawing CF_3 group at the other.



However, this olefin probably has a higher π -electron density in the olefinic double bond than those previously examined (see Page 177), and this may be the cause of such a facile bromine addition.

Conclusions.

The results of the photochemical addition of trifluoroiodomethane and hydrogen bromide to the olefins previously discussed are summarised in Table 22.

Table 22.

Orientation of Addition of the Br· and CF₃· Radicals.

Radical	olefin			
	δ^- CHCl	δ^+ CF ₂	δ^- CF ₃ ·CH	δ^+ CF ₂
CF ₃ ·	10	90	60	40
Br·	0	100	63	37*
	δ^- CF ₃ ·CH	δ^+ CHF	δ^- CF ₃ ·CH	δ^+ CH·CH ₃
CF ₃ ·	23	77	21	79
Br·	48	52*	(65	35) [†]

* Olefin dibromides also formed.

[†] Mean value of two experiments, ratio 57:48 and 74:26.

The 1:1 adduct ratios obtained from the addition of hydrogen bromide to 1,1,3,3,3-pentafluoropropene and 1,3,3,3-tetrafluoropropene are probably not accurate because of the formation of olefin dibromides. However, the ratios obtained are considered to be of the right order.

There are five factors that are considered important in determining the orientation of addition to unsymmetrical olefins:-

- 1) Steric effects.
- 2) The stability of the intermediate radical formed.
- 3) The strength of the bond formed.
- 4) The electrophilicity of the attacking radical.
- 5) The polarisation of the olefinic double bond.

These last two factors, together with steric effects, are only considered to be important when the stabilities of the two possible intermediate radicals (or the strength of the bonds formed) are of comparable magnitude.

1) Steric effects. From previously reported results, it has been shown that, in most cases, steric effects are relatively unimportant in determining the orientation of addition, and thus orientation based entirely on steric effects is probably not possible (as previously discussed on page 30).

However, the steric effects of very large groups on the olefin, or large attacking radicals, will affect the orientation of addition with olefins capable of bidirectional addition. It has been reported⁹¹ that, in the fast addition of the large bistrifluoromethylamino radical to hexafluoropropene, attack is solely on the less sterically hindered

CF_2 group of the olefin whereas bidirectional addition might be expected (see Page 30).

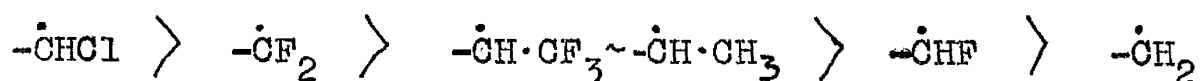
In the present work, steric effects do not appear to be important in determining the orientation of the slow addition reactions of the $\text{Br}\cdot$ and $\text{CF}_3\cdot$ radicals. For example, the preferred attack of both the $\text{Br}\cdot$ and $\text{CF}_3\cdot$ radicals on 1,1,3,3,3-pentafluoropropene is on what is probably the more sterically hindered site, i.e., the $\text{CF}_3\cdot\text{CH}$ group of the olefin.

However, the unidirectional addition of the $\text{Br}\cdot$ atom to what is probably the less sterically hindered CF_2 group of chloro-1,1-difluoroethylene is rather surprising, since bidirectional addition of the $\text{CF}_3\cdot$ radical does occur. Also, the CF_2 group is the more positively polarised group of the olefin and the $\text{Br}\cdot$ atom, which appears to be more electrophilic (from the other results in the present work) than the $\text{CF}_3\cdot$ radical, would not be expected to add exclusively to this group. This reaction was extremely fast (complete conversion in 20 min.), much faster than the corresponding addition of trifluoroiodomethane, and it may be that steric effects become important in such extremely fast additions, thus, causing addition to the more sterically hindered group not to occur.

2) Stability of the intermediate radical formed. The stabilities of the two possible intermediate radicals, formed

by the addition of a radical to an unsymmetrical olefin, are considered to be the dominant factor in determining the orientation of such an addition (see Page 25).

A series of the stabilising abilities of groups towards a lone electron is found, in the present work, to be



where the differences are only small. [The stability of the $-\dot{\text{C}}\text{H}_2$ radical is derived from the addition of trifluoroiodomethane to vinyl fluoride in the preparation of 1,3,3,3-tetrafluoropropene (Page 92).]

The results (Table 6, Page 36) from the additions to hexafluoropropene show that the $\text{CF}_3\cdot\dot{\text{C}}\text{F}-$ radical is more stable than the $-\dot{\text{C}}\text{F}_2$ radical, as would be expected from the above series, thus bidirectional addition to 1-chloro-2,3,3,3-tetrafluoropropene $\text{CF}_3\cdot\text{CF} : \text{CHCl}$ might be expected, with predominant attack on the $\text{CF}_3\cdot\text{CF}$ group of the olefin. Further bidirectional additions might be expected with 1-chloro-1,2,3,3,3-pentafluoropropene and 2-fluorobut-2-ene, though radical addition to the latter is reported¹²⁸ to be exclusively on the $\text{CH}\cdot\text{CH}_3$ group.

3) Strength of bond formed. Tedder and Walton¹²³ have proposed that the direction of radical addition to an olefin is determined, not by the stability of the possible intermediate

radicals formed by such an addition, but by the strength of the possible bonds that could be formed. However, as the authors pointed out, the only qualitative way of determining which new bond will be formed is to assume that the new bond is formed at the carbon atom which forms the least stable radical. Since, both theories lead to exactly the same predictions of orientation of radical addition, the theory of intermediate radical stability, with its theoretical shortcomings, is easier to apply than Tedder's more complicated theory, and serves as a simple empirical rule in forecasting the site of radical attack on an unsymmetrical olefin.

4) and 5) The electrophilicity of the attacking radical and the polarisation of the olefinic double bond. The electrophilicity of an attacking radical and the polarisation of an olefinic double bond are only considered to have significance when the stabilities of the two possible intermediate radicals which could be formed are comparable (see Page 31).

The electrophilicity of the attacking radical and the effect on the orientation of addition is amply illustrated in the additions of substituted silyl radicals ¹⁷³ to hexafluoropropene, as shown in Table 23.

Table 23. Addition of $R_3Si\cdot$ Radicals to Hexafluoropropene.

$R_3Si\cdot$	$\overset{\delta-}{CF_3} \cdot \overset{\delta-}{CF}$	$\overset{\delta+}{CF_2}$
$R_3=Me_3$	15	85
$R_3=Me_2Cl$	25	75
$R_3=MeCl_2$	47	53
$R_3=Cl_3$	65	35

The more electrophilic the radical is, then the greater is the attack on the more negatively polarised $CF_3\cdot CF$ group of the olefin. Similarly, two-way addition of the $Me_2P\cdot$ radical would not be expected with 1,1-difluoroethylene on the grounds of intermediate radical stability, but the nucleophilic character of the radical gives a high proportion of attack on the positively polarised CF_2 group of the olefin,¹⁷⁴ i.e.,

	$\overset{\delta-}{CH_2}$	$\overset{\delta+}{CF_2}$	
$Me_2P\cdot$	71	29	.

In the present work, the relative electrophilicities of the $Br\cdot$ and $CF_3\cdot$ radicals appear not to be very important in directing the orientation of addition, since an examination of Table 22 indicates that there is no direct evidence to show that one radical is more electrophilic

than the other, although, on balance, it would appear that the Br• atom is the more electrophilic.

Work on the orientation of addition, with olefins capable of bidirectional addition with these two radicals, has been concentrated on systems in which the π -electron density of the olefinic double bond has been diminished. In these reactions there seems to be no correlation between the results obtained.

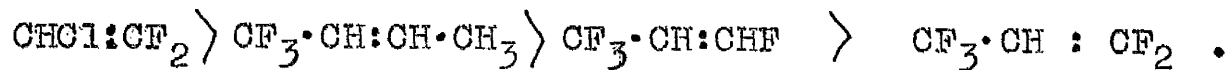
However, with 1,1,1-trifluorobut-2-ene, in which the π -bond probably has a relatively high electron density and is highly polarised, and in which the two possible intermediates $\text{CF}_3\cdot\dot{\text{C}}\text{H}\cdot\text{CHX}\cdot\text{CH}_3$ and $\text{CF}_3\cdot\text{CHX}\cdot\dot{\text{C}}\text{H}\cdot\text{CH}_3$ formed by initial attack might be expected to have similar stabilities, there is a very marked difference in the orientation of addition (Table 22). The preferred attack of the Br• atom is on the more negatively polarised $\text{CH}\cdot\text{CF}_3$ group of the olefin, whilst the CF_3 radical has a preferred attack at the more positively polarised group of the olefin. This seems good evidence that the bromine atom is the more electrophilic radical. It would also appear from the present results that the difference in radical electrophilicity is only brought out when the π -electron density of the olefinic double bond is relatively high. If this is the case, then vinyl fluoride, which might also be expected to have a relatively high π -electron density, ought to show, from the orientation of addition, that the Br• atom

has the greater electrophilicity.

	δ^- CH ₂	:	δ^+ CHF	
CF ₃ •	92		8	¹³²
Br•	81		19	⁹⁹

The results of such an investigation show that this is not the case.

The relative rates of addition of hydrogen bromide and trifluoroiodomethane to the olefins investigated in the present work was found to be in the order of:-



1,1,3,3,3-Pentafluoropropene is shown to be the least reactive olefin towards free-radical addition presumably due to the presence of strongly electron-withdrawing groups which decrease the π -electron density of the double bond.

In conclusion, therefore, it appears that the bromine atom is more electrophilic than the CF₃• radical, which agrees with Abell's work⁹⁹, but no definite conclusions with regard to orientation of the Br• and CF₃• radicals can be drawn.

A Compilation of Spectra.

- 1) The n.m.r. spectra are discussed on the following page .
- 2) The mass spectra are recorded on page 194 .
- 3) Some u.v. spectra are recorded on page 212 .
- 4) The i.r. spectra of pure compounds, if they are new, or if the spectra cannot be easily obtained from the literature, are listed in the appropriate places in the experimental section.

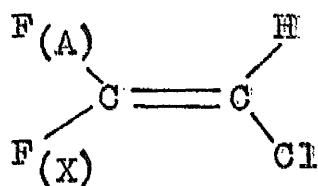
Nuclear Magnetic Resonance Spectroscopy.

N.m.r. spectroscopy proved to be the most valuable technique employed to elucidate the structures of the compounds under investigation. The spectra of certain compounds were often complex, but a first-order treatment of such spectra was usually sufficient to determine the structure.

The ^{19}F chemical shifts are recorded from trifluoroacetic acid as reference. A minus chemical shift is one to low field from the reference and a positive chemical shift is one to high field. The ^1H chemical shifts are taken from tetramethylsilane as reference at 10.00 γ .

The spectra of the products from the addition reactions are listed in the appropriate sections in the discussion. The spectra of the olefins dealt with in the present work are listed in the following pages together with a correlation chart of some of the ^{19}F chemical shifts observed.

Chloro-1,1-difluoroethylene.



^{19}F spectrum.

External reference $\text{CF}_3\cdot\text{COOH}$.

No solvent.

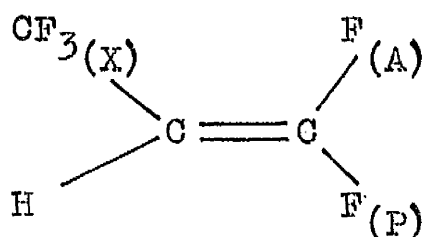
Band	Intensity	Chemical Shift (ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	1	+12.0	doublet of doublets	X-A=42.3 X-H=16.6	F(X)
2	1	+16.3	doublet of doublets	A-X=42.3 A-H=1.0	F(A)

^1H spectrum.

Internal reference Me_4Si . No solvent.

Band	Chemical Shift (γ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	5.2	doublet of doublets	H-X=16.6 H-A=1.0	H

1,1,3,3,3-Pentafluoropropene.



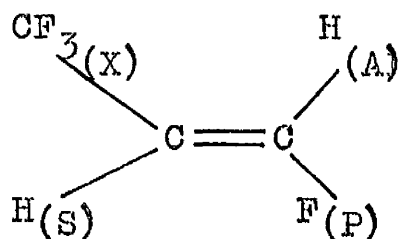
^{19}F spectrum. External reference $\text{CF}_3\cdot\text{COOH}$. No solvent.

Band	Intensity	Chemical Shift(ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	-16.8	doublet of doublets of doublets	X-A=17.5 X-P=11.4 X-H=6.7	F(X)
2	1	-2.5	doublet of quartets of doublets	A-H=21.7 A-X=17.5 A-P=14.2	F(A)
3	1	+2.7	doublet of quartets of doublets	P-A=14.2 P-X=11.4 P-H=1.6	F(P)

^1H spectrum. Internal reference Me_4Si . No solvent.

Band	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	5.26	doublet of quartets of doublets	H-A=21.7 H-X=6.7 H-P=1.6	H

Trans-1,3,3,3-tetrafluoropropene.



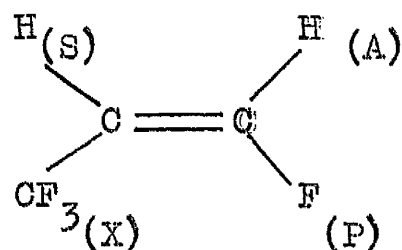
¹⁹F spectrum. External reference CF₃·COOH. No solvent.

Band	Intensity	Chemical Shift (ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	-14.8	doublet of doublets of doublets	X-P=8.9 X-S=6.8 X-A=2.2	F(X)
2	1	+46.0	doublet of doublets of quartets	P-A=78.3 P-S=14.8 P-X=8.9	F(P)

¹H spectrum. Internal reference Me₄Si. No solvent.

Band	Intensity	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	1	2.86	doublet of doublets of quartets	A-P=78.3 A-S=11.4 A-X=2.2	H(A)
2	1	4.41	doublet of doublets of quartets	S-P=14.8 S-A=11.4 S-X=6.8	H(S)

Cis-1,3,3,3-tetrafluoropropene.



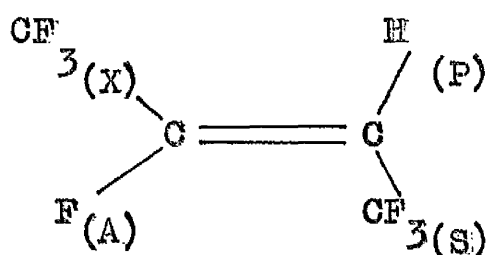
^{19}F spectrum. External reference $\text{CF}_3\cdot\text{COOH}$. No solvent.

Band	Intensity	Chemical Shift (ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	-17.6	doublet of doublets	X-P=17.5 X-S=7.5	$\text{F}(\text{X})$
2	1	+35.8	doublet of doublets of quartets	P-A=78.0 P-S=36.7 P-X=17.5	$\text{F}(\text{P})$

^1H spectrum. Internal reference Me_4Si . No solvent.

Band	Intensity	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	1	3.33	doublet of doublets	A-P=78.0 A-S=5.6	$\text{H}(\text{A})$
2	1	4.86	doublet of quartets of doublets	S-P=36.7 S-X=7.5 S-A=5.6	$\text{H}(\text{S})$

Trans-1,1,1,2,4,4,4-heptafluorobut-2-ene.



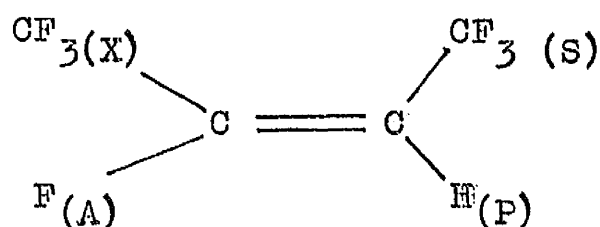
^{19}F spectrum. External reference $\text{CF}_3\cdot\text{COOH}$. No solvent.

Band	Intensity	Chemical Shift(ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	-15.8	doublet of doublets of quartets	S-A=18.0 S-P=6.9 S-X=1.6	$\text{F}(\text{S})$
2	3	-1.0	doublet of quartets of doublets	X-A=9.3 X-S=1.6 X-P=0.6	$\text{F}(\text{X})$
3	1	+42.2	doublet of quartets of quartets	A-P=29.8 A-S=18.0 A-X=9.3	$\text{F}(\text{A})$

^1H spectrum. Internal reference Me_4Si . No solvent.

Band	Chemical Shift (γ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	4.20	doublet of quartets of quartets	P-A=29.8 P-S=6.9 P-X=0.6	$\text{H}(\text{P})$

Cis-1,1,1,2,4,4,4-heptafluorobut-2-ene.



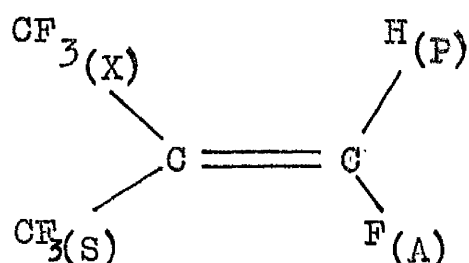
^{19}F spectrum. External reference $\text{CF}_3\cdot\text{COOH}$. No solvent.

Band	Intensity	Chemical Shift (ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	-19.4	doublet of quartets of doublets	S-A=11.3 S-X=9.9 S-P=7.8	$\text{F}(\text{S})$
2	3	-6.4	quartet of doublets of doublets	X-S=9.9 X-A=7.5 X-P=0.7	$\text{F}(\text{X})$
3	1	+38.0	doublet of quartets of quartets	A-P=17.8 A-S=11.3 A-X=7.5	$\text{F}(\text{A})$

^1H spectrum. Internal reference Me_4Si . No solvent.

Band	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	4.10	doublet of quartets of quartets	P-A=17.8 P-S=7.8 P-X=0.7	$\text{H}(\text{P})$

1,3,3,3-Tetrafluoro-2-trifluoromethylpropene.



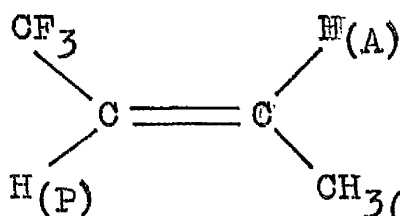
¹⁹F spectrum. External reference CF₃·COOH. No solvent.

Band	Intensity	Chemical Shift (ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	3	-16.3	doublet of quartets of doublets	S-A=19.5 S-X=6.7 S-P=0.9	F(S)
2	3	-12.9	quintet of doublets	X-AS=6.7 X-P=1.8	F(X)
3	1	+32.4	doublet of quartets of quartets	A-P=72.0 A-S=19.5 A-X=6.7	F(A)

¹H spectrum. Internal reference Me₄Si. No solvent.

Band	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	2.69	doublet of quartets of quartets	P-A=72.0 P-X=1.8 P-S=0.9	H(P)

Trans-1,1,1-trifluorobut-2-ene.



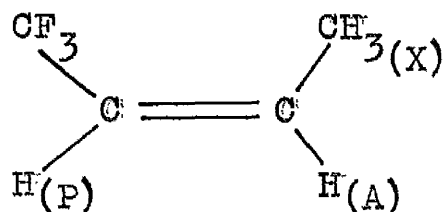
^{19}F spectrum. External reference $\text{CF}_3\cdot\text{COOH}$. No solvent.

Band	Chemical Shift (p.p.m.)	Multiplet Structure	Coupling J (c/s)	Assignment
1	-13.5	doublet of quartets of doublets	$\text{F-P}=6.0$ $\text{F-X}=2.6$ $\text{F-A}=2.1$	F

^1H spectrum. Internal reference Me_4Si . No solvent.

Band	Intensity	Chemical Shift (τ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	1	3.58	doublet of quartets of quartets	$\text{A-P}=15.9$ $\text{A-X}=6.3$ $\text{A-F}=2.1$	H(A)
2	1	4.40	doublet of quartets of quartets	$\text{P-A}=15.9$ $\text{P-F}=6.0$ $\text{P-X}=1.5$	H(P)
3	3	8.21	doublet of quartets of doublets	$\text{X-A}=6.3$ $\text{X-F}=2.6$ $\text{X-P}=1.5$	H(X)

Cis-1,1,1-trifluorobut-2-ene.

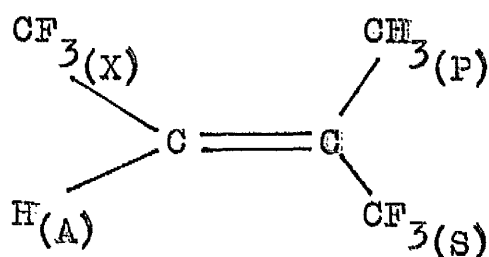


^{19}F spectrum. External reference $\text{CF}_3\cdot\text{COOH}$. Solvent Me_4Si .

Band	Chemical Shift (p.p.m)	Multiplet Structure	Coupling J (c/s)	Assignment
1	-19.8	doublet of quartets	$\text{F-P} = 8.5$ $\text{F-X} = 2.8$	F

The ^1H spectrum of the cis-olefin was masked by the bands of the trans-olefin present in the sample. Thus, the chemical shifts of the hydrogen nuclei in the cis-olefin must be very similar to those in the trans-olefin.

Trans-1,1,1-trifluoro-3-trifluoromethylbut-2-ene.



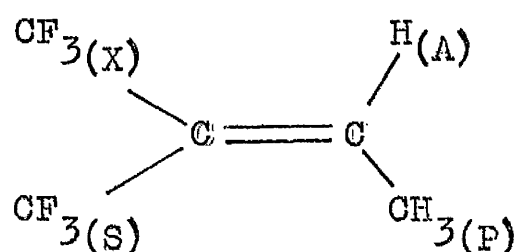
^{19}F spectrum. External reference $\text{CF}_3\cdot\text{COOH}$. Solvent Me_4Si .

Band	Intensity	Chemical Shift (p.p.m.)	Multiplet Structure	Coupling J (c/s)	Assignment
1	1	-17.6	doublet of septets	X-A=8.2 X-PS=1.9	$\text{F}'(\text{X})$
2	1	-5.3	quintet	S-AX=1.9	$\text{F}(\text{S})$

^1H spectrum. Internal reference and solvent Me_4Si .

Band	Intensity	Chemical Shift (γ)	Multiplet Structure	Coupling J (c/s)	Assignment
1	1	3.81	quartet of septets	A-X=8.2 A-PS=1.9	$\text{H}(\text{A})$
2	3	7.91	quintet	P-AX=1.9	$\text{H}(\text{P})$

1,1,1-Trifluoro-2-trifluoromethylbut-2-ene.



^{19}F spectrum. External reference $\text{CF}_3\cdot\text{COOH}$. No solvent.

Band	Intensity	Chemical Shift (ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	1	-17.7	quartet of quartets of doublets	S-X=7.2 S-P=2.4 S-A=1.1	F(S)
2	1	-11.6	quartet of quartets of doublets	X-S=7.2 X-P=2.3 X-P=1.8	F(X)

^1H spectrum. Internal reference Me_4Si . No solvent.

Band	Intensity	Chemical Shift (ppm)	Multiplet Structure	Coupling J (c/s)	Assignment
1	1	3.14	quartet	A-P=7.6	H(A)
2	3	7.98	doublet of septets	P-A=7.6 P-SX=2.3	H(P)

Some further small splitting is apparent in the $\text{H}(\text{A})$ band.

19
Chemical Shift Correlation

(p.p.m. from $\text{CF}_3\cdot\text{COOH}$)

Starred Fluorine Atom	Range	Average	No. of Compounds Investigated
$\text{CF}_3^*\cdot\text{CF}_2\cdot\text{CR}_3$	+0.7 to + 3.6	+1.4	3
$\text{CF}_3^*\cdot\text{CHCl}\cdot\text{CR}_3$	-7.6 to -14.0	-10.6	2
$\text{CF}_3^*\cdot\text{CHBr}\cdot\text{CR}_3$	-10.0 to - 4.9	-8.6	8
$\text{CF}_3^*\cdot\text{CHI}\cdot\text{CR}_3$	-14.6 to -9.6	-12.6	5
$\text{CF}_3^*\cdot\text{CH}(\text{CF}_3)\cdot\text{CR}_3$	-15.6 to -11.0	-13.3	5
$\text{CF}_3^*\cdot\text{CH}(\text{CH}_3)\cdot\text{CR}_3$	-8.2 to -5.8	-7.0	2
$\text{CF}_3^*\cdot\text{CH}_2\cdot\text{CR}_3$	-15.0 to -12.6	-13.5	5
$\text{CF}_3\cdot\text{CF}_2^*\cdot\text{CR}_3$	+24.6 to + 44.0	+37.1	3
$\text{CF}_2^*\text{Br}\cdot\text{CR}_3$	-30.5 to -24.8	-27.7	3
$\text{CF}_2^*\text{I}\cdot\text{CR}_3$	-38.3 to -27.6	-32.9	3
$\text{CF}_2^*\text{H}\cdot\text{CR}_3$		+44.0	1
$\text{CHF}^*\text{Br}\cdot\text{CR}_3$	+59.6 to +65.6	+61.8	3
$\text{CHF}^*\text{I}\cdot\text{CR}_3$		+80.6	1
$\text{CF}_3\cdot\text{CHF}^*\cdot\text{CR}_3$	+111.6 to +115.6	+113.6	2
$\text{CH}_2\text{F}^*\cdot\text{CR}_3$		+142.0	1

Some Reported ^{19}F Chemical Shifts

(p.p.m. from $\text{CF}_3\cdot\text{COOH}$)

Starred Fluorine Atom	Range	Reference
$\text{CF}_3^*\cdot\text{CF}_2\cdot\text{CR}_3$	+ 3.2 to + 11.9	138
$\text{CF}_3^*\cdot\text{CR}_3$	- 19.7 to + 7.7	138,175
$\text{CF}_2^*\cdot(\text{CR}_3)_2$	+ 21.9 to + 57.8	138
$\text{CF}_2^*\text{Br}\cdot\text{CR}_3$	- 22.0 to - 13.0	175
$\text{CHFBr}^*\cdot\text{CR}_3$	+ 70.0 to + 74.0	175
$\text{CH}_2\text{F}^*\cdot\text{CH}_2\cdot\text{CR}_3$	+145.5 to + 149.5	138

Mass Spectrometry.

Mass spectrometry proved helpful in elucidating the structures of various compounds, especially isomers. By an examination of the fragmental ions produced by the breakdown of two or more isomeric 1 : 1 adducts, it was possible to assign structures which proved to be correct in the light of further investigation.

Ions containing isotopic atoms, such as bromine or chlorine, showed isotope peaks in accordance with the natural abundance of such isotopes (Table 24).

Table 24 . Intensities of Isotope Peaks for Combinations of Bromine and Chlorine.

Halogen Present	P	P + 2	P + 4
Br	100	98	
Br ₂	100	195	96
Cl	100	33	
Cl ₂	100	65	11
Br Cl	100	130	32

The major peaks in the mass spectra of pure compounds prepared during this research are presented in tabular form in the following pages, in the same order as they are dealt with in the experimental section.

Table 25 .

3-Chloro-1,1,1,2,2-pentafluoro-3-iodopropane $\text{CF}_3 \cdot \text{CF}_2 \cdot \text{CHClI}$
and 2-Chloro-1,1,1,3,3-pentafluoro-3-iodopropane $\text{CF}_3 \cdot \text{CHCl} \cdot \text{CF}_2 \text{I}$.

m/e	Relative Intensity		Assignment
	$\text{CF}_3 \cdot \text{CF}_2 \cdot \text{CHClI}$	$\text{CF}_3 \cdot \text{CHCl} \cdot \text{CF}_2 \text{I}$	
31	1	12	CF^+
69	<u>100</u>	<u>100</u>	CF_3^+
85	10	42	CF_2Cl^+
87	3	12	CF_2Cl^+
112		46	C_3F_4^+
113	6	78	C_3HF_4^+
127	17	61	I^+
129	1	9	$\text{C}_3\text{HF}_3\text{Cl}^+$
131		4	$\text{C}_3\text{HF}_3\text{Cl}^+$
162		25	ICl^+
164		8	
167	37	67	$\text{C}_3\text{HF}_5\text{Cl}^+$
169	13	22	
177	4	10	CF_2I^+
190	4	19	$\text{C}_2\text{HF}_2\text{I}^+$
259	1	53	$\text{C}_3\text{HF}_5\text{I}^+$
294	50	<u>100</u>	Parent ⁺
296	17	33	

Table 26 .

3,3-Dichloro-1,1,1,2,2-pentafluoropropane $\text{CF}_3\text{CF}_2\text{CHCl}_2$
and 2,3-Dichloro-1,1,1,3,3-pentafluoropropane $\text{CF}_3\text{CHCl}\cdot\text{CF}_2\text{Cl}$.

m/e	Relative Intensity		Assignment
	$\text{CF}_3\cdot\text{CF}_2\cdot\text{CHCl}_2$	$\text{CF}_3\cdot\text{CHCl}\cdot\text{CF}_2\text{Cl}$	
67	19	10	CHFCl^+
69	55	75	$\text{CF}_3^+ \text{ CHFCl}^+$
83	97		CHCl_2^+
85	<u>100</u>	<u>100</u>	$\text{CF}_2\text{Cl}^+ + \text{CHCl}_2^+$
87	26	55	CF_2Cl^+
98	6	21	} $\text{C}_2\text{HF}_2\text{Cl}^+$
100		8	
112		8	C_3F_4^+
117	13		} C_2F_5^+
119	13		
167	10	50	} $\text{C}_3\text{HF}_5\text{Cl}^+$
169	3	18	
182		17	} $\text{C}_3\text{F}_4\text{Cl}_2^+$
184		12	
186		0.2	
197	14	8	} Parent ⁺
202	20	5	
204	13	3	
206	2	0.6	

Table 27 .

1-Bromo-2-chloro-1,1-difluoroethane $\text{CF}_2\text{Br}\cdot\text{CH}_2\text{Cl}$.

m/e	Relative Intensity	Assignment
49	11	CH_2Cl^+
51	4	$\text{CH}_2\text{Cl}^+ + \text{CHF}_2^+$
64	6	$\text{C}_2\text{H}_2\text{F}_2^+$
79	3	} Br^+
81	4	
99	<u>100</u>	$\text{C}_2\text{H}_2\text{F}_2\text{Cl}^+$
100	3	
101	31	$\text{C}_2\text{H}_2\text{F}_2\text{Cl}^+$
129	5	} CF_2Br^+
131	5	
178	1.8	} Parent ⁺
180	1.3	
182	0.8	

Table 28 . 1,1-Difluoroiodoethylene $\text{CF}_2\text{:CHI}$

Only one main peak at m/e 190 was shown, due to the parent ion.

Table 29 .

1,1,1,3,3-Pentafluoro-2-trifluoromethyl-3-iodopropaneand 1,1,1,2,2,4,4,4-Octafluoro-3-iodobutane $\text{CF}_3\text{CF}_2\text{CHI}\cdot\text{CF}_3$.

m/e	Relative Intensity		Assignment
	$(\text{CF}_3)_2\text{CH}\cdot\text{CF}_2\text{I}$	$\text{CF}_3\text{CF}_2\text{CHI}\cdot\text{CF}_3$	
31	3		CF^+
51	1		CHF_2^+
69	62	26	CF_3^+
82	2	5	C_2HF_2^+
93	3	2	C_3F_3^+
113	17	20	C_3HF_4^+
119		2	C_2F_5^+
127	22	34	I^+
133		2	
146		7	IF^+
163		8	C_4HF_6^+
177	45		CF_2I^+
181	3		C_4F_7^+
190		2	$\text{C}_2\text{HF}_2\text{I}^+$
201	<u>100</u>	1	C_4HF_8^+
208		10	$\text{C}_2\text{F}_3\text{I}^+$
221	2		$\text{C}_3\text{HF}_3\text{I}^+$
258		15	$\text{C}_3\text{F}_5\text{I}^+$
328	10	<u>100</u>	Parent ⁺

Table 30 .

3-Bromo-1,1,1,3,3-pentafluoropropane $\text{CF}_3\cdot\text{CH}_2\cdot\text{CF}_2\text{Br}$
and 2-Bromo-1,1,1,3,3-pentafluoropropane $\text{CF}_3\cdot\text{CHBr}\cdot\text{CHF}_2$.

m/e	Relative Intensity		Assignment
	$\text{CF}_3\cdot\text{CH}_2\cdot\text{CF}_2\text{Br}$	$\text{CF}_3\cdot\text{CHBr}\cdot\text{CHF}_2$	
31	14	22	CF^+
45	14	12	$\text{C}_2\text{H}_2\text{F}^+$
51	4	<u>100</u>	CHF_2^+
59	4	7	
69	85	11	CF_3^+
110		6	CFBr^+
112		15	$\text{C}_3\text{F}_4^+ + \text{CFBr}^+$
113	9		C_3HF_4^+
129	26	6	CF_2Br^+
131	26	6	
133	<u>100</u>	5	$\text{C}_3\text{H}_2\text{F}_5^+$
142		14	$\text{C}_2\text{HF}_2\text{Br}^+$
144		14	
161		27	$\text{C}_2\text{HF}_3\text{Br}^+$
163		27	
193	5	7	$\text{C}_3\text{H}_2\text{F}_4\text{Br}^+$
195	5	7	
212	1	54	Parent ⁺
214	1	54	

Table 31 .

2,3-Dibromo-1,1,1,3,3-pentafluoropropane $\text{CF}_3 \cdot \text{CHBr} \cdot \text{CF}_2\text{Br}$.

m/e	Relative Intensity	Assignment	
31	14	CF ⁺	
51	5	CHF ₂ ⁺	
69	68	CF ₃ ⁺	
79	4	}	Br ⁺
81	4		
82	6		C ₂ HF ₃ ⁺
113	12		C ₃ HF ₄ ⁺
129	24	}	CF ₂ Br ⁺
131	24		
142	6	}	C ₂ HF ₂ Br ⁺
144	6		
211	<u>100</u>	}	C ₃ HF ₅ Br ⁺
213	96		
270	2	}	C ₃ F ₄ Br ₂ ⁺
272	4		
274	2		

Table 32 .

1,1,1,2,4,4,4-pentafluoro-3-iodobutane $\text{CF}_3\text{-CHF}\cdot\text{CHI}\cdot\text{CF}_3$.

Isomer A and Isomer B .

m/e	Relative Intensity		Assignment
	isomer A	isomer B	
31	16	8	CF^+
51	55	16	CHF_2^+
69	<u>100</u>	79	CF_3^+
95	32	34	$\text{C}_3\text{H}_2\text{F}_3^+$
113	19	13	C_3HF_4^+
127	41	66	I^+
128	14	15	HI^+
145	21	20	$\text{C}_4\text{H}_2\text{F}_5^+$
148	12	5	
175	10		
177		10	CF_2I^+
209	6	6	$\text{C}_2\text{F}_4\text{I}^+$
219	10	4	
241	6	8	$\text{C}_3\text{H}_2\text{F}_4\text{I}^+$
310	79	<u>100</u>	Parent ⁺

Table 33 .

1,1,1,3-Tetrafluoro-3-iodo-2-trifluoromethylpropane

m/e	Relative Intensity	Assignment
31	17	CF^+
51	53	CHF_2^+
69	<u>100</u>	CF_3^+
75	11	C_3HF_2^+
95	20	$\text{C}_3\text{H}_2\text{F}_3^+$
113	43	C_3HF_4^+
114	58	$\text{C}_3\text{H}_2\text{F}_4^+$
127	70	I^+
128	13	HI^+
145	82	$\text{C}_4\text{H}_2\text{F}_5^+$
159	59	CHF_2I^+
163	35	C_4HF_6^+
177	17	CF_2I^+
183	55	$\text{C}_4\text{H}_2\text{F}_7^+$
196	30	CF_3I^+
272	10	$\text{C}_4\text{H}_2\text{F}_5\text{I}^+$
291	1	$\text{C}_4\text{H}_2\text{F}_6\text{I}^+$
310	59	Parent ⁺

Table 34.

1,1,1,2,4,4,4-Heptafluoro-2-iodobutane $\text{CF}_3\text{CFI}\cdot\text{CH}_2\text{CF}_3$.

m/e	Relative Intensity	Assignment
31	10	CF^+
45	7	$\text{C}_2\text{H}_2\text{F}^+$
51	9	CHF_2^+
69	<u>100</u>	CF_3^+
75	10	C_3HF_2^+
95	10	$\text{C}_3\text{H}_2\text{F}_3^+$
113	23	C_3HF_4^+
114	33	$\text{C}_3\text{H}_2\text{F}_4^+$
119	8	C_2F_5^+
127	66	I^+
128	30	HI^+
133	8	$\text{C}_3\text{H}_2\text{F}_5^+$
145	19	$\text{C}_4\text{H}_2\text{F}_5^+$
163	48	C_4HF_6^+
164	10	$\text{C}_4\text{H}_2\text{F}_6^+$
177	18	CF_2I^+
183	54	$\text{C}_4\text{H}_2\text{F}_7^+$
196	11	CF_3I^+
227	8	$\text{C}_2\text{F}_4\text{I}^+$
310	47	Parent ⁺

Table 35 .

3-Bromo-1,1,1,3-tetrafluoropropane $\text{CF}_3 \cdot \text{CH}_2 \cdot \text{CHFBr}$
and 2-Bromo-1,1,1,3-tetrafluoropropane $\text{CF}_3 \cdot \text{CHBr} \cdot \text{CH}_2\text{F}$.

m/e	Relative Intensity		Assignment
	$\text{CF}_3 \cdot \text{CH}_2 \cdot \text{CHFBr}$	$\text{CF}_3 \cdot \text{CHBr} \cdot \text{CH}_2\text{F}$	
27	11	23	C_2H_3^+
31	9	18	CF^+
33	3	36	CH_2F^+
45	11	27	$\text{C}_2\text{H}_2\text{F}^+$
51	56	<u>100</u>	CHF_2^+
64	10	27	$\text{C}_2\text{H}_2\text{F}_2^+$
65	5	10	$\text{C}_2\text{H}_3\text{F}_2^+$
69	57	91	CF_3^+
95	11	30	$\text{C}_3\text{H}_2\text{F}_3^+$
105	2	15	$\text{C}_2\text{H}_2\text{Br}^+$
107	2	15	
111	14	29	CHFBr^+
113	19	58	$\text{CHFBr}^+ + \text{C}_3\text{HF}_4^+$
114	5	69	$\text{C}_3\text{H}_2\text{F}_4^+$
115	<u>100</u>	46	$\text{C}_3\text{H}_3\text{F}_4^+$
125		15	
142		19	$\text{C}_2\text{HF}_2\text{Br}^+$
144		19	
194	9	70	Parent+
196	11	71	

Table 36 .

2,3-Dibromo-1,1,1,3-tetrafluoropropane $\text{CF}_3\cdot\text{CHBr}\cdot\text{CHFBr}$.Isomers E and F.

m/e	Relative Intensity		Assignment
	isomer E	Isomer F	
31	20	19	CF^+
45	17	17	$\text{C}_2\text{H}_2\text{F}^+$
51	59	57	CHF_2^+
64	20	16	$\text{C}_2\text{H}_2\text{F}_2^+$
69	74	64	CF_3^+
111	29	27	CHFBr^+
113	38	35	$\text{CHFBr}^+ + \text{C}_3\text{HF}_4^+$
129	10	10	CF_2Br^+
131	10	10	
193	<u>100</u>	<u>100</u>	$\text{C}_3\text{H}_2\text{F}_4\text{Br}^+$
195	100	100	
232	0.4	0.5	$\text{C}_3\text{F}_3\text{Br}_2^+$
234	0.8	1.0	
236	0.4	0.5	
253	0.7	0.6	$\text{C}_3\text{H}_2\text{F}_3\text{Br}_2^+$
255	1.2	1.1	
257	0.7	0.6	
272	4	1.5	Parent ⁺ ..
274	8	2.9	
276	4	1.5	

Table 37 .

1,1,1-Trifluoro-2-iodo-3-trifluoromethylbutaneIsomers C and D.

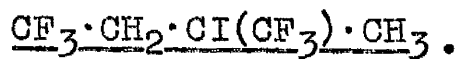
m/e	Relative Intensity		Assignment
	Isomer C	Isomer D	
27	4	6	C_2H_3^+
39	7	2	C_3H_3^+
47	3	11	$\text{C}_2\text{H}_4\text{F}^+$
51	20	27	CHF_2^+
64	4	6	$\text{C}_2\text{H}_2\text{F}_2^+$
65	15	22	$\text{C}_2\text{H}_3\text{F}_2^+$
69	18	26	CF_3^+
88		12	$\text{C}_4\text{H}_2\text{F}_2^+$
89	11	13	$\text{C}_4\text{H}_3\text{F}_2^+$
95	27	41	$\text{C}_3\text{H}_2\text{F}_3^+$
109	8	11	$\text{C}_4\text{H}_4\text{F}_3^+$
115	19	28	$\text{C}_3\text{H}_3\text{F}_4^+$
127	19	27	I^+
128	19	19	$\text{C}_4\text{H}_4\text{F}_4^+ + \text{HI}^+$
139	16	22	$\text{C}_5\text{H}_3\text{F}_4^+$
159	72	77	$\text{C}_5\text{H}_4\text{F}_5^+$
160	11	9	$\text{C}_5\text{H}_5\text{F}_5^+$
179	16	36	$\text{C}_5\text{H}_5\text{F}_6^+$
209	3	3	$\text{C}_2\text{HF}_3\text{I}^+$
306	<u>100</u>	<u>100</u>	Parent ⁺

Table 38 .

1,1,1-Trifluoro-3-iodo-2-trifluoromethylbutane

m/e	Relative Intensity	Assignment
27	9	C_2H_3^+
39	10	C_3H_3^+
47	89	$\text{C}_2\text{H}_4\text{F}^+$
51	8	CHF_2^+
59	5	$\text{C}_3\text{H}_4\text{F}^+$
64	6	$\text{C}_2\text{H}_2\text{F}_2^+$
65	7	$\text{C}_2\text{H}_3\text{F}_2^+$
69	30	CF_3^+
89	10	$\text{C}_4\text{H}_3\text{F}_2^+$
95	25	$\text{C}_3\text{H}_2\text{F}_3^+$
109	9	$\text{C}_4\text{H}_4\text{F}_3^+$
113	14	C_3HF_4^+
115	7	$\text{C}_3\text{H}_3\text{F}_4^+$
127	31	I^+
128	19	$\text{C}_4\text{H}_4\text{F}_4^+ + \text{HI}^+$
139	11	$\text{C}_5\text{H}_3\text{F}_4^+$
155	24	$\text{C}_2\text{H}_4\text{I}^+$
159	71	$\text{C}_5\text{H}_4\text{F}_5^+$
179	86	$\text{C}_5\text{H}_5\text{F}_6^+$
227	8	$\text{C}_2\text{F}_4\text{I}^+$
306	<u>100</u>	Parent +

Table 39.

1,1,1-Trifluoro-3-iodo-3-trifluoromethylbutane

m/e	Relative Intensity	Assignment
27	12	C_2H_3^+
39	16	C_3H_3^+
41	14	C_3H_5^+
43	13	C_2F^+
47	16	$\text{C}_2\text{H}_4\text{F}^+$
51	25	CHF_2^+
65	14	$\text{C}_2\text{H}_3\text{F}_2^+$
69	38	CF_3^+
91	60	$\text{C}_4\text{H}_5\text{F}_2^+$
95	25	$\text{C}_3\text{H}_2\text{F}_3^+$
111	<u>100</u>	$[\text{C}_4\text{H}_6\text{F}_3^+]$
113	14	$\text{C}_3\text{H}_4\text{F}_4^+$
115	19	$\text{C}_3\text{H}_3\text{F}_4^+$
127	34	I^+
128	20	$\text{C}_4\text{H}_4\text{F}_4^+ + \text{HI}^+$
139	9	$\text{C}_5\text{H}_3\text{F}_4^+$
155	10	$\text{C}_2\text{H}_4\text{I}^+$
159	39	$\text{C}_5\text{H}_4\text{F}_5^+$
179	13	$\text{C}_5\text{H}_5\text{F}_6^+$
227	28	$\text{C}_2\text{F}_4\text{I}^+$
238	57	$[\text{C}_4\text{H}_6\text{F}_3\text{I}^+]$
306	38	Parent $^+$

Table 40.

2-Bromo-1,1,1-trifluorobutane $\text{CF}_3 \cdot \text{CHBr} \cdot \text{CH}_2 \cdot \text{CH}_3$ -
 and 3-Bromo-1,1,1-trifluorobutane $\text{CF}_3 \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{CH}_3$.

m/e	Relative Intensity		Assignment
	$\text{CF}_3 \cdot \text{CHBr} \cdot \text{CH}_2 \cdot \text{CH}_3$	$\text{CF}_3 \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{CH}_3$	
27	33	39	C_2H_3^+
28	42	9	C_2H_4^+
29	54	21	C_2H_5^+
31	30	13	CF^+
40		49	C_3H_4^+
41	46	56	C_3H_5^+
45	28		$\text{C}_2\text{H}_2\text{F}^+$
47	58	<u>100</u>	$\text{C}_2\text{H}_4\text{F}^+$
51	9	18	$\text{CHF}_2^+ + \text{C}_4\text{H}_3^+$
59	16		$\text{C}_3\text{H}_4\text{F}^+$
64	14	14	$\text{C}_2\text{H}_2\text{F}_2^+$
69	13	53	CF_3^+
73	<u>100</u>		$\text{C}_4\text{H}_6\text{F}^+$
77	15	14	$\text{C}_3\text{H}_3\text{F}_2^+$
91	74	84	$\text{C}_4\text{H}_5\text{F}_2^+$
95	10	12	$\text{C}_3\text{H}_2\text{F}_3^+$
111	76	93	$\text{C}_4\text{H}_6\text{F}_3^+$
190	14	13	}
192	14	13	
			Parent*

Table 41.

Trans-4-bromo-1,1,1-trifluorobut-2-ene $\text{CF}_3 \cdot \text{CH} : \text{CH} \cdot \text{CH}_2 \text{Br}$.

m/e	Relative Intensity	Assignment
28	30	C_2H_4^+
29	33	
31	63	CF^+
32	20	CHF^+
38	10	C_3H_2^+
39	43	C_3H_3^+
41	9	
43	12	C_2F^+
45	32	$\text{C}_2\text{H}_2\text{F}^+$
47	11	$\text{C}_2\text{H}_4\text{F}^+$
59	48	$\text{C}_3\text{H}_4\text{F}^+$
69	18	CF_3^+
74	17	C_3F_2^+
89	40	$\text{C}_4\text{H}_3\text{F}_2^+$
90	13	$\text{C}_4\text{H}_4\text{F}_2^+$
91	10	
109	<u>100</u>	$\text{C}_4\text{H}_4\text{F}_3^+$
111	12	
169	5	}
171	5	
188	16	}
190	16	
		Parent +

Table 42.

2,3-Dibromo-1,1,1-trifluorobutane $\text{CF}_3 \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{CH}_3$.

Erythro and threo.

m/e	Relative Intensity		Assignment
	Erythro	Threo	
29	7		C_2H_5^+
31	4	10	CF^+
38		13	C_3H_2^+
39	7	17	C_3H_3^+
43	15	15	C_2F^+
45	18		$\text{C}_2\text{H}_2\text{F}^+$
47		30	$\text{C}_2\text{H}_4\text{F}^+$
59	3	24	$\text{C}_3\text{H}_4\text{F}^+$
69		27	CF_3^+
73	<u>100</u>		$[\text{C}_4\text{H}_6\text{F}^+]$
74	9		C_3F_2^+
75	4		C_3HF_2^+
89		36	$\text{C}_4\text{H}_3\text{F}_2^+$
90		10	$\text{C}_4\text{H}_4\text{F}_2^+$
95		13	$\text{C}_3\text{H}_2\text{F}_3^+$
107		16	$\text{C}_2\text{H}_2\text{Br}^+$
109	1.0	75	$\text{C}_2\text{H}_2\text{Br}^+ + \text{C}_4\text{H}_4\text{F}_3^+$
189	1.2	<u>100</u>	
191	1.2	<u>100</u>	$\text{C}_4\text{H}_5\text{F}_3\text{Br}^+$
268	0.1	3	
270	0.2	6	Parent ⁺
272	0.1	3	

Ultraviolet Spectra.

The ultraviolet spectra were recorded for the sake of posterity on any pure samples, containing a C-I bond, that remained towards the completion of the present work. The results are listed below.

Ultraviolet Spectra in the Vapour Phase.

Compound	$\lambda_{\text{Max.}}$	$\epsilon_{\text{Max.}}$	$\lambda_{\text{Min.}}$	$\epsilon_{\text{Min.}}$
$(\text{CF}_3)_2\text{CH}\cdot\text{CHFI}$	267-268	625	223	18
$\text{CF}_3\cdot\text{CHI}\cdot\text{CHF}\cdot\text{CF}_3$ (isomer A)	269-270	242	235	116
$\text{CF}_3\cdot\text{CHI}\cdot\text{CHF}\cdot\text{CF}_3$ (isomer B)	270-273	230	222	24
$\text{CF}_3\cdot\text{CHI}\cdot\text{CH}(\text{CF}_3)\cdot\text{CH}_3$ (isomer C)	267-269	199	234-235	26
$\text{CF}_3\cdot\text{CHI}\cdot\text{CH}(\text{CF}_3)\cdot\text{CH}_3$ (isomer D)	267-269	202	238	59
$\text{CF}_3\cdot\text{CF}_2\cdot\text{CHClI}$	278	607	226-227	14
$\text{CF}_3\cdot\text{CF}_2\cdot\text{CHI}\cdot\text{CF}_3$	268-269	196	256	177

The spectra were recorded on a Unicam S.P. 700 spectrophotometer.

E X P E R I M E N T A L
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EXPERIMENTAL

General Techniques

Many of the substances involved in this work were either gases or volatile liquids of undetermined toxicities, and were therefore manipulated in a conventional Pyrex vacuum-system. The system comprised a storage section of over 50 litres capacity, a section designed for the measurement of molecular weights by Regnault's method, and a set of interconnected traps suitable for the separation of mixtures of low-boiling substances by the technique of fractional condensation in vacuo. Each separate unit contained a mercury manometer and the units were connected by high-vacuum stopcocks. The apparatus was evacuated to pressures of 10^{-2} to 10^{-3} mm. of mercury by means of an Edwards two-stage Speedivac pump and to ca. 10^{-4} mm. of mercury by incorporating a mercury diffusion pump. The volume of each section of the system was determined prior to use, so that the volumes of reactants and products could be conveniently measured.

Reactions at pressures between one and eight atmospheres were conveniently carried out in sealed tubes of silica, Pyrex, or Dreadnought glass. The tube was attached to the vacuum-system by heavy-wall rubber tubing, evacuated, flamed with a bunsen burner to remove traces of moisture, cooled in liquid nitrogen, and then charged with the reactants. The tube was sealed in vacuo at -196° and

allowed to warm to room temperature in a steel guard tube. Irradiation was carried out by means of a Hanovia S.500 mercury vapour lamp, placed 10-15 cm. from the tube (unless stated to the contrary).

When reaction was complete, the tube was cooled in liquid nitrogen, attached to the vacuum-system by heavy-wall tubing, the seal broken in vacuo, and the volatile products were transferred to the vacuum-system.

Non-condensable gaseous products were absorbed on charcoal at -196° , which had previously been activated by heating in vacuo to 300° (30 min.). The volume of the gas absorbed was measured by heating the charcoal finger to 300° (30 min) and allowing the gas to expand into a bulb of known volume.

Separation of the condensable volatile material was affected by fractional condensation at low pressures (up to 3 mm.). The material to be separated was allowed to warm up slowly from -196° , and was then passed through a series of traps cooled in baths at successively lower temperatures. The baths used were organic solvents cooled with either liquid nitrogen or solid carbon dioxide until a stiff "slush" of the melting solvent was obtained.

The solvents used and their "slush-bath" temperatures are as follows:-

Melting carbon tetrachloride	-28°
" dichloroethane	-36°
" chlorobenzene	-45°
" chloroform	-64°
Methylated spirits/solid CO ₂	-78°
Melting toluene	-95°
" carbon disulphide	-112°
" 30°-40° petroleum ether	-130°
Liquid nitrogen	-196° .

A fraction which condensed in a trap cooled in methylated spirits containing solid carbon dioxide is described as the "-78° fraction" and similarly "-130° fraction" refers to the material which condensed in a trap cooled in melting 30°-40° petroleum ether.

Each fraction was normally examined by molecular weight determination, infrared spectroscopy, and gas-liquid chromatography.

Pure compounds were isolated by repeated fractional condensation, by distillation at atmospheric or reduced pressure, or by gas-liquid chromatographic separation. Preparative gas-liquid chromatography (g.l.c.) proved a very valuable technique for the separation of products with comparable boiling points.

Gas-liquid chromatographic analysis was carried out either on a Perkin-Elmer Vapour Fraktometer (Models 116, 154B, 451, or 452), or a Griffin and George D6 instrument fitted with a gas-density detector. The columns used for analysis were made of glass or aluminium (i.d. 4mm., length 2-8m.) packed with Celite impregnated with 30% (by weight) didecylphthalate (D.D.P.), trixylylphosphate (T.X.P.), dinonylphthalate (D.N.P.), or silicone oil (M.S. 550). These columns were also used for preparative work on the Perkin-Elmer Vapour Fraktometers. For large-scale preparative separations, a Wilkens Aerograph Autoprep, fitted with aluminium columns (i.d. 22mm., length 6m.) packed with Celite impregnated with 30% (by weight) of the appropriate stationary phase, was used. Gaseous samples (ca. 1ml. gas for analysis; 15-20 ml. gas for preparative work) were introduced on to the column from a gas-cell. Liquid samples were injected on to the column through a self-sealing Neoprene disc by means of a micro-hypodermic syringe. Where necessary, the various components of a mixture were individually collected by connecting "trapping-cells" to the gas-outlet of the Fraktometer. These consisted of a glass spiral tube immersed in a suitable "slush-bath" capable of condensing the issuing gas.

Infrared (i.r.) spectra were recorded on Perkin-Elmer model 137 (Infracord) or model 21 spectrophotometers, the latter machine being used to record the spectra of pure compounds. Vapours were examined in tapped cells (path length 10 cm.), liquids of low vapour pressure (\leq 3mm. at room temperature),

as films, and solids as mulls with both Nujol and hexachlorobutadiene.

Nuclear magnetic resonance (n.m.r.) spectra were recorded on a Perkin-Elmer R10 high-resolution nuclear magnetic resonance spectrometer operating at 60.00 Mc/s for ^1H spectra and 56.46 Mc/s for ^{19}F spectra using tetramethylsilane and trifluoroacetic acid as respective references.

Mass spectra were recorded on a A.E.I. M.S.2H mass spectrometer; spectra were produced by an electron beam of energy 70 eV. and were recorded using a constant accelerating voltage of 2 Kv. with electromagnetic scanning.

Preparation of Starting Materials.

Preparation of hydrogen bromide.

Bromine (160g., 1.0 mole) was added dropwise (6 hr.) to an excess of dried tetralin (400g.) at room temperature, though initial warming was required. The gas evolved was bubbled through tetralin to remove traces of bromine, passed over phosphorus pentoxide to remove traces of water, and purified by fractional condensation in vacuo to give hydrogen bromide (72g., 0.89 mole, 89%), (Found: \underline{M} , 81. Calc. for HBr: \underline{M} , 81) condensing at -196° .

Later a cylinder of hydrogen bromide was obtained for use in the department.

Preparation of silver trifluoroacetate, $\text{CF}_3\cdot\text{CO}_2 \text{Ag}$.

Sodium carbonate solution (2M., ca. 1,100ml.) was slowly added to a solution of silver nitrate (350g., 2.06moles) in water (ca. 700 ml.), in a blackened beaker, until no further pale yellow precipitate of silver carbonate was obtained. The precipitate was filtered off and washed several times with water until free from nitrate ions.

Trifluoroacetic acid (228g., 2.06 moles) was added slowly to a slurry of the silver carbonate in water (250 ml.) until a colourless solution was obtained. This solution was filtered and the water removed under reduced pressure, with the temperature kept below 50° . Blackened apparatus was used to avoid decomposition of the silver salt.

The silver trifluoroacetate (431g., 1.95 moles, 95%) so obtained was dried over phosphorus pentoxide in a vacuum-desiccator (2 weeks) before use.

Preparation of trifluoroiodomethane, CF_3I .

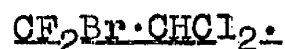
Silver trifluoroacetate (431g., 1.95 moles) and iodine (381g., 2.93 moles) were thoroughly dried, powdered, and intimately mixed. The mixture was transferred to a round-bottomed flask (3l.), fitted with a nitrogen inlet, and an air condenser attached to a scrubbing tower down which was passed an aqueous solution of sodium hydroxide (25% w/w.) and sodium thiosulphate (5% w/w). The scrubbing tower was connected to a Drechsel bottle, containing the alkaline

thiosulphate solution (200 ml.), and thence, via a drying train containing phosphorus pentoxide, to two traps cooled to -78° .

Dry nitrogen was passed through the apparatus (10 min.) and the mixture of silver trifluoroacetate and iodine was then heated gently until a steady evolution of gas was observed. Towards the end of the reaction (3 hr.), the mixture was heated more vigorously until the gas evolution ceased. The crude product (360g.) was taken into the vacuum-system and purified by fractional condensation in vacuo to give pure trifluoroiodomethane (360g., 1.84 moles, 94%) (Found: \underline{M} , 196. Calc. for CF_3I : \underline{M} , 196), condensing at -130° . The i.r. spectrum corresponded to that of a known pure sample, and g.l.c. (4m. D.D.P. at 20°) showed only one peak.

Further preparations of trifluoroiodomethane gave yields varying between 83% and 94%.

Preparation of 1-bromo-2,2-dichloro-1,1-difluoroethane,



Hydrogen bromide (36.4g., 0.45 mole) and 1,1-dichlorodifluoroethylene (60.0g., 0.45 mole) were introduced into a large photochemical reactor. The reactor was constructed from a Pyrex flask (20l) with a C.70 ground glass socket into which was fitted a water cooled, double-walled, silica insert with a Hanovia S.500 mercury vapour ultraviolet lamp. The reactants were admitted through a tapped side-arm, and the course of the reaction was followed by the pressure drop,

measured on a mercury manometer.

After being allowed to mix (20 min.), the reactants were irradiated until no further pressure drop was observed (90 min.). The products were transferred to an external trap cooled to -196° . Two similar runs were made.

Distillation of the combined products (280g.) at atmosphere pressure through a vacuum-jacketed silvered column (20cm.), packed with glass helices, gave 1-bromo-2,2-dichloro-1,1-difluoroethane (230g., 1.08 moles, 80%), b.p. $95-99^{\circ}$ (lit.¹⁷⁶ b.p. 88.5° at 621 mm.).

Dehalogenation of 1-bromo-2,2-dichloro-1,1-difluoroethane.

1-Bromo-2,2-dichloro-1,1-difluoroethane (230g., 1.08 moles) was added slowly to a stirred suspension of activated zinc dust (150g., 2.27 moles) in refluxing ethanol (400 ml.). The volatile products were swept from the reaction flask with dry nitrogen into a trap cooled to -130° . Subsequent purification of the volatile products by fractional condensation in vacuo gave pure chloro-1,1-difluoroethylene (90.8g., 0.93 mole, 86%), (Found : \underline{M} , 98. Calc. for C_2HF_2Cl : \underline{M} , 98.5) condensing at -130° . The i.r. spectrum and g.l.c. (4m. D.D.P. at 20°) examination showed no impurity.

Addition of Trifluoroiodomethane to Chloro-1,1-
difluoroethylene.

A. Photochemically.

1. For complete or almost complete conversion and further
irradiation.
- a) Irradiation period of 150 hr.

Trifluoroiodomethane (19.76g., 100.7 m moles) and chloro-1,1-difluoroethylene (4.83g., 49.2 m moles) were condensed in vacuo into two silica tubes (total capacity 700 ml.) and the vapour phase irradiated (150 hr.). The lower portions of the two tubes (5 cm.) were shielded from the ultraviolet light.

The volatile products were transferred to the vacuum-system and were separated by fractional condensation into the following fractions.

- i) Chlorotrifluoromethane (0.63g., 5.9m moles, 12%) (Found : M, 106. Calc. for CClF_3 : M, 104.5), condensing at -196° , and shown by i.r. spectroscopy to be contaminated with small amounts of hexafluoroethane and trifluoromethane.
- ii) Unchanged trifluoroiodomethane (11.2g., 56.9m moles, 56%) (Found : M, 195. Calc. for CF_3I : M, 196), condensing at -130° , and confirmed by a comparison of its i.r. spectrum and g.l.c. retention time (4m. D.D.P. at 200°) with those of an authentic pure sample.

iii) A -95° fraction (2.64g., 13.2 mmoles) (Found: M, 200) was shown by g.l.c. (2m. D.D.P. at 50°) to contain eight components. The i.r. spectrum showed bands at 3.35(w), 4.45(w), 5.80(doublet,m), 7.53(s), 7.95(s), 8.20(s), 8.50(s), 8.65(s), 9.0(m), 9.35(s), 9.70(s), 10.10(m), 10.48(m), 11.13(m), 11.83(m), 13.45(m), and 14.25(s) μ .

iv) A -78° fraction (6.84g., 29.7 mmoles) (Found: M, 230) was shown by g.l.c. (2m. D.D.P. at 102°) to contain the same eight components as in the previous fraction and six additional ones. The i.r. spectrum showed additional bands to those of the last fraction at 8.15(s), 8.88(s), 10.23(w), 11.38(w), 12.06(s), 12.80(w), and 13.55(w) μ .

Non-volatile material (3.0g.) remained in the reaction tubes, and its i.r. spectrum showed bands at 3.41(w), 5.72(m), 7.32(s), 7.45(s), 7.55(s), 7.75(s), 7.96(s), 8.14(s), 8.35(s), 8.86(s), 9.00(s), 9.30-9.74(broad, s), 10.24(s), 11.30-11.70(broad m), 12.10(m), 12.50(m), and 13.05(m) μ .

The two main components of the -78° fraction, comprising 64% of the fraction, and present in the ratio 72:28, were separated by g.l.c. (2m. D.D.P. at 95°).

The major component was identified as 3-chloro-1,1,1,2,2-pentafluoro-3-iodopropane, $\text{CF}_3 \cdot \text{CF}_2 \cdot \text{CHClI}$, (3.65g., 12.1 mmoles, 25%) (Found: C, 12.0; H, 0.3%; M, 294. Calc. for $\text{C}_3\text{HClF}_5\text{I}$: C, 12.2; H, 0.3%; M, 294.5) b.p.

(isoteniscope) $95.1 \pm 0.2^\circ$ (lit.¹⁴ b.p. 102°).

The i.r. spectrum showed bands at 3.30(w), 7.27(m), 7.47(s), 7.68(m), 7.83(s), 8.05(s), 8.15(s), 8.29(s), 8.70(s), 8.82(s), 9.00(s), 9.38(m), 9.75(s), 12.05(s), 12.65(m), 12.76(m), 12.85(m), 14.05(m), 14.18(s), 14.25(s), and 14.30(s) μ .

The ^{19}F and ^1H n.m.r. spectra (see Page 41) were consistent with the proposed structure. The ^{19}F spectrum showed three regions of absorption at 0.7 (singlet, intensity 35), 24.6 (doublet of doublets, intensity 8.5), and 41.7 (doublet of doublets, intensity 8) p.p.m. to high field from external trifluoroacetic acid. The ^1H spectrum showed one region of absorption at 4.04 (doublet of doublets-first order interpretation) γ from internal tetramethylsilane at 10.00 γ .

The mass spectrum (Table 25, Page 195) showed a strong parent peak at m/e 294, and the general breakdown pattern was consistent with the proposed structure.

The second component was identified as 2-chloro-1,1,1,3,3-pentafluoro-3-iodopropane, $\text{CF}_3\cdot\text{CHCl}\cdot\text{CF}_2\text{I}$, (1.38g., 4.7 mmoles, 10%) (Found: C, 12.4; H, 0.4%; \underline{M} , 293. $\text{C}_3\text{HClF}_5\text{I}$ requires C, 12.2; H, 0.3%; \underline{M} , 294.5) b.p. (isoteniscope) $98.6 \pm 0.2^\circ$.

The i.r. spectrum showed bands at 3.38(w), 7.47(s), 7.93(s), 8.06(s), 8.21(s), 8.30(s), 8.69(m), 8.74(m), 9.12(s), 9.32(m), 9.37(m), 9.75(s), 10.27(s), 11.12(w), 11.47(m),

11.69(m), 12.12(m), 12.65(m), 12.84(m), 13.60(w), and 14.22(m) μ .

The ^{19}F and ^1H n.m.r. spectra (see Page 46) were consistent with the proposed structure. The ^{19}F spectrum showed three regions of absorption at 28.4 (quartet of doublets, intensity 1), 27.6 (quartet of doublets, intensity 1), and 14.0 (triplet of doublets, intensity 3) p.p.m. to low field from trifluoroacetic acid. The ^1H spectrum showed one region of absorption at 5.12 (sextet-first order interpretation) τ from internal tetramethylsilane at 10.00 τ .

The mass spectrum (Table 25, Page 195) showed a strong parent peak at m/e 294 and the general pattern was consistent with the proposed structure.

Material Balance:- All of the olefin was consumed during reaction; 34% reacted to give the 1:1 adducts. The products represent a 99% recovery (by weight) of input material.

- b) Irradiation period of 192 hr.
- b) Irradiation period of 192 hr.

Trifluoroiodomethane (6.76g., 34.6m moles) and chloro-1,1-difluoroethylene (1.76g., 17.9m moles) were condensed into a silica tube (capacity 350ml.). The vapour phase was irradiated (192 hr.) and the products were worked up as in the previous experiment to give:-

i) a -196° fraction (0.28g., 2.5m moles) (Found : \underline{M} , 110) consisting of chlorotrifluoromethane (0.22g., 2.1m moles, 12%) and hexafluoroethane (0.06g., 0.4m mole) contaminated with an unknown component which contained a strong band at $9.8/\mu$ in the i.r. spectrum,

ii) unchanged trifluoriodomethane (3.56g., 18.2m moles, 53%) (Found : \underline{M} , 196. Calc for CF_3I : \underline{M} , 196),

iii) a higher-boiling fraction (3.09g.) shown by g.l.c. (2m. D.D.P. at 101°) to contain the same fourteen components as in the previous experiment, and

iv) non-volatile material (1.51g.).

The two major components of the higher-boiling fraction, present in the ratio 51 : 49, were identified as the 1 : 1 adducts $\text{CF}_3\cdot\text{CF}_2\cdot\text{CHClI}$ (1.00g., 3.39m moles, 19%) and $\text{CF}_3\cdot\text{CHCl}\cdot\text{CF}_2\text{I}$ (0.96g., 3.26m moles, 18%) respectively, by their g.l.c. retention times and i.r. spectra.

Material Balance:- All of the olefin was consumed during the reaction and 37% reacted to give the 1 : 1 adducts. The products represent a 99% recovery (by weight) of input material.

c) Irradiation period of 330 hr.

Trifluoriodomethane (7.42g., 37.7m moles) and chloro-1,1-difluoroethylene (1.93g., 19.9m moles) were

irradiated (330 hr) in a silica tube (capacity 350 ml.) and the products were worked up as in the previous experiments to give:-

i) a -196° fraction (0.23g., 2.0m moles) (Found: M, 115) shown by i.r. spectroscopy to be chlorotrifluoromethane and hexafluoroethane, contaminated with small amounts of trifluoromethane and an unknown component with an i.r. band at 9.8μ ,

ii) unchanged trifluoroiodomethane (3.00g., 15.3m moles, 41%) condensing at -130°,

iii) a mixture (0.81g., 4.1m moles) (Found : M, 198) condensing at -95°, and shown by g.l.c. (4m. D.D.P. at 20°) to be mainly trifluoroiodomethane (0.40g., 2.04m moles, 5%) contaminated with five other components,

iv) a -78° fraction (2.27g.), shown by g.l.c. (2m. D.D.P. at 102°) to contain the five components present in the previous fraction and six additional ones (all these components were present in the comparable fractions from the previous experiments), and

v) non-volatile material (2.6g.).

The two major components of the -78° fraction, present in the ratio 35 : 65, were identified as the 1 : 1 adducts $\text{CF}_3 \cdot \text{CF}_2 \cdot \text{CHClI}$ (0.473g., 1.61m moles, 8%) and $\text{CF}_3 \cdot \text{CHCl} \cdot \text{CF}_2 \text{ I}$ (0.878g., 2.98m moles, 15%) respectively.

Material Balance:- All of the olefin was consumed during the reaction, 23% reacting to give the

1 : 1 adducts. A total of 46% of the trifluoroiodomethane was recovered unchanged. The products represent a 95% recovery (by weight) of input material.

d) Irradiation period of 24 hr.

Trifluoroiodomethane (7.76g., 39.6m moles) and chloro-1,1-difluoroethylene (2.05g., 20.8m moles) were irradiated (24 hr) in an etched silica tube (capacity 350 ml) and the products worked up as in the previous experiments to give:-

i) a -196° fraction (0.10g., 0.7m moles) (Found : \underline{M} , 128) shown by i.r. spectroscopy to be mainly hexafluoroethane and chlorotrifluoromethane with a trace of trifluoromethane,

ii) a -130° fraction (7.58g., 46.2m moles) (Found : \underline{M} , 164) shown by g.l.c. (4m. D.D.P. at 21°) to be a mixture of unchanged trifluoroiodomethane (6.24g., 31.8m moles, 80%) and unchanged olefin (1.34g., 13.6m moles, 66%), and

iii) a -95° fraction (2.21g.) shown by g.l.c. to contain three major components (96%) and five minor components.

Two of the three major components were identified as the 1 : 1 adducts, $\text{CF}_3 \cdot \text{CF}_2 \cdot \text{CHClI}$ (1.80g., 6.12m moles, 85%) and $\text{CF}_3 \cdot \text{CHCl} \cdot \text{CF}_2\text{I}$ (0.15g., 0.50m moles, 7%) present in the ratio 92 : 8 (g.l.c.).

The third major component of the fraction was separated by g.l.c. (2m. D.D.P. at 90°) and identified as 1,1-difluoroiodoethylene, $\text{CF}_2 : \text{CHI}$ (0.05g., 0.29m mole, 4%)

(Found : C, 12.7; H, 0.5%; \underline{M} , 190. Calc. for C_2HF_2I : C, 12.6; H, 0.5%; \underline{M} , 190); the i.r. spectrum was similar to that reported in the literature.¹⁴⁰ The ^{19}F and 1H n.m.r. spectra (see Page 53) were consistent with the proposed structure; the ^{19}F spectrum showed two regions of absorption of equal intensity at 6.0 (doublet of doublets) and 1.7 (doublet of doublets) p.p.m. to low field from external trifluoroacetic acid, and the 1H spectrum showed one region of absorption at 5.27 (doublet of doublets) τ .

The mass spectrum (Table 28 see Page 197) showed a strong parent peak at m/e 190, and the general breakdown pattern was consistent with the proposed structure.

Material Balance:- 34% of the olefin was consumed during the reaction; 93% reacted to give the 1 : 1 adducts and 4% to give 1,1-difluoroiodoethylene. The products represent a 100% recovery (by weight) of input material.

Further similar irradiation reactions for periods of 72hr. and 96hr. resulted in all of the olefin reacting to give the 1 : 1 adducts in yields of 75% and 60% respectively. In the 72hr. reaction, the ratio of the 1 : 1 adducts $CF_3 \cdot CF_2 - CHClI$ and $CF_3 \cdot CHCl \cdot CF_2I$ was 89 : 11, and in the 96 hr. reaction the ratio was 83 : 17. Separation of the adducts on a large scale was carried out by g.l.c. (Autoprep, 6m.D.D.P. at 120°).

II For a small olefin conversion with varying irradiation period and distance from the irradiation source.

a) Irradiation period of 4 hr. at a distance of 50 cm.

Trifluoroiodomethane (10.5g., 53.6 mmoles) and chloro-1,1-difluoroethylene (2.64g., 26.8 mmoles) were sealed in a silica tube (capacity 350 ml.) in vacuo. The vapour phase ^{was} irradiated (4 hr.) at a distance of 50 cm. from the irradiation source, and the products worked up as in the previous experiments to give:-

- i) only a trace of a -196° fraction,
- ii) a -130° fraction (12.59g.) (Found: \underline{M} , 164) shown by i.r. spectroscopy and g.l.c. (4m. D.D.P. at 19°) to be a mixture of trifluoroiodomethane (10.11g., 51.7 mmoles, 96%) and chloro-1,1-difluoroethylene (2.48g., 25.0 mmoles, 93%), and
- iii) a -95° and -78° fraction (0.46g.) shown by g.l.c. (2m. D.D.P. at 100°) to contain six components. The two 1 : 1 adducts, $\text{CF}_3\text{CF}_2\cdot\text{CHClI}$ (0.34g., 1.16 mmoles, 65%) and $\text{CF}_3\cdot\text{CHCl}\cdot\text{CF}_2\text{I}$ (0.03g., 0.12 mmole, 6%), present in the ratio 91:9, and 1,1-difluoroiodoethylene (0.03g., 0.18 mmole, 10%) were the major products in this fraction.

Material Balance:- 6.7% of the olefin was consumed during the reaction; 71% of the reacted olefin gave the 1 : 1 adducts, and 10% gave 1,1-difluoroiodoethylene. The products represent a 99% recovery (by weight) of input material.

b) Irradiation period of 8 hr. at a distance of 10 cm.

Trifluoriodomethane (10.5g., 53.6m moles) and chloro-1,1-difluoroethylene (2.64g., 26.8m moles), sealed in a silica tube (capacity 350 ml.), were irradiated (vapour phase, 8 hr.) at a distance of 10 cm. from the lamp to give:-

- i) a -196° fraction (0.02g., 0.16m mole) (Found: M, 130) shown by i.r. spectroscopy to be mainly hexafluoroethane,
- ii) a -130° fraction (10.55g., 64.3m moles) (Found: M, 166) shown by i.r. spectroscopy and g.l.c. (4m. D.D.P. at 20°) to contain trifluoriodomethane (8.65g., 44.1m moles, 82%) and chloro-1,1-difluoroethylene (1.90g., 19.3m moles, 72%),
- iii) a -95° fraction (0.18g., 0.58m mole) (Found: M, 188) shown by i.r. spectroscopy and g.l.c. (2m. D.D.P. at 105°) to contain five components, the major one of which was identified as 1,1-difluoriodoethylene (0.09g., 0.46m mole, 6%),
- iv) a -78° fraction (1.71g.) shown by g.l.c. (2m.D.D.P. at 105°) to contain eight components, five of which were present in the previous fraction, and
- v) a trace of non-volatile material.

The major components of the -78° fraction were the 1 : 1 adducts $\text{CF}_3 \cdot \text{CF}_2 \cdot \text{CHClI}$ (1.30g., 4.40m moles, 59%) and $\text{CF}_3 \cdot \text{CHCl} \cdot \text{CF}_2\text{I}$ (0.14g., 0.49m mole, 7%) present in the ratio 90 : 10, 1,1-difluoriodoethylene (0.09g., 0.47m mole, 6%), and an unknown component (0.35m mole).

Material Balance:- 28% of the olefin was consumed during the reaction; 65% reacted to give the 1 : 1 adducts and 11% to give 1,1-difluoriodoethylene. The products represent a 95% recovery (by weight) of input material.

c) Irradiation period of 8 hr. at a distance of 50 cm.

Trifluoriodomethane (10.5g., 53.5m moles) and chloro-1,1-difluoroethylene (2.53g., 25.4m moles), sealed in a silica tube (capacity 350 ml.), were irradiated (vapour phase, 8hr.) at a distance of 50cm. from the irradiation source to give:-

- i) a -196° fraction (0.02g., 0.16m mole) (Found: \underline{M} , 128) shown by i.r. spectroscopy to be mainly hexafluoroethane,
- ii) a -130° fraction (12.02g., 71.9m moles) (Found: \underline{M} , 166) shown by i.r. spectroscopy and g.l.c. (4m. D.D.P. at 190°) to be a mixture of trifluoriodomethane (9.84g., 50.2m moles, 94%) and chloro-1,1-difluoroethylene (2.14g., 21.7m moles, 86%), and
- iii) a -95° and -78° fraction (0.84g.) shown by g.l.c. (2m. D.D.P. at 103°) to contain seven components.

The major components of the latter fraction were the 1 : 1 adducts $\text{CF}_3 \cdot \text{CF}_2 \cdot \text{CHClI}$ (0.69g., 2.35m moles, 64%) and $\text{CF}_3 \cdot \text{CHCl} \cdot \text{CF}_2\text{I}$ (0.08g., 0.26m mole, 7%) present in the ratio 90 : 10, 1,1-difluoriodoethylene (0.04g., 0.23m mole, 6%) and an unknown component (0.10m mole) having the same chromatographic retention time as the unknown component in the previous reaction.

Material Balance:- 14% of the olefin was consumed during the reaction; 71% of the reacted olefin gave 1 : 1 adducts and 6% gave 1,1-difluoroiodoethylene. The products represent a 99% recovery (by weight) of input material.

d) Irradiation period of 16 hr. at a distance of 100 cm.

Trifluoroiodomethane (10.5g., 53.6m moles) and chloro-1,1-difluoroethylene (2.64g, 26.8m moles), sealed in a silica tube (capacity 350 ml.), were irradiated (vapour phase, 16 hr.) at a distance of 100cm. from the irradiation source to give:-

i) a -196° fraction (0.01g., 0.08m mole) (Found : M, ca. 120) shown by i.r. spectroscopy to be a mixture of hexafluoroethane and chlorotrifluoromethane,

ii) a -130° fraction (12.24g., 74.4m moles) (Found : M, 165) shown by i.r. spectroscopy to be a mixture of trifluoroiodomethane (9.88g., 50.4m moles, 94%) and chloro-1,1-difluoroethylene (2.36g., 24.0m moles, 90%), and

iii) a combined -95° and -78° fraction (0.83g.) shown by g.l.c. (2m. D.D.P. at 105°) to contain eight components.

The major components of the latter fraction were the 1 : 1 adducts $\text{CF}_3 \cdot \text{CF}_2 \cdot \text{CHClI}$ (0.55g., 1.85m moles, 67%) and $\text{CF}_3 \cdot \text{CHCl} \cdot \text{CF}_2\text{I}$ (0.08g., 0.28m mole, 10%), present in the ratio 87 : 13, 1,1-difluoroiodoethylene

(0.04g., 0.21m mole , 8%), and an unknown component (0.15m mole) having the same chromatographic retention time as the unknown component in the previous reactions.

Material Balance:- 10% of the olefin was consumed during the reaction; 76% of the reacted olefin gave 1 : 1 adducts and 8% gave 1,1-difluoroiodoethylene. The products represent a 99% recovery (by weight) of the input material.

B Thermally.

a) At 195°.

Trifluoroiodomethane (5.76g., 29.4m moles) and chloro-1,1-difluoroethylene (1.55g., 15.7m moles) were recovered unchanged after being heated (195°, 100 hr.) in a Dreadnought tube (capacity 250 ml.).

b) At 225°.

Trifluoroiodomethane (5.89g., 30.3m moles) and chloro-1,1-difluoroethylene (1.50g., 15.2m moles), sealed in a Dreadnought tube (capacity 250 ml.), were heated (225°, 20 hr.) to give, after fractional condensation of the products, the following fractions:

i) a trace of a -196° fraction shown by i.r. spectroscopy to contain trifluoromethane, chlorotrifluoromethane, and hexafluoroethane,

ii) a -130° fraction (5.86g., 33.6 mmole) (Found: \underline{M} , 173) shown by i.r. spectroscopy to be a mixture of trifluoroiodomethane (5.08g., 25.7 mmoles, 85%) and chloro-1,1-difluoroethylene (0.78g., 7.90 mmoles, 52%), and

iii) a combined -95° and -78° fraction (0.45g.) shown by g.l.c. (2m. D.D.P. at 104°) to contain nine components.

The major components of the latter fraction were identified by their g.l.c. retention times as the 1 : 1 adducts $\text{CF}_3 \cdot \text{CF}_2 \cdot \text{CHClI}$ (0.25g., 0.85 mmole, 12%) and $\text{CF}_3 \cdot \text{CHCl} \cdot \text{CF}_2\text{I}$ (0.003g., 0.01 mmole, 1%), present in the ratio 98:2.

Free iodine and tar formed a layer on the inside of the reaction tube; this was not further investigated.

Material Balance: 48% of the olefin was consumed during the reaction; 13% reacted to give the 1 : 1 adducts. The volatile products represent an 85% recovery (by weight) of input material.

Irradiation of 3-chloro-1,1,1,2,2-pentafluoro-3-iodopropane.

A mixture of 3-chloro-1,1,1,2,2-pentafluoro-3-iodopropane (0.71g., 2.43 mmoles) and 2-chloro-1,1,1,3,3-pentafluoro-3-iodopropane (0.07g., 0.24 mmole) was sealed in a silica tube (capacity 100 ml.) and the vapour phase irradiated.

a) After 4 hr.

Fractional condensation gave:-

i) a trace of - 196° fraction shown by i.r. spectroscopy to be a mixture of trifluoriodomethane and chloro-1,1-difluoroethylene, and

ii) a - 36° fraction shown by spectroscopy to be little altered from the reactant mixture. This fraction was re-sealed in the silica tube and re-irradiated.

b) After 24 hr.

Fractional condensation of the volatile products gave:-

i) a - 196° fraction (0.08 g., 0.58 mmole) (Found: M, 136) shown by i.r. spectroscopy to be a mixture of chlorotrifluoromethane (0.04 g., 0.39 mmole, 63%) and trifluoriodomethane (0.04 g., 0.19 mmole, 31%) contaminated with a trace of chloro-1,1-difluoroethylene, and

ii) a -78° fraction (0.70 g.) shown by g.l.c. (2m.D.D.P. at 102°) to contain eight components; the major components were 3-chloro-1,1,1,2,2 - pentafluoro - 3 - iodopropane (0.55 g., 1.89 mmole, 78%), 2-chloro-1,1,1, 3,3 - pentafluoro -3- iodopropane (0.05 g., 0.16 mmole), and 1,1-difluoriodoethylene (0.05 g., 0.27 mmole, 44%).

A trace of non-volatile products and ~~the~~ free iodine were also obtained.

Material balance: The ratio of the halopropanes was unaltered and 23% of the reactants were consumed during the reaction; 63% reacted to give chlorotrifluoromethane, 44% to give 1,1- difluoriodoethylene, and 31% to give

trifluoroiodomethane. The volatile products represent a 100% recovery (by weight) of input material.

Reaction of 3-chloro-1,1,1,2,2-pentafluoro-3-iodopropane
with trifluoroiodomethane.

Reaction 1.

A mixture of trifluoroiodomethane (3.02g., 15.5m moles) and 3-chloro-1,1,1,2,2-pentafluoro-3-iodopropane (0.21g., 0.71m mole), sealed in a silica tube (capacity 100 ml.) and the vapour phase irradiated (47 hr), gave as volatile products the following fractions.

i) A -196° fraction (0.053g., 0.44m mole) (Found: M, 120) shown by i.r. spectroscopy to be chlorotrifluoromethane contaminated with traces of hexafluoroethane and an unknown component showing i.r. bands at 8.65, 8.70, and 9.70μ .

ii) A -130° fraction (2.98g., 15.2m moles, 99%) (Found: M, 196) shown by i.r. spectroscopy to be pure trifluoroiodomethane.

iii) A -95° and -78° fraction (0.195g.) shown by g.l.c. (2m. D. D.P. at 103°) to contain eight components. The major components were 3-chloro-1,1,1,2,2-pentafluoro-3-iodopropane (0.034g., 0.12m mole, 17%), 2-chloro-1,1,1,3,3-pentafluoro-3-iodopropane (0.042g., 0.14m mole, 24%), 1,1-difluoroiodoethylene (0.045g., 0.24m mole, 40%), and

an unknown component (0.23m mole, 25% of this fraction) having a similar g.l.c. retention time to the major ^{component} component in the previous reactions and showing strong i.r. bands at 8.2 and 8.3 μ .

iv) A trace of a non-volatile material.

Material Balance: 83% of the propane reacted; 24% of the reacted propane gave 2-chloro-1,1,1,3,3-pentafluoro-3-iodopropane, 40% gave 1,1-difluoroiodoethylene, and 38% gave the major unknown component. Trifluoroiodomethane (99%) was recovered unchanged. The volatile products represent a 99% recovery (by weight) of input material.

Reaction 2.

A mixture of trifluoroiodomethane (0.572g., 2.92m moles) and 3-chloro-1,1,1,2,2-pentafluoro-3-iodopropane (0.966g., 3.28m moles), sealed in a length of silica tubing (capacity 13 ml.) and the vapour phase irradiated (20 hr.), gave as volatile products the following fractions.

i) A -196° fraction (0.032g., 0.27m mole) (Found: \underline{M} , 124) shown by i.r. spectroscopy to be a mixture of chlorotrifluoromethane, hexafluoroethane, and a trace of an unknown component having i.r. bands at 8.65 and 9.70 μ .

ii) A -130° fraction (0.582g., 2.96m moles, 100%) (Found: \underline{M} , 196) shown by i.r. spectroscopy to be pure trifluoroiodomethane.

iii) a -95° and -78° fraction (0.945g.) shown by g.l.c. (2m. D.D.P. at 104°) to contain seven components. The major components were unchanged 3-chloro-1,1,1,2,2-pentafluoro-3-iodopropane (0.879g., 2.98m moles, 91%) and 1,1-difluoriodoethylene (0.046g., 0.24m mole, 80%). No 2-chloro-1,1,1,3,3-pentafluoro-3-iodopropane was detected.

Material Balance: 9% of the halopropane was consumed during the reaction; 80% reacted to give 1,1-difluoriodoethylene and chlorotrifluoromethane. Trifluoriodomethane (100%) was recovered unchanged. The products represent a 100% recovery (by weight) of input material.

Reactions 3 and 4.

Two further reactions involving trifluoriodomethane and 3-chloro-1,1,1,2,2-pentafluoro-3-iodopropane were carried out and in both cases no 2-chloro-1,1,1,3,3-pentafluoro-3-iodopropane was detected. The main product was, in both reactions, 1,1-difluoriodoethylene.

Reactions of 3-chloro-1,1,1,2,2-pentafluoro-3-iodopropane.

a) Reaction with chlorine.

3-chloro-1,1,1,2,2-pentafluoro-3-iodopropane (0.525g., 1.78m moles) and chlorine (1.26g., 17.8m moles) were condensed in vacuo into a silica tube (capacity 100ml) and the vapour phase was irradiated (36 hr.).

The products were shaken with mercury to remove excess chlorine and transferred to the vacuum-system.

Fractional condensation yielded only a -78° fraction (0.332g.) which was shown by g.l.c. (2m. D.D. P. at 70°) to contain one major component (99%) and a minor one with a shorter g.l.c. retention time.

The major component was identified as 3,3-dichloro-1,1,1,2,2-pentafluoropropane, $\text{CF}_3 \cdot \text{CF}_2 \cdot \text{CHCl}_2$, (0.33g., 1.65m moles, 93%) (Found: C, 17.6; H, 0.5%; $\underline{\text{M}}$, 201. Calc. for $\text{C}_3 \text{HCl}_2 \text{F}_5$: C, 17.7; H, 0.5%; $\underline{\text{M}}$, 203).

The i.r. spectrum showed bands at 3.35(w), 7.44(s), 7.56(m), 7.75(m), 8.12(vs), 8.28(vs), 8.44(s), 8.75(s), 9.39(m), 9.65(s), 10.15(w), 10.44(w), 11.05(w), 11.74(w), 11.94(s), 12.50(s), 13.22(m), 13.80(m), 13.99(s), 14.07(s), and 14.85(w) μ . This spectrum is in general agreement with that in the literature^{11a} though a strong band reported at 10.06 μ is absent.

The ^{19}F and ^1H n.m.r. spectra (see Page 44) were consistent with the proposed structure. The ^{19}F spectrum showed two regions of absorption at 44.0 (doublet of quartets, intensity 10.4) and 3.0 (triplet, intensity 14.5) p.p.m. to high field from external trifluoroacetic acid. The ^1H spectrum showed one region of absorption at 4.12 (triplet) γ .

The mass spectrum (Table 26, Page 196) showed a parent peak, a ^{peak at} m/e 83 corresponding to the ion CHCl_2^+ , and the general breakdown pattern was consistent with the proposed structure.

Material Balance: All of the iodopropane was consumed during the reaction; 93% reacted to give the dichloropropane. The products represent a 94% recovery (molar) of input material.

b) Reaction with powdered potassium hydroxide.

3-Chloro-1,1,1,2,2-pentafluoro-3-iodopropane (0.423g., 1.44 mmoles) was condensed in vacuo onto powdered potassium hydroxide (ca. 5g.) in a flask (10 ml.) and left at 20° for 20 mins.; no reaction occurred.

Reactions of 2-chloro-1,1,1,3,3-pentafluoro-3-iodopropane.

a) Reaction with chlorine.

2-Chloro-1,1,1,3,3-pentafluoro-3-iodopropane (0.256g., 0.87 mmole) and chlorine (0.63g., 8.9 mmoles) were condensed in vacuo into a silica tube (capacity 100 ml.) and the vapour phase was irradiated (40 hr.).

The products were shaken with mercury to remove excess chlorine and then transferred to the vacuum-system.

Fractional condensation yielded only a -78° fraction (0.173 g.) which was shown by g.l.c. (2m. D.D.P. at 70°) to contain only one component.

The product was identified as 2,3-dichloro-1,1,1,3,3-pentafluoropropane $\text{CF}_3 \cdot \text{CHCl} \cdot \text{CF}_2 \text{Cl}$ (0.173g., 0.85m mole, 98%) (Found: C, 17.8; H, 0.5%; $\underline{\text{M}}$, 202. Calc. for $\text{C}_3 \text{HCl}_2 \text{F}_5$: C, 17.7; H, 0.5%; $\underline{\text{M}}$, 203).

The i.r. spectrum was identical to that reported in the literature¹¹⁴ and identical to that of an authentic sample synthesised by an unambiguous route.

The ^{19}F and ^1H n.m.r. spectra (see Page 47) were consistent with the proposed structure. The ^{19}F spectrum showed three regions of absorption at 7.6 (triplet of doublets, intensity 3), and two overlapping bands (total intensity 2) at 19.8 (quartet of doublets) and 20.4 (quartet of doublets) p.p.m., all to low field from external trifluoroacetic acid. The ^1H spectrum showed one region of absorption at 5.48 (doublet of quintets) τ .

The mass spectrum (Table 26 , Page 196) showed a parent peak at m/e 202 and the general breakdown pattern was consistent with the proposed structure.

Synthesis of 2,3-dichloro-1,1,1,3,3-pentafluoropropane
 $\text{CF}_3 \cdot \text{CHCl} \cdot \text{CF}_2 \text{Cl}$

1,1,3,3,3-Pentafluoropropene (1.85g., 14.0m moles)

(preparation: see Page 246) and chlorine (0.63g., 8.9 mmoles) were condensed in vacuo into a silica tube (capacity 100 ml.) and the vapour phase irradiated (90 min.).

The products were transferred to the vacuum-system and fractional condensation gave:-

i) a -130° fraction shown by g.l.c. (4m. D.D.P. at 20°) to be unchanged 1,1,3,3,3-pentafluoropropene (0.67g., 5.1 mmoles, 36%), and

ii) a -78° fraction (1.81g.) shown by g.l.c. (2m. D.D.P. at 70°) to be pure 2,3-dichloro-1,1,1,3,3-pentafluoropropane (1.81g., 8.9 mmoles, 100%).

The i.r. spectrum and g.l.c. retention time were identical to the product of the previous reaction.

b) Reaction with potassium hydroxide.

2-Chloro-1,1,1,3,3-pentafluoro-3-iodopropane (0.187g., 0.64 mmole) was condensed in vacuo onto powdered potassium hydroxide (ca. 5g.) in a flask (10 ml.) and left at 20° for 20 min.

The products were transferred to the vacuum-system and fractional condensation gave:-

i) a -130° fraction (0.053g., 0.32 mmole, 91%) shown by g.l.c. (4m. D.D.P. at 20°) to contain one component, and

ii) unchanged reactant (0.085g., 0.29m mole, 45%),
condensing at -78° .

The product was identified as 2-chloropenta -
fluoropropene $\text{CF}_3\cdot\text{CCl}:\text{CF}_2$ (Found: C, 21.3; H, 0.2%; $\underline{\text{M}}$, 166.
Calc. for C_3ClF_5 : C, 21.6; H, 0.0%; $\underline{\text{M}}$, 166).

The i.r. spectrum showed bands at 3.58(w),
3.70(w), 3.86(w), 4.01(w), 4.17(w), 4.23(w), 4.38(w),
4.75(w), 5.50(w), 5.75(s), 6.00(w), 6.64(w), 6.76(w),
7.08(w), 7.40(s), 7.71(s), 7.89(s), 8.34(s), 8.54(s),
8.89(m), 9.10(w), 9.53(s), 10.05(s), 11.12(m), 11.69(w),
12.24(broad, w) 13.36(m), 13.44(m), 13.52(m), 14.10(w),
14.18(w), 14.56(w), 14.78(w), and 14.88(w) μ .

The ^{19}F n.m.r. spectrum was identical to that
reported in the literature.¹⁵⁹

Addition of Hydrogen Bromide to Chloro-1,1-difluoroethylene.

I. In the dark.

a) Hydrogen bromide (3.52g., 43.4m moles) and
chloro-1,1-difluoroethylene (2.14g., 21.7m moles) were
sealed in vacuo in a pyrex tube (capacity 300 ml.) and
left in the dark for 3 weeks; no reaction occurred.

b) Bromine (0.5g.) was added to the reaction mixture and
the reactants left in the dark for 8 weeks; again no reaction
occurred.

II Photochemically.

Hydrogen bromide (3.65g., 44.0m moles) and chloro-1,1-difluoroethylene (2.13g., 22.0m moles) were condensed in vacuo into a silica tube (capacity 350 ml.), and the vapour phase irradiated (20 min.). Immediate reaction was seen to occur.

The products were transferred to the vacuum-system and separated by fractional condensation into the following fractions.

i) Hydrogen bromide (1.74g., 21.5m moles, 49% recovered) (Found: M, 80. Calc. for HBr: M, 81), condensing at -196° , contaminated with a trace of an unknown component which had weak i.r. bands at 8.1, 8.71, 9.1, 10.6, and 13.5μ .

ii) A -95° fraction (3.94g.) which was shown by g.l.c. (2m. D.D.P. at 70°) to contain one major component (98% of this fraction) and three minor components with much shorter g.l.c. retention times.

The major component of the latter fraction was identified as 1-bromo-2-chloro-1,1-difluoroethane $\text{CF}_2\text{Br}\cdot\text{CH}_2\text{Cl}$

(3.85g., 21.5m moles, 97%) (Found: C, 13.1; H, 1.0%; M, 179. Calc. for $\text{C}_2\text{H}_2\text{BrClF}_2$: C, 13.4; H, 1.1%; M, 179); the i.r. spectrum was identical to that of an authentic sample.

The ^{19}F and ^1H n.m.r. spectra (see Page 65) were consistent with the proposed structure. The ^{19}F spectrum showed one region of absorption at 24.8 (triple -1st order interpretation) p.p.m. to low field from external trifluoroacetic acid. The ^1H spectrum showed one region of absorption at 5.92 (triple - 1st order interpretation) τ .

The mass spectrum (Table 27, Page 197) showed a strong parent peak at m/e 178 and the general breakdown pattern was consistent with the proposed structure.

Material Balance: All of the olefin was consumed during the reaction; 97% gave the 1 : 1 adduct . The products represent a 100% recovery (by weight) of input material.

Preparation of 1,1,1,3,3-pentafluoro-3-iodopropane



Trifluoriodomethane (12.6g., 64.2m moles) and 1,1-difluoroethylene (3.14g., 49.2m moles) were condensed in vacuo into two silica tubes (total capacity 700 ml.) and the vapour phase irradiated (90 hr.).

Fractional condensation of the products gave a -78° fraction (11.5g.) containing 1,1,1,3,3-pentafluoro-3-iodopropane as the major component, and a -130° fraction containing returned reactants.

Four similar reactions were carried out incorporating the returned reactants of the previous experiment.

Distillation of the combined -78° fractions (58g.) at atmospheric pressure through a vacuum-jacketed column (20cm) fitted with a fractional take-off head gave 1,1,1,3,3-pentafluoro-3-iodopropane (49g., 190m moles, 85%) b.p. 72° - 74° (lit.¹²⁹ b.p. 72°).

Dehydroiodination of 1,1,1,3,3-pentafluoro-3-iodopropane.

1,1,1,3,3-Pentafluoro-3-iodopropane (49g., 190m moles) was condensed in vacuo onto powdered potassium hydroxide (ca. 150g.) contained in a flask (500 ml.) which was connected to a trap of the vacuum-system so that pressure changes could

be observed.

On gentle heating a gas was evolved and this was taken off when the vapour pressure in the reaction vessel exceeded ca. 60cm. of mercury. When gas evolution ceased, the products were passed through a -78° bath, the contents of which were re-condensed onto fresh powdered potassium hydroxide and the reaction repeated.

Fractional condensation in vacuo gave pure 1,1,3,3,3-pentafluoropropene (22.3g., 169m moles, 89%) (Found: M, 132. Calc. for C_3HF_5 : M, 132), condensing at -130° . The i.r. spectrum and a g.l.c. (4m. D.D.P. at 21°) examination showed no impurity.

Addition of Trifluoroiodomethane to 1,1,3,3,3-Pentafluoro - propene.

A. Photochemically.

a) Irradiation period of 265 hr.

Trifluoroiodomethane (10.5g., 53.7m moles) and 1,1,3,3,3-pentafluoropropene (3.72g., 28.1m moles) were condensed in vacuo into a silica tube (capacity 350 ml.), and the vapour phase irradiated (265 hr.). The lower portion of the tube (5cm.) was shielded from the ultraviolet light.

The products were transferred to the vacuum-system and were separated by fractional condensation into the following fractions.

i) Hexafluoroethane (0.10g., 0.71m mole)(Found: M, 128. Calc. for C_2F_6 : M, 138), condensing at -196° , and shown by i.r. spectroscopy to be contaminated with silicon tetrafluoride and a trace of trifluoromethane.

ii) A -130° and -95° fraction (12.38g., 70.2m moles) (Found: M, 176) was shown by its i.r. spectrum and by g.l.c. (4m. D.D.P. at 20°) to be a mixture of unchanged trifluoroiodomethane (9.35g., 47.7m moles, 88%) and 1,1,3,3,3-pentafluoropropene (2.96g., 22.5m moles, 80%).

iii) A -78° fraction (1.78g.) was shown by g.l.c. (2m. D.D.P. at 90°) to contain 7 components. The i.r. spectrum showed bands at 5.82(w), 5.88(w), 7.08(w), 7.25(m), 7.42(s), 7.52(s), 7.81(s), 7.99(s), 8.06(s), 8.19(s), 8.30(s), 8.45(s), 8.90(m), 9.00(s), 9.12(s), 9.30(s), 9.74(s), 10.49(m), 10.90(m), 11.40(w), 11.67(w), 12.35(m), 13.50(m), 13.83(s), 14.08(m), 14.50(s), and 14.98(s) μ .

The two major components of the -78° fraction, comprising 82% of the fraction, and present in the ratio 55 : 45, were separated by g.l.c. (2m. D.D.P. at 80°).

The major component was identified as 1,1,1,3,3-pentafluoro-2-trifluoromethyl-3-iodopropane,

$(\text{CF}_3)_2\text{CH}\cdot\text{CF}_2$ I, (0.864g., 2.63m moles, 47%) (Found: C, 14.4; H, 0.3%; \underline{M} , 326. Calc. for C_4HF_5 I : C, 14.6; H, 0.3%; \underline{M} , 328) b.p. (isoteniscope) $79.8 \pm 0.2^\circ$ (lit.¹⁴⁷ b.p. 80°).

The i.r. spectrum showed bands at 3.34(w), 4.38(w), 4.56(w), 4.63(w), 4.85(w), 5.80(w), 6.92(w), 7.39(VS), 7.78(VS), 8.04(VS), 8.22(VS), 8.30(VS), 8.43(s), 8.60(m), 8.98(VS), 9.12(VS), 9.73(s), 10.30(m), 10.48(s), 10.92(s), 11.41(m), 11.68(m), 12.36(s), 13.50(m), 13.85(s), 14.14(s), 14.54(s), and 14.98(s) μ .

The ^{19}F and ^1H n.m.r. spectra (see Page 69) were consistent with the proposed structure. The ^{19}F spectrum showed two regions of absorption at 37.4 (septet of doublets, intensity 1) and 15.2 (triplet of doublets, intensity 3) p.p.m. to low field from external trifluoroacetic acid. The ^1H spectrum showed one region of absorption at 6.24 (triplet of septets) τ from internal tetramethylsilane at 10.00 τ .

The mass spectrum (Table 29, Page 198) showed a parent peak at m/e 328, and the general breakdown pattern was consistent with the proposed structure.

The second component was identified as

1,1,1,2,2,4,4,4-octafluoro-3-iodobutane, $\text{CF}_3\cdot\text{CF}_2\cdot\text{CHI}\cdot\text{CF}_3$, (0.706g., 2.15m moles, 38%) (Found: C, 14.8; H, 0.5%; \underline{M} , 329. C_4HF_8 I requires C, 14.6; H, 0.3%; \underline{M} , 328) b.p.

(isoteniscope) $71.0 \pm 0.2^\circ$.

The i.r. spectrum showed bands at 3.30(w), 4.11(w), 4.35(w), 4.42(w), 5.80(w), 6.10(w), 6.84(w), 7.19(m), 7.36(s), 7.56(vs), 7.88(vs), 8.14(vs), 8.27(vs), 8.35(vs), 8.60(s), 9.10(vs), 9.35(s), 9.78(vs), 11.34(m), 11.65(m), 12.00(m), 12.90(w), 13.44(s), 13.93(s), 14.45(s), and 15.00 (s) μ .

The ^{19}F and ^1H n.m.r. spectra (see Page 72) were consistent with the proposed structure. The ^{19}F spectrum showed four regions of absorption at 14.6 (doublet of doublets^{of doublets}/of quartets, intensity 13)p.p.m. to low field, 3.6 (quartet, intensity 13), 25.0 (doublet of doublets of quartets, intensity 4), and 36.0 (doublet of quintets, intensity 4)p.p.m. to high field from external trifluoroacetic acid; the latter two bands showed an AB system. The ^1H spectrum showed one region of absorption at 5.32 (triplet of quartets) τ from internal tetramethylsilane at 10.00 τ .

The mass spectrum (Table 29, Page 198) showed a parent peak at m/e 328, and the general breakdown pattern was consistent with the proposed structure.

Material Balance: 20% of the olefin was consumed during the reaction; 85% reacted to give the 1 : 1 adducts. The products represent a 100% recovery (by weight) of input material.

b) Irradiation Period of 192 hr. at a distance of 2cm.

from the irradiation source.

Trifluoroiodomethane (10.5g., 53.7m moles) and 1,1,3,3,3-pentafluoropropene (3.88g., 29.4m moles) were condensed into a silica tube (capacity 350 ml.). The vapour phase was irradiated (192 hr.) at a distance of 2cm. from an ultraviolet lamp, and the products were worked up as in the previous experiment to give:-

i) a -196° fraction (0.20g., 2.05m moles) (Found: M, 100) shown by i.r. spectroscopy to contain hexafluoroethane, trifluoromethane, and silicon tetrafluoride, which when washed with aqueous potassium hydroxide solution (2M.) gave a mixture (0.115g., 1.18m moles) (Found: M, 98) of hexafluoroethane (0.07g., 0.48m mole) and trifluoromethane (0.05g., 0.7m mole, 8%),

ii) a -130° fraction (11.40g., 64.5m moles) (Found: M, 177) shown by g.l.c. (4m. D.D.P. at 20°) to be a mixture of trifluoroiodomethane (8.63g., 44.0m moles, 82%) and 1,1,3,3,3-pentafluoropropene (2.71g., 20.5m moles, 70%), and

iii) a higher-boiling fraction (2.43g.) shown by g.l.c. (2m. D.D.P. at 90°) to contain 7 components as in the previous reaction.

The two major components of the higher-boiling fraction, present in the ratio 58 : 42, were identified as the 1 : 1 adducts, $(\text{CF}_3)_2\text{CH}\cdot\text{CF}_2\text{I}$ (1.29g., 3.95m moles, 44%) and $\text{CF}_3\cdot\text{CF}_2\cdot\text{CHI}\cdot\text{CF}_3$ (0.94g., 2.86m moles, 32%) respectively, by their g.l.c. retention times and i.r. spectra.

Material Balance: 30% of the olefin was consumed during the reaction; 76% reacted to give the 1 : 1 adducts.

The products represent a 98% recovery (by weight) of input material.

c) Irradiation period of 216hr. at 100°.

Trifluoroiodomethane (10.5g., 53.7m moles) and 1,1,3,3,3-pentafluoropropene (3.52g., 26.7m moles) were sealed in a silica tube (capacity 350 ml.). The tube was placed vertically in a wire furnace (100°) with the blackened neck of the tube protruding beneath the furnace. The vapour phase was irradiated (216hr.) and the products worked up to give:-

i) a -196° fraction (0.23g., 2.05m moles) (Found: M, 102) shown by i.r. spectroscopy, molecular weight measurements, and washing with aqueous potassium hydroxide solution to contain hexafluoroethane (0.06g., 0.83m mole), trifluoromethane (0.04g., 0.29m mole, 3%) and silicon tetrafluoride (0.12g., 1.15m moles),

ii) a -130° fraction (10.13g., 56.7m moles)
(Found: M, 179) shown by g.l.c. (4m. D.D.P. at 20°) to
be a mixture of trifluoriodomethane (8.2g., 41.8m moles,
78%) and 1,1,3,3,3-pentafluoropropene (1.97g., 14.9m moles,
56%), and

iii) a -95° and -78° fraction (3.32g.) shown by g.l.c.
to contain 7 components, identical to those of the previous
reactions.

The major components of the latter fraction
were identified as the 1 : 1 adducts $(\text{CF}_3)_2 \text{CH} \cdot \text{CF}_2 \text{I}$
(1.89g., 5.76m moles, 49%) and $\text{CF}_3 \cdot \text{CF}_2 \cdot \text{CHI} \cdot \text{CF}_3$ (1.11g.,
3.38m moles, 29%), present in the ratio 63 : 37 respectively.

Material Balance: 44% of the olefin was consumed during the
reaction, 78% reacted to give the 1 : 1 adducts. The products
represent a 97% recovery (by weight) of input material.

d) Irradiation period of 144hr. at a distance of 2cm. from
a 250 W. Hanovia lamp.

Trifluoriodomethane (10.5g., 53.60m moles)
and 1,1,3,3,3-pentafluoropropene (3.53g., 26.71m moles)
were sealed in a silica tube (capacity 350ml.) and irradiated
(144 hr.) at a distance of 2cm. from a 250 W. Hanovia lamp, and
gave products which were worked up as in the previous
experiments to give:-

i) a -196° fraction (0.10g., 1.05m moles) (Found:M, 99) shown by i.r. spectrometry to be a mixture of hexafluoro - ethane, trifluoromethane and silicon tetrafluoride in similar proportions to experiment (b),

ii) a -130° fraction (12.56g., 71.40m moles) (Found:M, 176) shown by g.l.c. (4m. D.D.P. at 20°) to be a mixture of trifluoroiodomethane (9.63g., 49.10m moles, 93%) and 1,1,3,3,3-pentafluoropropene (2.93g., 22.2m moles, 83%), and

iii) a higher-boiling fraction (1.31g.) shown by g.l.c. (2m. D.D.P. at 90°) to contain 2 major components and 5 minor components.

The major components were identified as the 1 : 1 adducts $(\text{CF}_3)_2 \text{CH} \cdot \text{CF}_2 \text{I}$ (0.71g., 2.16m moles, 48%) and $\text{CF}_3 \cdot \text{CF}_2 \cdot \text{CHI} \cdot \text{CF}_3$ (0.47g., 1.44m moles, 32%), present in the ratio 60 : 40 respectively.

Material Balance: 17% of the olefin was consumed during the reaction; 80% reacted to give the 1 : 1 adducts. The products represent a 100% recovery (by weight) of input material.

B. Thermally.

Trifluoroiodomethane (6.29g., 32.1m moles) and 1,1,3,3,3-pentafluoropropene (2.12g., 16.0m moles) were

sealed in a Dreadnought tube (capacity 250 ml.) and heated (212°, 70hr.) to give volatile products which were fractionally condensed to give:-

i) a -196° fraction (0.10g., 1.52m moles) (Found: M, 66) shown by i.r. spectroscopy to be a mixture of trifluoro - methane, silicon tetrafluoride and an unknown component having strong i.r. bands at 7.89, 8.17, 8.45, 9.32, and 10.30 μ .

ii) a - 130° fraction (5.22g., 28.5m moles) (Found: M, 183) shown by g.l.c. (4m. D.D.P. at 20°) to be a mixture of trifluoriodomethane (4.45g., 22.70m moles, 71%) and 1,1,3,3,3-pentafluoropropene (0.76g., 5.75m moles, 36%) with a trace of a higher-boiling component identified from the i.r. spectrum of the mixture as perfluoroisobutene,

iii) a -95° fraction (0.43g., 2.13m moles) (Found: M, 202) shown by i.r. spectroscopy to be a mixture of perfluoro - isobutene (0.40g., 1.92m moles, 19%) and 1,1,3,3,3-penta - fluoropropene (0.03g., 0.21m mole, 1%), and

iv) a -78° fraction (1.45g.) shown by g.l.c. (2m. D.D.P. at 84°) to contain thirteen components, seven of which had similar g.l.c. retention times to the products of the irradiation reactions.

A few crystals of iodine and a trace of non-condensable material were also obtained.

The two major components of the -78° fraction were identified as the 1 : 1 adducts $(\text{CF}_3)_2 \text{CH} \cdot \text{CF}_2 \text{I}$ (0.20g., 0.61m mole, 6%) and $\text{CF}_3 \cdot \text{CF}_2 \cdot \text{CHI} \cdot \text{CF}_3$ (0.99g., 3.02m moles, 30%) present in the ratio 17 : 83 respectively.

Material Balance: 63% of the olefin was consumed during the reaction; 36% reacted to give the 1 : 1 adducts and over 19% gave perfluoroisobutene. The volatile products represent an 86% recovery (by weight) of input material.

A preliminary experiment at 216° for 260hr. gave 1 : 1 adducts (28%) $(\text{CF}_3)_2 \text{CH} \cdot \text{CF}_2 \text{I}$ and $\text{CF}_3 \cdot \text{CF}_2 \cdot \text{CHI} \cdot \text{CF}_3$ in the ratio 12 : 88. A black tar and free iodine were also obtained and the main breakdown product was identified by i.r. spectroscopy as perfluoroisobutene.

Reaction of the 1 : 1 Adducts with Powdered Potassium

Hydroxide.

I. 1,1,1,3,3-Pentafluoro-2-trifluoromethyl-3-iodopropane.

1,1,1,3,3-Pentafluoro-2-trifluoromethyl-3-iodopropane (0.75g., 2.29m moles) was condensed in vacuo onto powdered potassium hydroxide (ca. 5g.) and left at 20° for 30 min. The products were fractionally condensed to give:-

- i) a -130° fraction (0.23g., 1.15m moles) (Found: M, 200)

shown by g.l.c. (4m. D.D.P. at 20°) to contain one component, and

ii) unchanged reactant (0.06g., 0.18m mole, 8% recovered), condensing at -78°.

The product was identified as perfluoroisobutene $(\text{CF}_3)_2\text{C} : \text{CF}_2$ (0.23g., 1.15m moles, 55%) (Found: C, 24.1; H, 0.1%; \underline{M} , 200. Calc. for C_4F_8 : C, 24.0; H, 0.0%; \underline{M} , 200). The i.r. spectrum was identical to that reported in the literature.¹⁴⁸

II. 1,1,1,2,2,4,4,4-Octafluoro-3-iodobutane.

1,1,1,2,2,4,4,4-Octafluoro-3-iodobutane (0.42g., 1.28m moles) was condensed in vacuo onto powdered potassium hydroxide (ca. 5g.) and left at 20° for 30 min.; no observable reaction occurred and 97% of the reactant was recovered.

Addition of Bromine to 1,1,3,3,3-pentafluoropropene.

Bromine (0.66g., 4.12m moles) and 1,1,3,3,3-pentafluoropropene (1.18g., 8.90m moles) were sealed in vacuo in a Pyrex tube (capacity 250ml.) and left in the dark (16hr.); no reaction took place. On exposure to a 100W. bulb (10hr.) reaction did occur.

The products were shaken with mercury to remove unreacted bromine and transferred to the vacuum-system.

Fractional condensation yielded:-

i) unreacted 1,1,3,3,3-pentafluoropropene (0.82g., 6.21m moles, 70% recovered), condensing at -130° and identified by its i.r. spectrum, and

ii) a -78° fraction (0.77g.) shown by g.l.c. (2m. D.D.P. at 70°) to contain one major component (98% of fraction) contaminated with two minor unknown components (2% of fraction) having much shorter g.l.c. retention times.

The major component of the latter fraction was identified as 1,2-dibromo-1,1,3,3,3-pentafluoropropane $\text{CF}_3\cdot\text{CHBr}\cdot\text{CF}_2$ Br (0.77g., 2.64m moles, 98%) (Found: C, 12.5; H, 0.5%; $\underline{\text{M}}$, 290. Calc. for $\text{C}_3\text{HBr}_2\text{F}_5$: C, 12.3; H, 0.3%; $\underline{\text{M}}$, 292) b.p. (Siwoloboff) 87° (lit. b.p. 87° ¹⁴⁷; 88° ¹⁷⁷).

The i.r. spectrum showed bands at 3.30(w), 7.46(s), 7.91(s), 8.06(s), 8.08(s), 8.22(s), 8.30(s), 8.67(m), 8.83(s), 8.94(s), 9.70(s), 10.34(s), 10.39(s), 10.71(w), 11.36(m), 11.54(m), 12.35(m), 13.10(m), 14.20(m), and 15.32(m) μ .

The ^{19}F and ^1H n.m.r. spectra (see Page 84) were consistent with the proposed structure. The ^{19}F spectrum showed two regions of absorption at 27.8 (doublet of quartets- first order interpretation, intensity 2) and 10.0 (triplet of doublets, intensity 3) p.p.m. to low field from external trifluoroacetic acid. The ^1H spectrum showed

one region of absorption at 5.38 (triplet of quartets - first order interpretation) γ .

The mass spectrum (Table 31 , Page 200) showed no parent peak but the general breakdown pattern was consistent with the proposed structure.

Material Balance: 30% of the olefin was consumed during the reaction; 98% reacted to give the dibromide. The products represent a 100% (molar) recovery.

Addition of Hydrogen Bromide to 1,1,3,3,3-Pentafluoropropene.

Hydrogen bromide (3.88g., 48.01m moles) and 1,1,3,3,3-pentafluoropropene (3.49g., 26.40m moles) were sealed in a silica tube (capacity 350 ml.) and irradiated (48 hr.) to give products which, after being washed with mercury, were separated by fractional condensation into the following fractions.

i) Hydrogen (0.01g., 5.13m. moles) (Found: \underline{M} , 2.0 Calc. for H_2 : \underline{M} , 2.0) was obtained as a non-condensable gas.

ii) Hydrogen bromide (0.31g., 3.47m. moles, 7% recovered) (Found: \underline{M} , 89. Calc. for HBr : \underline{M} , 81), condensing at -196° , which was shown by i.r. spectroscopy to be contaminated with bromotrifluoromethane and an unknown component having i.r. bands at 7.42, 8.02, 8.77, and 9.82 μ .

iii) A -130° fraction (2.82g., 29.01 mmoles) (Found:M, 97) which was shown by i.r. spectroscopy and g.l.c. (4m. D.D.P. at 21°) to be a mixture of unchanged hydrogen bromide (1.63g., 20.11 mmoles, 42% recovered) and 1,1,3,3,3-pentafluoropropene (1.18g., 8.90 mmoles, 33% recovered).

iv) A -95° fraction (0.17g., 1.03 mmoles) (Found:M, 167) which contained i.r. bands at 3.4(w), 5.68(m), 7.06(s), 7.28(s), 7.49(s), 7.84(s), 7.92(s), 8.22(s), 8.48(s), 8.86(s), 9.30(s), 9.70(w), 10.00(w), 10.40(m), 10.70(w), 11.20(broad,m), 11.70(m), 12.40(m), and 14.75(m) μ . None of the i.r. bands were identified and the fraction was not investigated further.

v) A combined -45° and -78° fraction (3.36g.) was shown by g.l.c. (2m. D.D.P. at 80°) to contain five major components G,H,I,J, and K, present in the ratio 28:11:1:54:5 respectively, and three minor components ($< 1\%$) with shorter g.l.c. retention times. The i.r. spectrum showed bands at 5.80(w), 7.05(w), 7.25(m), 7.48(s), 7.90(s), 8.06(s), 8.20(s), 8.64(m), 8.80(s), 8.94(s), 9.05(s), 9.68(m), 10.27(m), 10.38(m), 10.71(m), 11.30(m), 11.51(m), 11.93(w), 12.34(m), 12.80(w), 13.56(m), and 14.17(m) μ .

The five major components were separated by g.l.c. (2m. D.D.P. at 700°).

Component G was identified as 1-bromo-1,1,3,3,3-pentafluoropropane $\text{CF}_2\text{Br}\cdot\text{CH}_2\cdot\text{CF}_3$ (0.79g., 3.72 mmoles, 21%) (Found: C, 16.9; H, 1.0%; $\underline{\text{M}}$, 212. Calc. for $\text{C}_3\text{H}_2\text{BrF}_5$: C, 16.9; H, 0.9%; $\underline{\text{M}}$, 213) b.p. (isoteniscope) $47.5 \pm 0.2^\circ$ (lit. b.p. 44.0° ¹⁴⁷; 47.0° ¹²⁸).

The i.r. spectrum showed bands at 4.45(w), 4.53(w), 4.62(w), 4.74(w), 5.06(w), 6.36(w), 6.80(m), 7.04(s), 7.25(vs), 7.38(s), 7.50(s), 7.84(vs), 8.26(vs), 8.50(vs), 8.64(vs), 9.01(m), 9.23(s), 9.75(m), 10.08(s), 10.50(s), 10.75(s), 11.09(s), 11.89(s), 11.95(s), 12.49(s), 13.90(m), 14.50(m), and 14.94 (broad, s) μ .

The ^{19}F and ^1H n.m.r. spectra (see Page 80) were consistent with the proposed structure. The ^{19}F spectrum showed two regions of absorption at 30.5 (triplet with further splitting evident, intensity 2) and 13.5 (triplet with further splitting evident, intensity 3) p.p.m. to low field^{from}/external trifluoroacetic acid. The ^1H spectrum showed one region of absorption at 6.78 (triplet of quartets) τ .

The mass spectrum (Table 30, Page 199) showed a strong parent peak at m/e 212 and the general breakdown pattern was consistent with the proposed structure.

Component H was identified as 2-bromo-1,1,1,3,3-pentafluoropropane $\text{CF}_3\text{:CHBr}\cdot\text{CHF}_2$ (0.31g., 1.47 mmoles, 9%) (Found : C, 17.0; H, 1.1%; M, 214. $\text{C}_3\text{H}_2\text{BrF}_5$ requires C, 16.9; H, 0.9%; M, 213) b.p. (isoteniscope) $56.1 \pm 0.2^\circ$.

The i.r. spectrum showed bands at 3.35(m), 4.16(w), 4.46(w), 4.57(w), 4.64(w), 4.70(w), 5.78(w), 7.04(m), 7.20(s), 7.24(s), 7.39(s), 7.56(s), 7.81(s), 7.96(s), 8.26(s), 8.32(s), 8.89(s), 9.10(s), 9.14(s), 9.45(m), 10.25(m), 10.50(w), 11.45(m), 11.71(w), 12.55(m), 12.89(m), and 14.40(broad, m) μ .

The ^{19}F and ^1H n.m.r. spectra (see Page 82) were consistent with the proposed structure. The ^{19}F spectrum showed three regions of absorption at 7.7 (doublet of triplets - first order interpretation, intensity 2.9) p.p.m. to low field, and 43.6 (doublet of quintets, intensity 1.0) and 44.4 (doublet of doublets of quartets, intensity 1.0) p.p.m. to high field from external trifluoroacetic acid. The ^1H spectrum showed two regions of absorption at 4.03 (triplet of doublets, intensity 1) and 5.68 (doublet of doublets of quartets of doublets, intensity 1) τ .

The mass spectrum (Table 30, Page 199) showed a parent peak at m/e 212, and the general breakdown pattern was consistent with the proposed structure.

Component I showed i.r. bands at 5.80(s), 7.28(m), 7.52(s), 7.91(s), 8.10(s), 8.22(s), 8.68(m), 8.84(s), 8.98(m), 9.08(m), 9.60(s), 9.94(s), 10.36(m), 11.99(s), 12.34(m), 13.10(m), and 14.22(m) μ . The mass spectrum showed peaks at m/e values (assignments and relative abundances in parentheses) of 274 ($C_3F_4^{81}Br_2^+$, 2.6), 272 ($C_3F_4^{81}Br^{79}Br^+$, 4.8), 270 ($C_3F_4^{79}Br_2^+$, 2.6), 255 ($C_3F_3^{81}Br_2^+$, 2.4), 253 ($C_3F_3^{81}Br^{79}Br^+$, 4.5), 251 ($C_3F_3^{79}Br_2^+$, 2.4), 193 ($C_3F_4^{81}Br^+$, 98), 191 ($C_3F_4^{79}Br^+$, 100), 133 (-, 12), 131 ($CF_2^{81}Br^+$, 10), 129 ($CF_2^{79}Br^+$, 10), 112 ($C_3F_4^+$, 36), 93 ($C_3F_3^+$, 32), and 69 (CF_3^+ , 61). This evidence indicates that component I is 1,2-dibromo-1,3,3,3-tetrafluoropropene $CF_3 \cdot CBr:CFBr$ (0.05g., 0.14 mmole, 1%).

Component J was identified as 1,2-dibromo-1,1,3,3,3-pentafluoropropane (2.15g., 7.39 mmoles, 48%) by its i.r. spectrum and g.l.c. retention time.

Component K showed i.r. bands at 7.05(w), 7.49(m), 7.92(s), 8.05(s), 8.21(s), 8.55(w), 8.64(w), 8.82(s), 8.99(s), 9.10(s), 9.31(s), 9.70(s), 10.08(s), 10.38(m), 10.68(s), 11.50(w), 12.45(broad,m), 13.13(m), 13.23(m), and 13.60(m) μ , and it appeared to be contaminated with 1,2-dibromo-1,1,3,3,3-pentafluoropropane. The mass spectrum showed strong peaks at m/e values (assignments and relative abundances in parentheses) of 275 ($C_3HF_4^{81}Br_2^+$, 5), 273 ($C_3HF_4^{81}Br^{79}Br^+$, 9.0), 271 ($C_3HF_4^{79}Br_2^+$, 5.0), 224 ($C_2F_2^{81}Br_2^+$, 13.6), 222 ($C_2F_2^{81}Br^{79}Br^+$, 26),

$220(\text{C}_2\text{F}_2^{79}\text{Br}_2^+, 13.6)$, $213(\text{C}_3\text{HF}_5^{81}\text{Br}^+, 42)$,
 $211(\text{C}_3\text{HF}_5^{79}\text{Br}^+, 42)$, $198(-, 23)$, $193(\text{C}_3\text{F}_4^{81}\text{Br}^+, 13.6)$,
 $191(\text{C}_3\text{F}_4^{79}\text{Br}^+, 13.6)$, $145(\text{C}_2\text{H}_2\text{F}_2^{81}\text{Br}^+, 100)$, 143
 $(\text{C}_2\text{H}_2\text{F}_2^{79}\text{Br}^+, 97)$, $69(\text{CF}_3^+, 32)$, and $64(\text{C}_2\text{H}_2\text{F}_2^+, 30)$,
 suggesting a dihydrodibromocompound (0.73mmole, 5%).

Material Balance: 67% of the olefin was consumed during the reaction; 33% reacted to give the 1 : 1 adducts and 48% to give the dibromide. The products represent a 91% (by weight) of input material.

A further reaction (140hr. irradiation period) gave complete olefin conversion. The 1 : 1 adducts, present in the ratio $\text{CF}_3\text{CHBr}\cdot\text{CHF}_2$: $\text{CF}_3\text{CH}_2\text{CF}_2\text{Br}$ of 64 : 36, were given in a yield of ca. 32%, and the dibromide was given in a yield of ca. 60%.

Addition of Hydrogen Bromide to 1,1,3,3,3-Pentafluoro - propene in the presence of Silver Powder.

Hydrogen bromide (1.34g., 16.85 mmoles) and 1,1,3,3,3-pentafluoropropene (1.08g., 8.20 mmoles) were condensed into a silica tube (capacity 100 ml.) containing silver powder (0.10g.) and irradiated (12 hr.).

All of the silver powder was consumed, and the products were washed with mercury to remove free bromine

and fractionally condensed to give:-

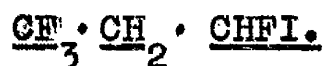
- i) hydrogen (1.25 mmoles),
- ii) a combined -196° and -130° fraction (2.21g., 22.15 mmoles) (Found: M, 100) shown by i.r. spectroscopy to be a mixture of unchanged hydrogen bromide (1.15g., 14.14 mmoles, 84% recovered) and 1,1,3,3,3-pentafluoropropene (1.06g., 8.01 mmoles, 98% recovered), and
- iii) a -78° fraction (0.05g., 0.18 mmole).

The latter fraction was condensed into a tapped ampoule fitted with a serum cap and by means of a gas-syringe injected onto a g.l.c. column (2m. D.D.P. at 80°) which showed the presence of 1-bromo-1,1,3,3,3-pentafluoropropane (ca. 0.001g., 0.042 mmole, 22%), 2-bromo-1,1,1,3,3-pentafluoro - propane (ca. 0.001g., 0.076 mmole, 37%), and 1,2-dibromo-1,1,3,3,3-pentafluoropropane (ca. 0.002g., 0.076 mmole, 40%), present in the ratio 22:37:40 respectively, and identified by their g.l.c. retention times.

Material Balance: 2% of the olefin was consumed during the reaction; 59% reacted to give the 1 : 1 adducts and 40% to give the dibromide. The products represent a 94% (by weight) recovery of input material.

A further reaction in the presence of 1gm. of silver powder gave only hydrogen and silver bromide apart from recovered reactants.

Preparation of 1,1,1,3-Tetrafluoro-3-iodopropane,



Trifluoroiodomethane (19.3g., 98.3 mmoles) and vinyl fluoride (1.8g., 40.0 mmoles) were condensed in vacuo into two silica tubes (capacity 700 ml.) and the vapour phase irradiated (60 hr.).

Fractional condensation of the products gave a -78° fraction (7.1g.) containing 1,1,1,3-tetrafluoro-3-iodopropane, as the major component and a -130° fraction containing returned reactants.

Three similar reactions were carried out incorporating the returned reactants of the previous experiment.

Distillation of the combined -78° fractions (28g.) at atmospheric pressure through a vacuum-jacketed column (40 cm.) fitted with a fractional take-off head gave a fraction (25g., 103 mmoles, 90%) boiling at 85-88° containing 1,1,1,3-tetrafluoro-3-iodopropane (lit.¹²⁵ b.p. 86°).

Dehydroiodination of 1,1,1,3-Tetrafluoro-3-iodopropane.

The fraction (25g., 103 mmoles) containing 1,1,1,3-tetrafluoro-3-iodopropane was condensed in vacuo onto powdered potassium hydroxide (ca. 150g.) contained in

a flask (500 ml.) which was connected to a trap of the vacuum-system so that pressure changes could be observed.

On warming a gas was evolved which was taken off into a -196° trap when the pressure in the reaction vessel exceeded ca. 60 cm. of mercury. When the gas evolution ceased, the products were passed through a -78° trap, the contents of which were condensed onto fresh powdered potassium hydroxide and the reaction repeated.

Fractional condensation in vacuo gave products (8.82g., 77.4 mmoles, 75%) (Found : C, 31.8; H, 1.8%; M, 114. Calc. for $C_3H_2F_4$: C, 31.6; H, 1.8%; M, 114), condensing at -130° , shown by g.l.c. (4m. D.D.P. at 20°) to be a mixture of three components in the ratio 57:39:4. This mixture of olefins was separated by g.l.c. (4m. D.D.P. at 20°).

The major component was identified as trans - 1,3,3,3-tetrafluoropropene (5.03g., 44.1 mmoles, 43%) (Found : M, 114. $C_3H_2F_4$ requires M, 114) b.p. (isoteniscope) $-19.5 \pm 0.2^{\circ}$.

The i.r. spectrum showed bands at 3.21(w), 3.30(w), 3.46(w), 3.57(w), 3.75(w), 4.00(w), 4.10(w), 4.37(w), 4.51(w), 4.80(w), 5.03(w), 5.40(w), 5.55(w), 5.70(m), 5.90(s), 6.56(w), 6.94(w), 7.22(m), 7.50(s), 7.99(s), 8.26(m), 8.47(s), 8.63(s), 9.03(vs), 9.08(vs), 9.78(w), 10.04(w), 10.80(s), 11.80(m), 11.86(m), 11.93(m),

12.02(m), 14.28(s), 14.40(s), and 14.52(s) μ .

The ^{19}F and ^1H n.m.r. spectra (see Page 183) were consistent with the proposed structure. The ^{19}F spectrum showed two regions of absorption at 14.8 (doublet of doublets of doublets, intensity 2.8) p.p.m. to low field, and 46.0 (doublet of doublets of quartets, intensity 1) p.p.m. to high field from external trifluoroacetic acid. The ^1H spectrum showed two regions of absorption at 2.86 (doublet of doublets of doublets, intensity 1) and 4.41 τ (doublet of doublets of quartets, intensity 1) from internal tetramethylsilane at 10.00 τ .

The second component was identified as cis-1,3,3,3-tetrafluoropropene (3.44g., 30.2 mmoles, 29%) (Found: \underline{M} , 114. $\text{C}_3\text{H}_2\text{F}_4$ requires \underline{M} , 114) b.p. (isoteniscope) $9.3 \pm 0.2^\circ$.

The i.r. spectrum showed bands at 3.21(w), 3.27(w), 3.68(w), 3.95(w), 4.10(w), 4.36(w), 4.53(w), 4.69(w), 4.84(w), 4.92(w), 5.17(w), 5.45(w), 5.81(m), 5.92(s), 6.55(w), 7.05(s), 7.80(s), 7.88(vs), 8.17(m), 8.56(vs), 9.75(m), 10.32(w), 11.58(m), 11.66(m), 13.00(m), 13.08(m), 13.29(m), and 13.44(m) μ .

The ^{19}F and ^1H n.m.r. spectra were consistent with the proposed structure. The ^{19}F spectrum showed two regions of absorption at 17.6 (doublet of doublets, intensity 3)

p.p.m. to low field, and 35.8 (doublet of doublets of quartets, intensity 1) p.p.m. to high field from external trifluoroacetic acid. The ^1H spectrum showed two regions of absorption at 3.33 (doublet of doublets, intensity 1) and 4.86 τ (doublet of quartets of doublets, intensity 1) from internal tetramethylsilane at 10.00 τ .

The minor component was identified as 2,3,3,3-tetrafluoropropene (0.35g., 3.1 mmoles, 3%) (Found : \underline{M} , 114, Calc. for $\text{C}_3\text{H}_2\text{F}_4$: \underline{M} , 114); its i.r. spectrum was identical with that of an authentic sample prepared in this department.¹⁵⁴

The mixture of trans-1,3,3,3-tetrafluoropropene (59%), cis-1,3,3,3-tetrafluoropropene (39%), and 2,3,3,3-tetrafluoropropene (4%) was used for addition reactions unless stated otherwise, and henceforth called tetrafluoropropene.

Irradiation of Trans-1,3,3,3-tetrafluoropropene.

Trans-1,3,3,3-tetrafluoropropene (0.29g., 2.58 mmoles) was sealed in a length of silica tubing (15 ml.) and irradiated (115 hr.).

The volatile products (0.21g., 1.88 mmoles) condensed at -130° and were shown by g.l.c. (4m. D.D.P. at 20°) to be a mixture of unchanged trans-1,3,3,3-tetrafluoro -

propene (0.18g., 1.60 mmoles, 62%, recovered) and cis-1,3,3,3-tetrafluoropropene (0.03g., 0.28 mmole, 11%), present in the ratio 85 : 15 respectively, and identified by their g.l.c. retention times and i.r. spectra.

A small amount of non-volatile material remained in the reaction tube.

Material Balance: 38% of the trans- propene was consumed during the reaction; 11% reacted to give the cis-propene. The volatile products represent a 73% recovery (by weight) of input material.

Addition of Trifluoriodomethane to Tetrafluoropropene.

Reaction 1.

Trifluoriodomethane (10.48g., 53.50 mmoles) and a mixture of the isomeric tetrafluoropropenes (3.05g., 26.75 mmoles) consisting of trans-1,3,3,3-tetrafluoropropene (1.74g., 15.24 mmoles), cis-1,3,3,3-tetrafluoropropene (1.19g., 10.47 mmoles), and 2,3,3,3-tetrafluoropropene (0.11g., 1.06 mmoles) were condensed in vacuo into a silica tube (capacity 350 ml.) and the vapour phase irradiated (30 hr.).

The products were transferred to the vacuum-system and separated into the following fractions.

i) A trace of a -196° fraction (0.01 mmole) which showed a strong i.r. band at $7.97/\mu$.

ii) A combined -130° and -95° fraction (12.83g., 77.00 mmoles) (Found : \underline{M} , 168) was shown by its i.r. spectrum and g.l.c. (4m. D.D.P. at 20°) to be a mixture of unchanged trifluoroiodomethane (9.97g., 51.88 mmoles, 95% recovered), trans-1,3,3,3-tetrafluoropropene (1.68g., 14.66 mmoles, 96% recovered), cis-1,3,3,3-tetrafluoropropene (1.13g., 9.86 mmoles, 93% recovered), and 2,3,3,3-tetrafluoropropene (0.06g., 0.51 mmoles, 48% recovered).

iii) A -78° fraction (0.67g.) was shown by g.l.c. (2m. D.D.P. at 80°) to contain six components (A-F). The i.r. spectrum showed bands at 3.25(w), 3.40(w), 5.90(m), 7.05(m), 7.58(s), 7.80(s), 7.92(s), 8.05(m), 8.18(m), 8.34(s), 8.55(s), 9.00(s), 9.10(s), 9.31(s), 9.70(m), 10.10(w), 10.75(w), 11.60(broad, m), 13.00(m), 13.40(m), 13.50(m), and $13.91/\mu$.

The four major components of the latter fraction (C-F) comprised 92% of the fraction (g.l.c. peak areas), and were present in the ratio C:D:E:F of 27:32:17:16. These major components were separated by g.l.c. (2m. D.D.P. at 80°) from the combined -78° fractions of this and similar reactions; the minor components A and B were not separated.

Component C was identified as

1,1,1,2,4,4,4-heptafluoro-2-iodobutane $\text{CF}_3 \cdot \text{CFI} \cdot \text{CH}_2 \cdot \text{CF}_3$

(0.18g., 0.58 mmole, 100%) (Found: C, 15.7; H, 0.6%; $\underline{\text{M}}$, 305. $\text{C}_4\text{H}_2\text{F}_7\text{I}$ requires C, 15.5; H, 0.6%; $\underline{\text{M}}$, 310) b.p. (isoteniscope) $83.3 \pm 0.2^\circ$

The i.r. spectrum showed bands at 3.36(w), 4.97(w), 5.40(w), 5.72(w), 6.77(w), 7.00(m), 7.18(m), 7.26(m), 7.43(m), 7.54(m), 7.76(s), 7.87(s), 8.15(s), 8.35(vs), 8.58(vs), 8.80(m), 9.13(w), 9.52(w), 9.93(m), 10.65(m), 11.15(w), 11.55(m), 11.86(m), 12.36(w), 13.01(w), and 13.84(m) μ .

The ^{19}F and ^1H n.m.r. spectra (see Page 94) were consistent with the proposed structure. The ^{19}F spectrum showed three regions of absorption at 16.2 (doublet of triplets of quartets, intensity 3) to low field, and 3.0 (doublet of quartets, intensity 3) and 55.0 (doublet of octets, intensity 1) p.p.m. to high field from external trifluoroacetic acid. The ^1H spectrum showed one region of absorption at 7.00 (complex AB portion of an ABPX_3 - type system) γ .

The mass spectrum (Table 34, Page 203) showed a strong parent peak at m/e 310 and the general breakdown pattern was consistent with the proposed structure.

Component D was identified as one of the isomeric

1,1,1,2,4,4,4-heptafluoro-3-iodobutanes $\text{CF}_3 \cdot \text{CHF} \cdot \text{CHI} \cdot \text{CF}_3$

(isomer I, threo or erythro) (0.21g., 0.67 mmole, 56%)
(Found: C, 15.7; H, 0.7%; M, 312. $\text{C}_4\text{H}_2\text{F}_7\text{I}$ requires C, 15.5; H, 0.6%; M, 310) b.p. (isoteniscope) $90.0 \pm 0.2^\circ$.

The i.r. spectrum showed bands at 3.22(w), 3.34(w), 6.25(w), 7.10(m), 7.46(s), 7.55(s), 7.70(s), 7.90(vs), 8.20(s), 8.34(vs), 8.41(vs), 8.57(vs), 8.80(s), 9.15(s), 10.18(m), 11.24(w), 11.85(m), 13.59(m), 13.91(m), and 15.38(vs) μ .

The ^{19}F and ^1H n.m.r. spectra (see Page 97) were consistent with the proposed structure. The ^{19}F spectrum showed three regions of absorption at 9.6 (doublet of doublets of quartets, intensity 3), and 0.6 (doublet of doublets of quartets, intensity 3)p.p.m. to low field, and 115.6 (doublet of doublets of quartets of quartets, intensity 1)p.p.m. to high field from external trifluoroacetic acid. The ^1H spectrum showed two overlapping regions of absorption at 5.35 (doublet of quartets of doublets) and 5.48 (doublet of quartets of doublets) τ .

The mass spectrum (Table 32, Page 201) showed a strong parent peak at m/e 310 and the general breakdown was consistent with the proposed structure.

Component E was identified as the second isomer of

1,1,1,2,4,4,4-heptafluoro-3-iodobutane $\text{CF}_3\text{CHF}\cdot\text{CHI}\cdot\text{CF}_3$
(isomer II, erythro or threo) (0.11g., 0.36 mmole, 30%)
(Found: C, 15.7; H, 0.7%; M, 311. $\text{C}_4\text{H}_2\text{F}_7\text{I}$ requires
C, 15.5; H, 0.6%; M, 310) b.p. (isoteniscope) $92.3 \pm 0.2^\circ$.

The i.r. spectrum showed bands at 3.32(w),
3.34(w), 7.10(w), 7.26(m), 7.42(s), 7.55(s), 7.67(vs),
7.81(s), 7.89(s), 8.02(vs), 8.25(vs), 8.32(vs), 8.57(s),
8.75(vs), 9.03(s), 9.14(s), 9.50(m), 10.14(w), 11.41(m),
11.88(m), 13.04(w), 13.38(m), 14.00(m), 14.97(m), and
15.35(vs) μ .

The ^{19}F and ^1H n.m.r. spectra (see Page 99)
were consistent with the proposed structure. The ^{19}F
spectrum showed three regions of absorption at 12.6
(doublet of doublets of quartets, intensity 3) and 2.2
(doublet of doublets of quartets, intensity 3) p.p.m. to
low field, and 111.6 (doublet of quartets of doublets of
quartets, intensity 1) p.p.m. to high field from external
trifluoroacetic acid. The ^1H spectrum showed two regions
of absorption at 5.04 (doublet of doublets of quartets),
and 5.44 (doublet of doublets of quartets) τ .

The mass spectrum (Table 32, Page 201) showed
a strong parent ion at m/e 310 and the general breakdown
pattern was consistent with the proposed structure.

Component F was identified as 1,1,1,3-tetrafluoro-3-iodo-2-trifluoromethylpropane $(\text{CF}_3)_2\text{CH}\cdot\text{CHF}\text{I}$ (0.10g.,

0.34 mmole, 28%) (Found: C, 15.5; H, 0.7%; $\underline{\text{M}}$, 312.

$\text{C}_4\text{H}_2\text{F}_7\text{I}$ requires C, 15.5; H, 0.6%; $\underline{\text{M}}$, 310) b.p. (isoten - iscope) $98.2 \pm 0.2^\circ$.

The i.r. spectrum showed bands at 3.34(w), 7.04(w), 7.22(s), 7.53(s), 7.75(s), 7.90(s), 8.11(s), 8.30(s), 8.39(s), 8.54(m), 9.04(s), 9.12(s), 9.67(m), 10.30(m), 11.07(m), 11.80(m), 13.06(m), 13.46(m), 14.05(s), 14.83(s), and 15.35(s) μ .

The ^{19}F and ^1H n.m.r. spectra (see Page 102) were consistent with the proposed structure. The ^{19}F spectrum showed three regions of absorption at 12.2 (doublet of quartets of doublets of doublets, intensity 3) and 11.0 (quartet of doublets of doublets, intensity 3)p.p.m. to low field, and 80.6 (doublet of doublets of quartets of quartets, intensity 1)p.p.m. to high field from external trifluoroacetic acid. The ^1H spectrum showed two regions of absorption at 2.82 (doublet of doublets, intensity 1) and 6.40 (doublet of septets of doublets, intensity 1) τ .

The mass spectrum (Table 33, Page 202) showed a strong parent ion at m/e 310 and the general breakdown pattern was consistent with the proposed structure.

Material Balance: 5% of the isomeric 1,3,3,3-tetrafluoropropenes, and 52% of the 2,3,3,3-tetrafluoropropene were consumed during the reaction; all of the reacted olefins was recovered as 1 : 1 adducts. The products represent a 100% recovery (by weight) of input material.

Reaction 2.

Trifluoriodomethane (10.52g., 53.80 mmoles) and a mixture of the isomeric tetrafluoropropenes (3.05g., 26.75 mmoles) consisting of trans-1,3,3,3-tetrafluoropropene (1.74g., 15.24 mmoles), cis-1,3,3,3-tetrafluoropropene (1.19g., 10.47 mmoles), and 2,3,3,3-tetrafluoropropene (0.11g., 1.06 mmoles), sealed in a silica tube (capacity 350 ml.), were irradiated (140 hr.) to give the following fractions:

i) a -196° fraction (0.05g., 0.47 mmole) (Found: M, 115) shown by i.r. spectroscopy to be a mixture of hexafluoroethane, trifluoromethane, and an unknown component showing strong i.r. bands at 8.45, 9.30, and 9.73 μ .

ii) a combined -130° and -95° fraction (11.59g., 67.40 mmoles) (Found: M, 172) shown by g.l.c. (4m. D.D.P. at 20°) to be a mixture of unchanged trifluoriodomethane (9.22g., 47.00 mmoles, 87% recovered), trans-1,3,3,3-tetrafluoropropene (1.56g., 13.76 mmoles, 90% recovered), cis-1,3,3,3-tetrafluoropropene (0.76g., 6.67 mmoles, 64% recovered), and a trace of an unknown component, and

iii) a -78° fraction (1.70g.) shown by g.l.c. (2m. D.D.P. at 80°) to contain five components (B-F, as in the previous reaction).

The four major components of the latter fraction, present in the ratio C:D:E:F of ~~the~~ 19:40:22:17, were identified as 1,1,1,2,4,4,4-heptafluoro-2-iodobutane (0.32g., 1.04 mmoles, 97%), 1,1,1,2,4,4,4-heptafluoro-3-iodobutane (isomer I) (0.68g., 2.18 mmoles, 41%), 1,1,1,2,4,4,4-heptafluoro-3-iodobutane (isomer II) (0.37g., 1.20 mmoles, 23%), and 1,1,1,3-tetrafluoro-3-iodo-2-trifluoromethylpropane (0.29g., 0.93 mmole, 18%) respectively.

Material Balance: 21% of the isomeric 1,3,3,3-tetrafluoropropenes, and 100% of the 2,3,3,3-tetrafluoropropene were consumed during the reaction; 82% of the former and 97% of the latter reacted to give 1 : 1 adducts. The products represent a 98% recovery (by weight) of input material.

Reaction 3.

The -130° fraction from the previous reaction was re-irradiated in order to obtain more 1 : 1 adducts.

The -78° fraction of this reaction showed three major components in the ratio D:E:F of 42:26:27.

Addition of Trifluoroiodomethane to Trans-1,3,3,3-
tetrafluoropropene.

Trifluoroiodomethane (2.36g., 12.10 mmoles) and trans-1,3,3,3-tetrafluoropropene (0.35g., 3.04 mmoles), sealed in a silica tube (capacity 100 ml.), were irradiated (140 hr.) to give:-

i) a -130° fraction (2.31g., 12.78 mmoles) (Found: M, 181) shown by g.l.c. (4m. D.D.P. at 20°) to contain unchanged trifluoroiodomethane (2.03g., 10.36 mmoles, 85% recovered), trans-1,3,3,3-tetrafluoropropene (0.20g., 1.72 mmoles, 57% recovered) and cis-1,3,3,3-tetrafluoropropene (0.08g., 0.67 mmole, 51%), and

ii) a -78° fraction (0.23g.) shown by g.l.c. (2m. D.D.P. at 80°) to contain five components (A,B,D,E,F as in previous reactions).

The three major components of the latter fraction, present in the ratio D:E:F of 49:21:20, were identified as 1,1,1,2,4,4,4-heptafluoro-3-iodobutane (isomer I) (0.11g., 0.37 mmole, 28%), and (isomer II) (0.05g., 0.16 mmole, 12%) and 1,1,1,3-tetrafluoro-3-iodo-2-trifluoromethyl - propane (0.05g., 0.15 mmole, 11%) respectively.

Material Balance: 43% of the trans-olefin was consumed during the reaction; half reacting to give the cis-olefin

and half to give the 1 : 1 adducts. The products represent a 95% recovery (by weight) of input material.

Addition of Trifluoroiodomethane to Cis-1,3,3,3-
tetrafluoropropene.

Trifluoroiodomethane (0.91g., 4.64 mmoles) and cis-1,3,3,3-tetrafluoropropene (0.14g., 1.25 mmoles), sealed in a silica tube (capacity 100 ml.), were irradiated (148 hr.) to give:-

- i) a trace of a -196° fraction,
- ii) a -130° fraction (0.93g., 4.91 mmoles) (Found: M, 189) shown by g.l.c. (4m. D.D.P. at 20°) to contain unchanged trifluoroiodomethane (0.83g., 4.16 mmoles, 90% recovered), cis-1,3,3,3-tetrafluoropropene (0.06g., 0.53 mmole, 42% recovered), and trans-1,3,3,3-tetrafluoropropene (0.03g., 0.24 mmole, 33%), and
- iii) a -78° fraction (0.08g.) shown by g.l.c. (2m. D.D.P. at 80°) to contain five components (A,B,D,E,F as in previous reactions).

The three major components of the latter fraction, present in the ratio D:E:F of 57:22:14, were identified as 1,1,1,2,4,4,4-heptafluoro-3-iodobutane (isomer I) (0.04g., 0.14 mmole, 20%) and (isomer II) (0.02g., 0.06 mole, 8%),

and 1,1,1,3-tetrafluoro-3-iodo-2-trifluoromethylpropane (0.01g., 0.03 mmole, 4%) respectively.

Material Balance: 58% of the cis-olefin was consumed during the reaction; 33% reacted to give the trans - olefin, and 32% reacted to give the 1 : 1 adducts. The products represent a 96% recovery (by weight) of input material.

Reaction of a Mixture of 1 : 1 Adducts with Powdered Potassium Hydroxide.

A mixture of 1 : 1 adducts (2.51g., 8.12 mmoles) consisting of 1,1,1,2,4,4,4-heptafluoro-2-iodobutane (0.15g., 0.49 mmole), 1,1,1,2,4,4,4-heptafluoro-3-iodobutane (isomer I) (1.13g., 3.65 mmoles) and (isomer II) (0.58g., 1.87 mmoles), and 1,1,1,3-tetrafluoro-3-iodo-2-trifluoromethylpropane (0.50g., 1.62 mmoles) were condensed in vacuo onto powdered potassium hydroxide (ca. 20g.) and gently warmed (30 min.).

Fractional condensation of the products yielded:-

i) a low-boiling fraction (1.05g., 6.21 mmoles) (Found: M, 169) which was shown by g.l.c. (4m. D.D.P. at 20°) to contain five components in the ratio L:M:N:O:P of 67:3:15:3:12, and

ii) a high-boiling fraction (0.31g., 1.00 mmole, 12% recovered), presumed to be returned reactants, which was not examined further.

The five components in the low-boiling fraction were separated by g.l.c. (4m. D.D.P. at 20°).

Component L was identified as hexafluorobut-2-yne (0.67g., 4.16 mmoles, 58%) (Found: M, 162. Calc. for C_4F_6 : M, 162). The i.r. spectrum was identical to that of an authentic sample.

Component M (0.03g., 0.19mmole, 3%) (Found: M, 170) was shown by i.r. spectroscopy to be a mixture of an allene (presumably hexafluorobut-1,2-diene $CF_2=C:CF\cdot CF_3$) showing strong bands at 4.93 and 6.70 μ , and an unknown olefin showing a strong band at 5.70 μ .

The i.r. spectrum showed bands at 3.30(w), 4.25(w), 4.47(w), 4.93(s), 5.70(s), 6.70(m), 7.24(s), 7.56(s), 7.70(s), 7.78(s), 8.18(s), 8.37(s), 8.62(s), 8.92(s), 9.40(w), 10.17(s), 10.26(s), 10.63(s), 11.40(m), 12.75(m), 12.91(m), 13.20(w), and 14.16(s) μ .

Component N was identified as trans-1,1,1,2,4,4,4-heptafluorobut-2-ene $CF_3\cdot CF:CH\cdot CF_3$ (0.17g., 0.92 mmole, 13%) (Found: M, 182. Calc. for C_4HF_7 : M, 182).

The i.r. spectrum showed bands at 3.20(w),

4.21(w), 4.42(w), 4.88(w), 5.74(s), 6.24(w), 6.56(w), 6.96(m), 7.13(s), 7.63(vs), 7.84(vs), 8.22(vs), 8.37(vs), 9.18(w), 9.42(s), 10.17(w), 11.58(s), 12.14(m), 13.53(s), 13.59(s), 13.65(s), 14.60(w), and 15.44(s) μ , and was identical to that of a sample prepared simultaneously by another route in this department¹⁴⁵ (Found: C, 26.2; H, 0.7%. Calc. for $C_4H_7F_7$: C, 26.4; H, 0.5%).

The ^{19}F and 1H n.m.r. spectra (see Page 185) were consistent with the proposed structure. The ^{19}F spectrum showed three regions of absorption at 15.8 (doublet of doublets of quartets, intensity 6) and 1.0 (doublet of quartets of doublets, intensity 6) p.p.m. to low field, and 42.2 (doublet of quartets of quartets, intensity 2) p.p.m. to high field from external trifluoroacetic acid. The 1H spectrum showed one region of absorption at 4.20 (doublet of quartets with further splitting evident) τ . The shifts in the fluorine spectrum are identical to those reported in the literature.¹⁷⁸ Component O was identified as cis-1,1,1,2,4,4,4-heptafluoro-but-2-ene $CF_3 \cdot CF:CH \cdot CF_3$ (0.03g., 0.19 mmole, 3%) (Found: M, 181. Calc. for $C_4H_7F_7$: M, 182).

The i.r. spectrum showed bands at 3.25(w), 4.13(w), 4.39(w), 4.53(w), 4.82(w), 5.05(w), 5.50(w),

5.56(w), 5.69(w), 5.81(s), 6.77(w), 6.83(w), 6.92(m),
 6.94(m), 7.04(m), 7.20(s), 7.63(s), 7.94(s), 8.15(s),
 8.48(vs), 8.56(vs), 8.96(vs), 10.35(w), 11.13(s), 11.88(m),
 12.68(w), 14.05(s), 14.13(s), 14.20(s), and 15.38(s) μ ,
 and was identical to that of a sample prepared simultaneously
 by another route in this department¹⁴⁵ (Found : C, 26.6; H,
 0.8%. Calc. for $C_4H_7F_7$: C, 26.4; H, 0.5%).

The ^{19}F and 1H n.m.r. spectra (see Page 186)
 were consistent with the proposed structure. The ^{19}F
 spectrum showed three regions of absorption at 19.4
 (doublet of quartets of doublets, intensity 3) and
 6.4 (quartet of doublets of doublets, intensity 3) p.p.m.
 to low field, and 38.0 (doublet of quartets of quartets,
 intensity 1) p.p.m. to high field from external trifluoro -
 acetic acid. The 1H spectrum showed one region of absorption
 at 4.10 (doublet of quartets of quartets) γ .

Component P was identified as 1,3,3,3-tetrafluoro-2-
 trifluoromethylpropene $(CF_3)_2C : CHF$ (0.14g., 0.75 mmole,
 10%) (Found: C, 26.4; H, 0.7%; \underline{M} , 182. Calc. for $C_4H_7F_7$:
 C, 26.4; H, 0.5%; \underline{M} , 182) b.p. $16.3 \pm 0.2^\circ$ (lit.¹⁵⁵ 17°).

The i.r. spectrum showed bands at 3.20(w),
 3.55(w), 4.19(w), 4.35(w), 4.64(w), 5.08(w), 5.49(m), 5.67(m),
 5.90(s), 6.63(w), 6.86(w), 7.13(s), 7.57(s), 7.88(s), 8.18(s),
 8.39(vs), 8.87(s), 9.38(m), 10.08(s), 10.95(m), 11.85(m),
 12.64(w), 12.82(w), 13.62(s), 13.69(s), 13.79(s), and 14.32(w) μ .

The ^{19}F and ^1H n.m.r. spectra (see Page 187) were consistent with the proposed structure. The ^{19}F spectrum showed three regions of absorption at 16.3 (doublet of quartets of doublets, intensity 3) and 12.9 (a quintet of doublets, intensity 3) p.p.m. to low field, and 32.4 (doublet of quartets of quartets, intensity 1) p.p.m. to high field from external trifluoroacetic acid. The ^1H spectrum showed one region of absorption at 2.69 (doublet of quartets of quartets) τ .

Material Balance: 88% of the 1 : 1 adducts was consumed during the reaction; 87% was recovered as the low-boiling fraction.

Reaction of 1,1,1,2,4,4,4-Heptafluoro-2-iodobutane with
Powdered Potassium Hydroxide.

1,1,1,2,4,4,4-Heptafluoro-2-iodobutane (0.10g., 0.32 mmole) was condensed in vacuo onto powdered potassium hydroxide (ca. 5g.) and left at room temperature (2hr.).

The products (0.05g., 0.27 mmole) (Found: M, 180), condensing at -130° , were shown by i.r. spectroscopy and g.l.c. (4m. D.D.P. at 20°) to be trans-1,1,1,2,4,4,4-heptafluorobut-2-ene (0.05g., 0.25 mmole, 84%) contaminated with an unknown minor component (0.01 mmole, 2%) with a

shorter g.l.c. retention time, present in the ratio 96:4.

Material Balance: All of the butane was consumed during the reaction; 84% reacted to give trans-1,1,1,2,4,4,4-heptafluorobut-2-ene. The products represent an 85% (molar) recovery of input material.

Reaction of 1,1,1,2,4,4,4-Heptafluoro-3-iodobutane (isomer I)
with Powdered Potassium Hydroxide.

1,1,1,2,4,4,4-Heptafluoro-3-iodobutane (isomer I) (0.20g., 0.65 mmole) was condensed in vacuo onto powdered potassium hydroxide (ca. 5g.) and left at room temperature (20 min.) to give:-

i) a -130° fraction (0.09g., 0.48 mmole) (Found: M, 175) shown by i.r. spectroscopy and g.l.c. (4m. D.D.P. at 20°) to be a mixture of trans-1,1,1,2,4,4,4-heptafluorobut-2-ene (0.06g., 0.34 mmole, 69%) and hexafluorobut-2-yne (0.02g., 0.14 mmole, 29%), present in the ratio 70:30 respectively, and

ii) a -78° fraction (0.05g., 0.16 mmole, 25% recovered) shown by i.r. spectroscopy to be unchanged 1,1,1,2,4,4,4-heptafluoro-3-iodobutane contaminated with an unknown component showing strong i.r. bands at 6.02, 7.39, 7.60, 7.98, 10.40, 11.62, and 13.71 μ .

Material Balance: 75% of the butane was consumed during the reaction; 69% reacted to give trans-1,1,1,2,4,4,4-heptafluorobut-2-ene and 29% to give hexafluorobut-2-yne. The products represent a 98% (molar) recovery of input material.

A further experiment required warming before reaction occurred but gave trans-1,1,1,2,4,4,4-heptafluorobut-2-ene (70%) and hexafluorobut-2-yne (28%), though a third reaction gave the alkyne (83%) and the trans-olefin (13%) and again required warming.

Reaction of 1,1,1,2,4,4,4-Heptafluoro-3-iodobutane (isomer I)
with Aqueous Potassium Hydroxide.

1,1,1,2,4,4,4-Hepta-3-iodobutane (isomer I) (0.11g., 0.36 mmole) was condensed in vacuo into a flask (10 ml.) fitted with a tap through which aqueous potassium hydroxide (5 ml., 3M.) was allowed to run in. The reaction was left (15 min.) with frequent shaking, then the volatile products were transferred to the vacuum-system and fractionally condensed to give:-

i) a -130° fraction (0.03g., 0.14 mmole) shown by i.r. spectroscopy and g.l.c. (4m. D.D.P. at 200°) to be a mixture of hexafluorobut-2-yne (0.02g., 0.13mmole, 63%), trans - (ca. 0.003g., 0.014 mmole, 4%), and cis-1,1,1,2,4,4,4-

heptafluorobut-2-ene (ca. 0.003g., 0.014 mmole, 4%), present in the ratio 88:6:6 respectively, and

ii) a -78° fraction (0.05g., 0.16 mmole), after drying over phosphorus pentoxide, which was shown by i.r. spectroscopy to be a mixture of unchanged reactant and the unknown component from the previous reaction with powdered potassium hydroxide.

Material Balance: About 60% of the butane was consumed during the reaction; 63% reacted to give the alkyne and 8% to give the cis- and trans-olefins. The products represent an 83% (molar) recovery of input material.

Reaction of 1,1,1,2,4,4,4-Heptafluoro-3-iodobutane (isomer II)
with Powdered Potassium Hydroxide.

1,1,1,2,4,4,4-Heptafluoro-3-iodobutane (isomer II) (0.31g., 1.00 mmole) was condensed onto powdered potassium hydroxide (ca. 5g.). On warming (20 min.) reaction occurred to give:-

i) a -130° fraction (0.12g., 0.75 mmole) (Found: M, 161) shown by i.r. spectroscopy and g.l.c. (4m. D.D.P. at 20°) to be a mixture of hexafluorobut-2-yne (0.09g., 0.56 mmole, 56%), trans-1,1,1,2,4,4,4-heptafluorobut-2-ene (0.02g., 0.07 mmole, 7%), and an unknown component (0.11 mmole, 11%) having a slightly longer retention time than the alkyne and showing

strong i.r. bands at 5.80, 7.30, 9.45, 11.68, and 12.53 μ , present in the ratio 75:9:16 respectively, and

ii) a -78° fraction (0.04 mmole) which was not investigated.

Material Balance: 96% of the butane was consumed during the reaction; 56% reacted to give the alkyne, 7% to give the trans-olefin, and 11% to give the unknown component. The products represent a 79% (molar) recovery of input material.

A further reaction gave a similar ratio of products. The products were hexafluorobut-2-yne, the unknown component, trans-olefin, and cis-olefin in the ratio of 74:16:8:2 respectively.

Reaction of 1,1,1,3-Tetrafluoro-3-iodo-2-trifluoromethyl - propane with Powdered Potassium Hydroxide.

1,1,1,3-Tetrafluoro-3-iodo-2-trifluoromethyl - propane (0.31g., 1.00 mmole) was condensed in vacuo onto powdered potassium hydroxide (ca. 5g.) and left at room temperature (15 min.). The products, on fractional condensation, gave:-

i) a -130° fraction (0.16g., 0.89 mmole) (Found: M, 181)

shown by i.r. spectroscopy and g.l.c. (4m. D.D.P. at 20°) to be pure 1,3,3,3-tetrafluoro-2-trifluoromethylpropene (0.16g., 0.89 mmole, 95%), and

ii) a -78° fraction (0.02g., 0.06 mmole, 6% recovered) shown by i.r. spectroscopy to be unchanged reactant.

Material Balance: 94% of the butane was consumed in the reaction; 95% reacted to give the olefin. The products represent a 95% recovery (molar) of input material.

The Addition of Bromine to Tetrafluoropropene.

Bromine (1.41g., 8.80 mmoles) and a mixture of the isomeric tetrafluoropropenes (1.36g., 11.9 mmoles) consisting of trans-1,3,3,3-tetrafluoropropene (0.77g., 6.78 mmoles), cis-1,3,3,3-tetrafluoropropene (0.53g., 4.64 mmoles), and 2,3,3,3-tetrafluoropropene (0.05g., 0.48 mmole) were sealed in vacuo in a silica tube (capacity 100 ml.) and left in the dark (100 hr.); no reaction occurred. Reaction did occur when the mixture was irradiated (110 hr.).

The products were shaken with mercury and fractionally condensed to give:-

i) a -196° fraction (0.02g., 0.20 mmole) (Found: M, ca. 100) which contained i.r. bands at 5.94(w), 7.52(w), 7.67(w),

7.99(m), 8.20(m), 8.64(m), 8.90(m), 9.04(s), 9.20(s), 9.26(s), 9.68(s), 9.76(s), 10.06(w), 10.82(w), 11.40(w), 13.03(w), 13.12(w), and 13.30(w) μ ,

ii) a -130° fraction (0.79g., 6.88 mmoles) shown by g.l.c. (4m. D.D.P. at 20°) to be a mixture of unchanged trans-1,3,3,3-tetrafluoropropene (0.71g., 6.19 mmoles, 91% recovered), cis-1,3,3,3-tetrafluoropropene (0.08g., 0.69 mmole, 15% recovered), and with a trace of 2,3,3,3-tetrafluoropropene, and

iii) a -64° fraction (1.23g.) containing i.r. bands at 3.45(w), 7.43(m), 7.54(s), 7.65(m), 7.88(s), 8.00(s), 8.28(s), 8.41(s), 8.67(m), 8.88(s), 9.06(m), 9.20(m), 9.63(m), 10.40(m), 11.48(broad, m), 12.82(broad, m), 13.30(m), and 14.38(m) μ , and shown by g.l.c. (2m. D.D.P. at 95°) to contain four components, present in the ratio 6:3:30:57 respectively; the two minor components had much shorter g.l.c. retention times than the major components.

The two major components were separated by g.l.c. (2m. D.D.P. at 90°).

The larger component was identified as one of the isomeric 1,2-dibromo-1,3,3,3-tetrafluoropropanes $\text{CF}_3\cdot\text{CHBr}\cdot\text{CHFBr}$ (isomer II, threo or erythro) (0.67g., 2.46 mmoles, 58%) (Found: C, 133; H, 0.7%; M, 273. $\text{C}_3\text{H}_2\text{Br}_2\text{F}_4$

requires C, 13.1; H, 0.7%; M, 274) b.p. (isoteniscope) $107.9 \pm 0.2^\circ$.

The i.r. spectrum showed bands at 3.34(w), 3.37(w), 7.16(w), 7.34(m), 7.50(s), 7.62(m), 7.85(s), 8.07(m), 8.21(m), 8.28(m), 8.42(s), 8.64(m), 9.06(m), 9.28(m), 9.39(m), 9.65(m), 10.43(m), 11.46(m), 11.50(m), 12.90(m), 12.95(m), 13.30(m), 14.43(broad, m), and 14.71(m) μ .

The ^{19}F and ^1H n.m.r. spectra (see Page 124) were consistent with the proposed structure. The ^{19}F spectrum showed two regions of absorption at 9.2(doublet of doublets, intensity 2.8) p.p.m. to low field, and 65.6 (doublet of doublets of quartets, intensity 1.0) p.p.m. to high field from external trifluoroacetic acid. The ^1H spectrum showed two regions of absorption at 3.35(doublet of doublets, intensity 1) and 5.62 (doublet of quartets of doublets, intensity 1) γ .

The mass spectrum (Table 36 , Page 205) showed a strong parent peak at m/e 272 and the general breakdown was consistent with the proposed structure.

The second component was identified as the other isomeric 1,2-dibromo-1,3,3,3-tetrafluoropropane $\text{CF}_3 \cdot \text{CHBr} \cdot \text{CHFBr}$ (isomer I, erythro or threo) (0.36g., 1.32 mmoles, 31%)

(Found: C, 13.3; H, 0.7%; M, 275. $C_3H_2Br_2F_4$ requires C, 13.1; H, 0.7%; M, 274) b.p. (isoteniscope) $107.5 \pm 0.2^\circ$.

The i.r spectrum showed bands at 3.34(w), 3.41(w), 7.13(w), 7.20(w), 7.26(w), 7.39(s), 7.60(s), 7.83(s), 7.98(s), 8.04(s), 8.26(s), 8.44(s), 8.67(s), 8.86(s), 9.18(m), 9.22(m), 9.42(m), 9.63(m), 10.43(w), 11.37(m), 11.58(m), 11.84(w), 12.78(m), 12.85(m), 13.34(m), 13.40(m), 13.45(m), 14.41(m), and 14.71(m) μ .

The ^{19}F and 1H n.m.r. spectra (see Page 122) were consistent with the proposed structure. The ^{19}F spectrum showed two regions of absorption at 10.0 (doublet of doublets, intensity 3) p.p.m. to low field, and 60.2 (doublet of quartets of doublets, intensity 1) p.p.m. to high field from external trifluoroacetic acid. The 1H spectrum showed two regions of absorption at 3.47 (doublet of doublets, intensity 1) and 5.50 (doublet of quartets of doublets, intensity 1) τ .

The mass spectrum (Table 36 , Page 205) showed a strong parent peak at m/e 272 and the general breakdown pattern was consistent with the proposed structure.

Material Balance: All of the 2,3,3,3-tetrafluoropropene was consumed during the reaction without showing any olefin dibromide. 9% of the trans- and 85% of the cis-1,3,3,3-tetrafluoropropene were consumed during the reaction; 89%

going to the 1 : 1 adducts. The products represent a 100% (molar) recovery of input olefins.

The Addition of Hydrogen Bromide to Tetrafluoropropene.

Reaction 1.

Hydrogen bromide (4.33g., 53.5 mmoles) and a mixture of the isomeric tetrafluoropropenes (3.05g., 26.75 mmoles) consisting of trans-1,3,3,3-tetrafluoropropene (1.74g., 15.51 mmoles), cis-1,3,3,3-tetrafluoropropene (1.15g., 10.01 mmoles), and 2,3,3,3-tetrafluoropropene (0.12g., 1.01 mmoles) were sealed in a silica tube (capacity 350 ml.) and irradiated (26 hr.).

The products were transferred to the vacuum - system and fractional condensation gave the following fractions.

i) Hydrogen (0.02g., 11.1 mmoles) (Found:M, 2.0. Calc. for H_2 : M, 2.0).

ii) A -196° fraction (2.12g., 26.77 mmoles) (Found:M, 79) which was shown by i.r. spectroscopy to be unchanged hydrogen bromide (2.12g., 26.30 mmoles, 49% recovered) contaminated with an unknown component showing weak i.r. bands at 5.90, 7.29, 8.27, 8.69, 9.18, 9.24, and 9.70 μ .

iii) A -130° fraction (1.80g., 15.90 mmoles) (Found:M, 113)

which was shown by i.r. spectroscopy and g.l.c. (4m. D.D.P. at 20°) to be a mixture of hydrogen bromide (0.7g., 0.81 mmole, 2% recovered), trans-1,3,3,3-tetrafluoropropene (1.50g., 13.12 mmoles, 85% recovered), cis-1,3,3,3-tetrafluoropropene (0.23g., 1.98 mmoles, 20% recovered), and a trace of an unknown component with a slightly longer g.l.c. retention time.

iv) A -95° fraction (0.01g., 0.85 mmole) was shown by i.r. spectroscopy and g.l.c. (4m. D.D.P. at 20°) to contain trans-1,3,3,3-tetrafluoropropene (ca. 0.007g., 0.59 mmole, 4% recovered), cis-1,3,3,3-tetrafluoropropene (ca. 0.003g., 0.26 mmole, 3% recovered), and a trace of an unknown component (3% of this fraction) with a longer g.l.c. retention time.

v) A -78° fraction (2.19g., after shaking with mercury) which was shown by g.l.c. (2m. D.D.P. at 80°) to contain six components; three major ones (96% of fraction), present in the ratio R:S:T of 29:29:37, and three minor components (4% of fraction) with much shorter g.l.c. retention times.

The three major components of the latter fraction were separated by g.l.c. (2m. D.D.P. at 70°).

Component R was identified as 1-bromo-1,3,3,3-tetrafluoropropane $\text{CF}_3 \cdot \text{CH}_2 \cdot \text{CHFBr}$ (0.57g., 2.94 mmoles, 27%) (Found: C, 18.7; H, 1.6%; M, 195. Calc. for $\text{C}_3 \text{H}_3 \text{BrF}_4$: C, 18.5; H, 1.5%; M, 195) b.p. (isotenscope) $61.0 \pm 0.2^\circ$

(lit.¹²⁸ b.p. 59.3°).

The i.r. spectrum showed bands at 3.33(w), 3.36(w), 6.82(w), 7.01(m), 7.21(s), 7.43(s), 7.53(m), 7.75(s), 7.90(s), 8.13(s), 8.35(m), 8.54(s), 8.77(s), 9.38(w), 9.65(m), 9.99(m), 11.33(m), 11.81(3), 13.45(s), and 14.80(broad, w) μ .

The ^{19}F and ^1H n.m.r. spectra (see Page 119) were consistent with the proposed structure. The ^{19}F spectrum showed two regions of absorption at 12.6 (triplet of doublets, intensity 3) p.p.m. to low field, and 59.6 (doublet of doublets of doublets of quartets, intensity 1) p.p.m. to high field from external tri-fluoroacetic acid. The ^1H spectrum showed two regions of absorption at 3.38 (doublet of doublets of doublets, intensity 1) and 7.08 (complex, intensity 2) τ .

The mass spectrum (Table 35, Page 204) showed a parent peak at m/e 194 and the general breakdown pattern was consistent with the proposed structure.

Component S was identified as 2-bromo-1,1,1,3-tetrafluoropropane $\text{CF}_3\cdot\text{CHBr}\cdot\text{CH}_2\text{F}$ (0.57g., 2.94 mmoles, 27%) (Found: C, 18.6; H, 1.5%; $\underline{\text{M}}$, 195. $\text{C}_3\text{H}_3\text{BrF}_4$ requires C, 18.5; H, 1.5%; $\underline{\text{M}}$, 195) b.p. (isoteniscope) $65.5 \pm 0.2^\circ$.

The i.r. spectrum showed bands at 3.33(w),

3.41(w), 6.78(w), 7.12(w), 7.32(m), 7.53(s), 7.77(m), 7.91(s), 8.35(s), 8.87(s), 9.18(m), 9.56(s), 10.00(m), 11.54(w), 12.22(w), 12.78(m), 12.84(m), 12.90(m), and 14.60(m) μ .

The ^{19}F and ^1H n.m.r. spectra (see Page 120) were consistent with the proposed structure. The ^{19}F spectrum showed two regions of absorption at 6.8 (triplet(distorted), intensity 3.2) p.p.m. to low field, and 142.2 (triplet of doublets of quartets, intensity 1) p.p.m. to high field from external trifluoroacetic acid. The ^1H spectrum showed two overlapping regions of absorption at 5.32 (an ABMX system) and 5.71 (masked by ABMX system) γ .

The mass spectrum (Table 35, Page 204) showed a strong parent peak at m/e 194 and the general breakdown was consistent with the proposed structure.

Component T was shown by i.r. spectroscopy to be a mixture of the isomeric 1,2-dibromo-1,3,3,3-tetrafluoropropanes (1.02g., 3.74 mmoles, 35%).

Material Balance: All of the 2,3,3,3-tetrafluoropropene was consumed during the reaction, none of which was observed as adducts. 37% of the 1,3,3,3-tetrafluoropropenes was consumed; 54% reacted to give the 1 : 1 adducts and 35%

to give the dibromides. The products (after the removal of bromine) represent an 83% (by weight) recovery of input material.

Reaction 2.

Hydrogen bromide (3.90g., 48.11 mmoles) and a mixture of the isomeric tetrafluoropropenes (3.61g., 31.74 mmoles) consisting of trans-1,3,3,3-tetrafluoro - propene (2.06g., 18.13 mmoles), cis-1,3,3,3-tetrafluoro - propene (1.41g., 12.39 mmoles), and 2,3,3,3-tetrafluoro - propene (0.14g., 1.27 mmoles) were sealed in a silica tube (capacity 350 ml.) and irradiated (7hr.) to give products which were separated by fractional condensation into the following fractions:-

i) hydrogen (ca. 0.006 g., 2.79 mmoles) present as a non-condensable gas,

ii) a combined -196° and -130° fraction (6.82g., 72.05 mmoles) (Found: M, 95) shown by i.r. spectroscopy and g.l.c. (4m. D.D.P. at 20°) to be a mixture of unchanged hydrogen bromide (3.43g., 42.32 mmoles, 88% recovered), trans-1,3,3,3-tetrafluoropropene (3.04g., 26.62 mmoles, 150% recovered), cis -1,3,3,3-tetrafluoropropene (0.29g., 2.56 mmoles, 21% recovered) and 2,3,3,3-tetrafluoro - propene (0.06g., 0.55 mmole, 43% recovered),

iii) a combined -95° and -78° fraction (0.35g.) shown by g.l.c. (2m. D.D.P. at 70°) to contain ten components, and

iv) bromine (0.09g., 1.10 mmoles) estimated by shaking with mercury.

The major components of the combined -95° and -78° fraction were identified by their g.l.c. retention times and shown to be 1-bromo-1,3,3,3-tetrafluoropropane (ca. 0.092g., 0.47 mmole, 30%), 2-bromo-1,1,1,3-tetrafluoropropane (ca. 0.056g., 0.29 mmole, 19%), 1,2-dibromo-1,3,3,3-tetrafluoropropane (isomer I) (ca. 0.116g., 0.43 mmole, 28%) and (isomer II) (ca. 0.041g., 0.15 mmole, 10%), present in the ratio 31:19:27:10 respectively. Some unreacted olefins (5% of this fraction) were also observed.

Material Balance: 57% of the 2,3,3,3-tetrafluoropropene was consumed during the reaction, none of which appeared as adducts. 4% of the 1,3,3,3-tetrafluoropropene was consumed during the reaction; 49% reacted to give the 1 : 1 adducts and 38% to give the dibromides. The products represent a 97% (by weight) recovery of input material.

Reaction 3.

In a further experiment (72 hr. irradiation period) almost all of the olefins were consumed to give

products comprising 1-bromo-1,3,3,3-tetrafluoropropane, 2-bromo-1,1,1,3-tetrafluoropropane, and 1,2-dibromo-1,3,3,3-tetrafluoropropane (isomer I) and (isomer II), present in the ratio 14:12:39:23 respectively, and representing 88% of the liquid fraction.

Addition of Hydrogen Bromide to Tetrafluoropropene
in the Presence of Silver Powder.

Hydrogen bromide (1.85g., 13.41 mmoles) and a mixture of the isomeric tetrafluoropropenes (0.82g., 7.13 mmoles) consisting of trans-1,3,3,3-tetrafluoropropene (0.46g., 4.06 mmoles), cis-1,3,3,3-tetrafluoropropene (0.32g., 2.78 mmoles), and 2,3,3,3-tetrafluoropropene (0.03g., 0.28 mmole), and silver powder (1g.) were sealed in a silica tube (capacity 100 ml.) and irradiated (7 hr.). The only reaction was hydrogen bromide breakdown.

After a further irradiation (9hr), drops of free bromine were observed and fractional condensation of the products gave:

i) hydrogen (ca. 0.007g., 3.50 mmoles) (Found: M, 2.0. Calc. for H_2 : M, 2.0),

ii) a combined -196° and -95° fraction (1.29g., 13.40 mmoles) (Found: M, 96) shown by i.r. spectroscopy and g.l.c.

(4m. D.D.P. at 20°) to be a mixture of unchanged hydrogen bromide (0.53g., 6.51 mmoles, 48% recovered), trans-1,3,3,3-tetrafluoropropene (0.68g., 5.93 mmoles, 150% recovered), cis-1,3,3,3-tetrafluoropropene (0.06g., 0.55 mmole, 20% recovered), and 2,3,3,3-tetrafluoropropene (0.02g., 0.14 mmole, 49% recovered) contaminated with a trace of an unknown component with a longer g.l.c. retention time, and iii) a -78° fraction (0.17 mmole) coloured brown by bromine.

The latter fraction was shown by g.l.c. (2m. D.D. P. at 70°; injection by gas syringe) to contain the 1 : 1 adducts, $\text{CF}_3 \cdot \text{CH}_2 \cdot \text{CHBr}$ and $\text{CF}_3 \cdot \text{CHBr} \cdot \text{CH}_2\text{F}$, and the dibromides, $\text{CF}_3 \cdot \text{CHBr} \cdot \text{CHBr}$ (isomer I) and (isomer II), present in the ratio 32:44:18:3 respectively. A shoulder (3% of the fraction) on the g.l.c. peak corresponding to 1-bromo-1,3,3,3-tetrafluoropropene was probably due to 3-bromo-1,1,1,2-tetrafluoropropene.

Material Balance: 51% of the 2,3,3,3-tetrafluoropropene was consumed during the reaction; 4% reacted to give the probable 1 : 1 adduct. 4% of the 1,3,3,3-tetrafluoropropene was consumed; 55% of which was recovered as the product fraction. The products represent a 98% (molar) recovery of input material.

Preparation of 1,1,1-Trifluoro-3-iodobutane, $\text{CF}_3\text{CH}_2\text{CHI}\cdot\text{CH}_3$.

Trifluoroiodomethane (43.7g., 224 mmoles) and propene (5.73g., 134 mmoles) were condensed in vacuo into four silica tubes (total capacity 1,400 ml.) and the vapour phase irradiated (160 hr.).

Fractional condensation of the products gave a -78° fraction (31g.) containing 1,1,1-trifluoro-3-iodobutane as the major component, and a -130° fraction containing unchanged trifluoroiodomethane.

Distillation of the -78° fraction at atmospheric pressure through a vacuum-jacketed column (40 cm.) fitted with a fractional take-off head gave a fraction (29g., 91% by weight) boiling between 102° and 106° and containing 1,1,1-trifluoro-3-iodobutane (lit. ¹²⁵ b.p. 103.5°).

Dehydroiodination of 1,1,1-Trifluoro-3-iodobutane.

The fraction (29g.) containing 1,1,1-trifluoro-3-iodobutane was condensed in vacuo onto powdered potassium hydroxide (ca. 150g.) contained in a flask (500 ml.) which was connected to a trap of the vacuum-system so that pressure changes could be observed.

On warming a gas was evolved which was condensed into a -196° trap when the pressure in the reaction vessel

exceeded ca. 60 cm. of mercury. When the gas evolution ceased, the products were passed through a -78° trap, the contents of which were re-condensed onto fresh powdered potassium hydroxide and the reaction repeated.

Fractional condensation in vacuo gave products (12.6g., 115 mmoles, 91%) (Found: M, 110. Calc. for $C_3H_5F_3$: M, 110), condensing at -130° , shown by g.l.c. (4m. D.D.P. at 20°) to be a mixture of three components in the ratio 79 : 17 : 4. This mixture of olefins was separated by g.l.c. (4m. D.D.P. at 20°).

The major component was identified as trans-1,1,1-trifluorobut-2-ene $CF_3 \cdot CH : CH \cdot CH_3$ (9.99g., 90.8 mmoles, 79%) (Found: C, 43.3; H, 4.5%; M, 110. $C_4H_5F_3$ requires C, 43.6; H, 4.5%; M, 110) b.p. (isoteniscope) $17.6 \pm 0.2^{\circ}$.

The i.r. spectrum showed bands at 3.20(w), 3.26(m), 3.36(s), 3.41(s), 3.48(m), 3.64(w), 3.78(w), 3.93(w), 4.06(w), 4.17(w), 4.34(w), 4.41(w), 4.60(w), 4.72(w), 4.98(w), 5.42(w), 5.50(w), 5.71(w), ^{5.88(s),} 5.92(s), 6.60(w), 6.87(s), 6.90(s), 7.20(s), 7.34(s), 7.38(s), 7.56(vs), 7.87(vs), 8.61(vs), 8.72(vs), 9.27(s), 10.42(s), 10.50(s), 11.79(m), 14.05(w), 14.59(s), 14.70(s), and 14.82(s) μ .

The ^{19}F and 1H n.m.r. spectra (see Page 188)

were consistent with the proposed structure. The ^{19}F spectrum showed one region of absorption at 13.5 (doublet of quartets of doublets) p.p.m. to low field from external trifluoroacetic acid. The ^1H spectrum showed three regions of absorption at 3.58 (doublet of quartets of quartets, intensity 1), 4.40 (doublet of quartets of quartets, intensity 1), and 8.21 (doublet of quartets of doublets, intensity 3) τ .

The second component was identified as cis -1,1,1-trifluorobut-2-ene $\text{CF}_3 \cdot \text{CH} : \text{CH} \cdot \text{CH}_3$ (2.15g., 19.5 mmoles, 17%) (Found: C, 43.3; H, 4.5%; M, 110. Calc. for $\text{C}_4\text{H}_5\text{F}_3$: C, 43.6; H, 4.5%; M, 110) b.p. (isoteniscope) $16.0 \pm 0.2^\circ$.

The i.r. spectrum showed bands at 3.26(m), 3.31(m), 3.38(m), 3.45(m), 4.00(w), 4.15(w), 4.38(w), 4.47(w), 5.07(w), 5.30(w), 5.60(w), 5.70(w), 5.80(m), 5.96(s), 6.45(w), 6.53(w), 6.60(w), 6.86(s), 6.88(s), 7.04(s), 7.19(s), 7.22(s), 7.55(s), 7.83(vs), 8.08(vs), 8.56(vs), 8.70(vs), 9.40(s), 10.40(w), 10.49(w), 10.71(m), 12.04(m), 12.12(m), and 14.03(s) μ .

It was difficult to obtain enough cis-olefin to enable the n.m.r. spectra to be run on the pure compound. The small amount of pure cis-olefin obtained was mixed with the olefin mixture to obtain a large enough sample. The ^{19}F spectrum (see Page 189) was consistent with the proposed

structure and showed one region of absorption at 19.8 (doublet of quartets) p.p.m. to low field from external trifluoroacetic acid. The ^1H spectrum showed that the shifts of the hydrogen nuclei in the cis-olefin were very similar to the shifts in the trans-olefin; a complex spectrum resulted from which no information could be drawn.

The minor component was identified as 2-trifluoro - methyl propene $\text{CH}_3\cdot\text{C}(\text{CF}_3) : \text{CH}_2$ (0.51g., 4.6 mmoles, 4%) (Found: $\underline{\text{M}}$, 110. Calc. for $\text{C}_4\text{H}_5\text{F}_3$: $\underline{\text{M}}$, 110); its i.r. spectrum was identical to that of an authentic sample prepared in this department.¹⁵⁴

The mixture of olefins was generally used for addition reactions, unless stated otherwise, and is henceforth called trifluorobutene.

Irradiation of Trans-1,1,1-trifluorobut-2-ene.

Trans-1,1,1-trifluorobut-2-ene (0.21g., 1.87 mmoles) contaminated with cis-1,1,1-trifluorobut-2-ene (4%) was irradiated (70 hr.) in a silica tube (capacity 100 ml.).

The products (0.20g., 1.82 mmoles, 97% recovered) were shown by g.l.c. (4m. D.D.P. at 200) to be trans-1,1,1-trifluorobut-2-ene and cis-1,1,1-trifluorobut-2-ene in the ratio 96:4.

Addition of Trifluoriodomethane to Trifluorobutene.

Reaction 1.

Trifluoriodomethane (21.0g., 107.1 mmoles) and a mixture of the isomeric trifluorobutenes (5.88g., 53.55 mmoles) consisting of trans-1,1,1-trifluorobut-2-ene (4.66g., 42.31 mmoles), cis-1,1,1-trifluorobut-2-ene (1.00g., 9.10 mmoles), and 2-trifluoromethylpropene (0.24g., 2.15 mmoles) were condensed in vacuo into two silica tubes (total capacity 700 ml.) and the vapour phase irradiated (96 hr.).

The products were transferred to the vacuum-system and fractional condensation gave the following fractions.

i) A -196° fraction (0.19g., 1.95 mmoles) (Found: M, 97) which was shown by i.r. spectroscopy to be a mixture of trifluoromethane (0.088g., 1.20 mmoles) and hexafluoroethane (0.11g., 0.75 mmole).

ii) A combined -130° and -95° fraction (23.05g., 135.5 mmoles) (Found: M, 170) which was shown by i.r. spectroscopy and g.l.c. (4m. D.D.P. at 20°) to be a mixture of unchanged trifluoriodomethane (18.51g., 94.6 mmoles, 88% recovered), trans-1,1,1-trifluorobut-2-ene (3.90g., 35.42 mmoles, 83% recovered), cis-1,1,1-trifluorobut-2-ene (0.54g., 4.89 mmoles,

53% recovered), and 2-trifluoromethylpropene (0.07g., 0.61 mmole, 28% recovered).

iii) A combined -78° and -24° fraction (3.51g.) which was shown by g.l.c. (2m. D.D.P. at 115°) to contain six components, together with a trace of unchanged olefins with extremely short g.l.c. retention times. The i.r. spectrum showed bands at $3.40(w)$, $6.84(m)$, $7.0(w)$, $7.18(m)$, $7.20(m)$, $7.53(s)$, $7.62(s)$, $7.80(s)$, $7.94(s)$, $8.19(s)$, $8.31(s)$, $8.45(s)$, $8.65(s)$, $8.93(s)$, $9.12(s)$, $9.28(m)$, $9.45(m)$, $9.84(m)$, $10.02(w)$, $10.85(w)$, $11.20(w)$, $11.69(m)$, $12.05(w)$, $13.48(m)$, and $14.21(m)$ μ .

The four major components U, V, W, and X were separated by g.l.c. (4m. D.D.P. at 120°) from the liquid fraction which comprised of the six components U, V, W, X, Y, and Z present in the ratio 40:8:22:25:2:2 respectively.

Component U was identified as

1,1,1-trifluoro-2-iodo-3-trifluoromethylbutane $CF_3 \cdot CHI \cdot CH - (CF_3) \cdot CH_3$ (isomer I) (erythro or threo) (1.40g., 4.58 mmoles, 41%) (Found: C, 19.9; H, 1.9%; \underline{M} , 306. $C_5H_5F_6I$ requires C, 20.0; H, 1.7%; \underline{M} , 306) b.p. (isoteniscope) $107.5 \pm 0.2^{\circ}$.

The i.r. spectrum showed bands at $3.30(w)$, $3.34(w)$, $6.80(m)$, $6.95(w)$, $7.21(m)$, $7.51(s)$, $7.55(s)$, $7.82(s)$, $7.92(vs)$, $8.32(vs)$, $8.44(vs)$, $8.66(vs)$, $8.94(s)$, $9.10(s)$, $9.27(m)$, $9.47(m)$, $9.85(m)$, $10.38(w)$, $11.73(w)$, and

14.38(m) μ .

The ^{19}F and ^1H n.m.r. spectra (see Page 138) were consistent with the proposed structure. The ^{19}F spectrum showed two regions of absorption at 10.4 (doublet, intensity 2.9) and 5.8 (doublet, intensity 3) p.p.m. to low field from external trifluoroacetic acid. The ^1H spectrum showed three regions of absorption at 5.40 (quartet, intensity 1.0), 7.64 (septet, intensity 1.0), and 8.70 (doublet, intensity 3.0) τ .

The mass spectrum (Table 37, Page 206) showed a strong parent peak at m/e 306 and the general breakdown pattern was consistent with the proposed structure.

Component V was identified as 1,1,1-trifluoro-3-iodo-3-trifluoromethylbutane $\text{CF}_3 \cdot \text{CH}_2 \cdot \text{CI} (\text{CF}_3) \cdot \text{CH}_3$ (0.28g., 0.92 mmole, 60%) (Found: C, 20.2; H, 2.0%; $\underline{\text{M}}$, 304. $\text{C}_5\text{H}_5\text{F}_6\text{I}$ requires C, 20.0; H, 1.7%; $\underline{\text{M}}$, 306) b.p. (isoteniscope) $111.0 \pm 0.2^\circ$.

The i.r. spectrum showed bands at 3.34(w), 3.38(w), 6.85(m), 6.96(m), 7.14(m), 7.30(s), 7.51(s), 7.61(s), 7.83(vs), 7.95(vs), 8.22(s), 8.38(vs), 8.46(vs), 8.65(vs), 8.95(s), 9.14(s), 9.22(m), 10.00(m), 10.88(w), 12.10(w), 13.53(w), 14.15(w), and 14.88(w) μ .

The mass spectrum (Table 39, Page 208) showed a strong parent peak at m/e 306 and the general breakdown pattern was reasonably consistent with the proposed structure.

Component W was identified as 1,1,1-trifluoro-3-iodo-2-trifluoromethylbutane $(CF_3)_2 CH \cdot CHI \cdot CH_3$ (0.77g., 2.52 mmole, 23%) (Found: C, 20.3; H, 1.6%; \underline{M} , 305. $C_5H_5F_6I$ requires C, 20.0; H, 1.7%; \underline{M} , 306) b.p. (isotenis - cope) $98.1 \pm 0.2^\circ$.

The i.r. spectrum showed bands at 3.31(w), 3.36(w), 6.83(w), 6.87(w), 7.16(m), 7.52(s), 7.60(s), 7.78(s), 7.96(s), 8.18(s), 8.35(s), 8.55(s), 8.65(s), 8.94(m), 9.13(m), 9.48(m), 10.04(m), 10.50(w), 10.90(w), 11.20(m), 12.10(w), 13.52(w), and 14.35(m) μ .

The ^{19}F and 1H n.m.r. spectra (see Page 141) were consistent with the proposed structure. The ^{19}F spectrum showed two regions of absorption at 15.6 (quintet, intensity 3.0) and 12.6 (quintet, intensity 3.0) p.p.m. to low field from external trifluoroacetic acid. The 1H spectrum showed three regions of absorption at 5.45 (quartet of doublets, intensity 1.0), 6.62 (septet of doublets, intensity 1.0), and 7.96 (doublet, intensity 3.0) τ .

The mass spectrum (Table 38, Page 207) showed a strong parent peak at m/e 306 and the general breakdown pattern was consistent with the proposed structure.

Component X was identified as 1,1,1-trifluoro-2-iodo-3-trifluoromethylbutane (isomer II) (threo or erythro) (0.87g., 2.87 mmoles, 26%) (Found: C, 20.2; H, 1.8%; M, 304. $C_5H_5F_6I$ requires C, 20.0; H, 1.7%; M, 306) b.p. (isoteniscope) $116.3 \pm 0.2^\circ$.

The i.r. spectrum showed bands at 3.31(w), 3.36(w), 6.78(m), 7.15(m), 7.28(s), 7.52(s), 7.63(s), 7.82(vs), 7.96(vs), 8.20(s), 8.36(vs), 8.46(vs), 8.65(vs), 8.90(s), 9.14(s), 9.44(m), 9.87(m), 10.50(w), 10.88(m), 11.23(w), 11.94(w), 13.52(m), and 14.35(m) μ .

The ^{19}F and 1H n.m.r. spectra (see Page 143) were consistent with the proposed structure. The ^{19}F spectrum showed two regions of absorption at 14.3 (quintet, intensity 3) and 8.2 (quintet, intensity 3)p.p.m. to low field from external trifluoroacetic acid. The 1H spectrum showed three regions of absorption at 5.54 (quartet of doublets, intensity 1.0), 7.34 (heptet of doublets, intensity 1.0), and 8.75 (doublet, intensity 3.0) γ .

The mass spectrum (Table 37, Page 206) showed a strong parent peak at m/e 306, and the general breakdown pattern was consistent with the proposed structure.

Material Balance: 72% of the 2-trifluoromethylpropene was consumed during the reaction; 60% reacted to give the 1 : 1 adduct. 20% of the 1,1,1-trifluorobut-2-ene was consumed;

90% reacted to give the 1:1 adducts. The products represent a 99% (by weight) recovery of input material.

Reaction 2.

The combined -130° and -95° fraction from the previous experiment was irradiated (170 hr.) to give 60% olefin conversion. The liquid products ^{were} shown by g.l.c. (4m.D.D.P. at 117°) to contain 1:1 adducts (95% of the liquid fraction) $\text{CF}_3 \cdot \text{CHI} \cdot \text{CH}(\text{CF}_3) \cdot \text{CH}_3$ (isomer I), $\text{CF}_3 \cdot \text{CH}_2 \cdot \text{CI}(\text{CF}_3) \cdot \text{CH}_3$, $(\text{CF}_3)_2 \text{CH} \cdot \text{CHI} \cdot \text{CH}_3$, and $\text{CF}_3 \cdot \text{CHI} \cdot \text{CH}(\text{CF}_3) \cdot \text{CH}_3$ (isomer II) in the ratio 49:1:22:27 respectively. No components corresponding to Y and Z of the previous experiment were observed.

The ratio of 1:1 adducts was checked on a D6 gas density instrument and found to be identical to that obtained above.

Addition of Trifluoroiodomethane to Trans-1,1,1-trifluorobut-2-ene.

Trifluoroiodomethane (3.50g., 17.4 mmoles) and trans-1,1,1-trifluorobut-2-ene (0.22g., 1.99 mmoles) were sealed in a silica tube (capacity 100 ml.) and irradiated (100 hr.) to give products which on fractional condensation gave the following fractions:-

i) a -196° fraction (0.06g., 0.42 mmole) (Found: M, 136) shown by i.r. spectroscopy to be hexafluoroethane contaminated with trifluoromethane,

ii) a combined -130° and -95° fraction (3.43g., 17.89 mmoles) (Found: M, 192) shown by i.r. spectroscopy and g.l.c. (4m. D.D.P. at 20°) to be a mixture of unchanged trifluoroiodomethane (3.33g., 16.98 mmoles, 97%) and trans-1,1,1-trifluorobut-2-ene (0.10g., 0.91 mmole, 46%), and

iii) a -78° fraction (0.30g.) shown by g.l.c. (2m D.D.P. at 115°) to contain three components.

The components were identified by their g.l.c. retention times as the 1 : 1 adducts $\text{CF}_3 \cdot \text{CHI} \cdot \text{CH}(\text{CF}_3) \cdot \text{CH}_3$ (isomer I) (0.17g., 0.56 mmole, 52%), $(\text{CF}_3)_2\text{CH} \cdot \text{CHI} \cdot \text{CH}_3$ (0.05g., 0.17 mmole, 15%), and $\text{CF}_3 \cdot \text{CHI} \cdot \text{CH}(\text{CF}_3) \cdot \text{CH}_3$ (isomer II) (0.08g., 0.25 mmole, 23%) present in the ratio 57:17:25 respectively.

Material Balance: 54% of the olefin was consumed during the reaction; 90% reacted to give the 1 : 1 adducts. The products represent a 99% (by weight) recovery of input material.

Reaction of a Mixture of 1 : 1 Adducts with Powdered

Potassium Hydroxide.

A mixture of 1 : 1 adducts (2.49g., 7.81 mmoles) consisting of 1,1,1-trifluoro-2-iodo-3-trifluoromethyl - butane (isomer I) (1.17g., 3.83 mmoles) and (isomer II) (0.65g., 2.11 mmoles), and 1,1,1-trifluoro-3-iodo-2-trifluoromethylbutane (0.53g., 1.72 mmoles) were condensed in vacuo onto powdered potassium hydroxide (ca. 20g.) and gently warmed (30 min.).

Fractional condensation of the products yielded:-

i) a low-boiling fraction (1.08g., 6.12 mmoles) (Found: M, 177) shown by g.l.c. (4m. D.D.P. at 20°) to contain seven components present in the ratio A:B:C:D:E:F:G of 0.5:0.5:57:5:6:6:25, and

ii) a high-boiling fraction (0.21g., 0.69 mmole, 9% recovered) presumed to be unchanged reactants which was not examined further.

The four major components of the low-boiling fraction (C,E,F,and G) were separated by g.l.c. (4m. D.D. P. at 20°).

Component C was identified as trans-1,1,1-trifluoro-3-trifluoromethylbut-2-ene $\text{CF}_3 \cdot \text{CH} : \text{C}(\text{CF}_3) \cdot \text{CH}_3$ (0.62g., 3.49

mmoles, 49%) (Found: C, 33.7; H, 2.4%; M, 179. $C_5H_4F_6$ requires C, 33.7; H, 2.3%; M, 178) b.p. (isoteniscope) $31.4 \pm 0.2^\circ$ (lit.¹⁷⁹ b.p. for 1,1,1-trifluoro-3-trifluoro-methylbut-2-ene is reported as 31°).

The i.r. spectrum showed bands at 3.22(w), 3.29(w), 3.37(m), 3.46(w), 4.34(w), 4.41(w), 4.98(w), 5.65(w), 5.83(m), 5.89(m), 6.86(s), 6.94(s), 7.16(s), 7.28(s), 7.61(vs), 7.80(vs), 8.38(vs), 8.57(vs), 9.20(vs), 10.12(s), 11.69(s), 12.52(w), 13.88(m), 13.94(m), and 14.01(m) μ .

The ^{19}F and 1H n.m.r. spectra (see Page 190) were consistent with the proposed structure. The ^{19}F spectrum showed two regions of absorption at 17.6 (doublet of septets, intensity 3) and 5.3 (quintet, intensity 3) p.p.m. to low field from external trifluoroacetic acid. The 1H spectrum showed two regions of absorption at 3.81 (quartet of septets, intensity 1) and 7.94 (quintet, intensity 3) τ .

Component E (0.37 mmole, 5%) was not identified; its i.r. spectrum showed bands at 5.80(w), 6.77(m), 6.85(m), 7.25(m), 7.75(s), 8.02(m), 8.33(m), 8.59(s), 9.12(m), 9.73(m), 11.70(m), 12.59(w), and 14.20(w) μ .

Component F (0.37 mmole, 5%) was not identified; its i.r. spectrum showed bands at 3.40(m), 3.55(m), 5.80(s), 6.98(w), 7.92(broad, s), 8.16(s), 8.32(s), 8.58(s), 9.52(m), 9.72(s), 12.60(w), and 13.95(w) μ .

Component G was identified as 1,1,1-trifluoro-2-trifluoromethylbut-2-ene $(\text{CF}_3)_2\text{C} : \text{CH} \cdot \text{CH}_3$ (0.27g., 1.53 mmoles, 21%) (Found: C, 33.9; H, 2.3%; M, 178. $\text{C}_5\text{H}_4\text{F}_6$ requires C, 33.7; H, 2.3%; M, 178) b.p. (isoteniscope) $53.7 \pm 0.2^\circ$.

The i.r. spectrum showed bands at 3.29(w), 3.38(m), 3.46(w), 4.32(w), 4.38(w), 4.61(w), 4.77(w), 5.14(w), 5.23(w), 5.30(w), 5.36(w), 5.82(m), 5.92(s), 6.41(w), 6.53(w), 6.84(m), 6.87(m), 7.10(vs), 7.21(s), 7.60(vs), 8.02(vs), 8.19(s), 8.49(vs), 9.05(vs), 9.39(m), 9.75(m), 10.09(s), 10.56(s), 11.56(s), 13.05(m), 13.93(s), 14.02(s), 14.10(s), and 14.78(w) μ .

The ^{19}F and ^1H n.m.r. spectra (see Page 191) were consistent with the proposed structure. The ^{19}F spectrum showed two regions of absorption at 17.7 (quartet of quartets of doublets, intensity 3) and 11.6 (quartet of quartets of doublets, intensity 3) p.p.m. to low field from external trifluoroacetic acid. The ^1H spectrum showed two regions of absorption at 3.14 (quartet of quartets of quartets, intensity 0.9) and 7.98 (doublet

of septets, intensity 3.0) γ .

Material Balance: 91% of the mixture of 1 : 1 adducts were consumed during the reaction; 49% reacted to give trans-1,1,1-trifluoro-3-trifluoromethylbut-2-ene, and 21% to give 1,1,1-trifluoro-2-trifluoromethylbut-2-ene. The products represent an 87% (molar) recovery of input material.

Reaction of 1,1,1-Trifluoro-3-iodo-2-trifluoromethylbutane
with Powdered Potassium Hydroxide.

1,1,1-Trifluoro-3-iodo-2-trifluoromethylbutane (0.51g., 1.67 mmoles) was condensed in vacuo onto powdered potassium hydroxide (ca. 5g.) and left at room temperature (20 min.) to give as products:

i) a low-boiling fraction shown by i.r. spectroscopy and g.l.c. (4m. D.D.P. at 20°) to be 1,1,1-trifluoro-2-trifluoromethylbut-2-ene (0.29g., 1.62 mmoles, 97%) contaminated with a trace of a lower-boiling component (2% of this fraction), and

ii) a trace of a higher-boiling fraction presumed to be unchanged reactant.

Material Balance: All of the butane was consumed during the reaction; 97% reacted to give the olefin. The products represent a 98% (molar) recovery of input material.

Reaction of 1,1,1-Trifluoro-2-iodo-3-trifluoromethylbutane
(isomer I) with Powdered Potassium Hydroxide.

1,1,1-Trifluoro-2-iodo-3-trifluoromethylbutane (isomer I) (1.04g., 0.34 mmole) was condensed in vacuo onto powdered potassium hydroxide (ca. 5g.) and left at room temperature (30 min.); no reaction occurred. On warming (100°, 15 min) reaction did occur to give the following products:

- i) a low-boiling fraction shown by i.r. spectroscopy and g.l.c. (4m. D.D.P. at 20°) to be trans^{-1,1,1-}trifluoro-3-trifluoromethylbut-2-ene (0.28g., 0.16 mmole, 70%) contaminated with the two unknown components, E (0.02 mmole, 10%) and F (0.01 mmole, 2%) (see Page 312), present in the ratio 85:12:3, and
- ii) unchanged reactant (0.33g., 0.11 mmole, 32% recovered).

The i.r. spectrum of component E isolated from this reaction showed strong additional ^{bands} at 4.90 and 6.72 μ suggesting contamination with an allene presumably 1,1-difluoro-3-trifluoromethylbut-1,2-diene $\text{CF}_2\text{:C:C}(\text{CF}_3)\cdot\text{CH}_3$.

Material Balance: 68% of the butane was consumed during the reaction; 70% reacted to give the trans-olefin. The products represent a 91% (molar) recovery of input material.

Reaction of 1,1,1-Trifluoro-2-iodo-3-trifluoromethylbutane
(isomer II) with Powdered Potassium Hydroxide.

1,1,1-Trifluoro-2-iodo-3-trifluoromethylbutane (isomer II) (0.68g., 0.22 mmole) was condensed in vacuo onto powdered potassium hydroxide (ca. 5g.) and left at room temperature (30 min.); no reaction occurred. On warming (100°, 15 min.) reaction did occur to give the following products:

i) a low-boiling fraction (0.22g., 0.13 mmole) (Found: M, 170) shown by i.r. spectroscopy and g.l.c. (4m. D.D.P. at 20°) to be a mixture of trans-1,1,1-trifluoro-3-trifluoromethylbut-2-ene (0.07g., 0.04 mmole, 25%) and component E (0.07 mmole, 40%) contaminated with component F (0.01 mmole, 8%), and

ii) unchanged reactant (0.15g., 0.05 mmole, 23% recovered).

Component E, presumed to be cis-1,1,1-trifluoro-3-trifluoromethylbut-2-ene was shown by i.r. spectroscopy to be contaminated with the same allene as in the previous experiment and could not be isolated in a pure state.

Material Balance: 77% of the butane was consumed during the reaction; and the products represent an 82% (molar) recovery of input material.

Addition of Bromine to Trifluorobutene.

Bromine (1.61g., 10.0 mmoles) and a mixture of the isomeric trifluorobutenes (1.23g., 11.15 mmoles), consisting of trans-1,1,1-trifluorobut-2-ene (0.98g., 8.82 mmoles), cis-1,1,1-trifluorobut-2-ene (0.21g., 1.90 mmoles), and 2-trifluoromethylpropene (0.05g., 0.44 mmole), were sealed in vacuo in a silica tube (capacity 100 ml.) and left in the dark.

Immediate reaction was observed in the liquid phase and when only gaseous olefins remained reaction appeared to cease, estimated by bromine coloration. The tube was left in the dark for a further 8 hr. to give products which, after being shaken with mercury to remove the unreacted bromine, gave the following fractions on fractional condensation.

i) A low-boiling fraction (0.24g., 2.22 mmoles) (Found: M, 110) which was shown by i.r. spectroscopy and g.l.c. (4m. D.D.P. at 20°) to be a mixture of unreacted olefins comprising trans-1,1,1-trifluorobut-2-ene (0.23g., 2.06 mmoles, 23% recovered), cis-1,1,1-trifluorobut-2-ene (ca. 0.005g., 0.04 mmole, 2% recovered), and 2-trifluoromethylpropene (ca. 0.012g., 0.11 mmole, 25% recovered).

ii) A high-boiling fraction (2.25g.) which was shown by g.l.c. (2m. D.D.P. at 100°) to contain 2 components in the ratio 80 : 20.

The major component was identified as erythro-2,3-dibromo-1,1,1-trifluorobutane $\text{CF}_3 \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{CH}_3$ (1.80g., 6.67 mmoles, 98% of trans-olefin) (Found: C, 18.0; H, 1.9%. $\text{C}_4\text{H}_5\text{Br}_2\text{F}_3$ requires C, 17.8; H, 1.8%) b.p. (Siwoloboff) 135°.

The i.r. spectrum showed bands at 3.32(w), 3.38(w), 6.86(w), 6.90(w), 7.20(w), 7.49(s), 7.68(w), 7.92(s), 8.15(m), 8.20(m), 8.25(m), 8.47(s), 8.88(s), 8.98(s), 9.28(w), 9.51(m), 9.93(m), 10.35(w), 11.08(w), 11.70(m), 13.69(m), and 14.13(m) μ .

The ^{19}F and ^1H n.m.r. spectra (see Page 165) were consistent with the proposed structure. The ^{19}F spectrum showed one region of absorption at 9.9 (doublet of quartets) p.p.m. to low field from external trifluoroacetic acid. The ^1H spectrum showed two regions of absorption at 5.45 (complex AB pattern, intensity 2.0) and 8.19 (doublet of quartets, intensity 3.1) τ .

The mass spectrum (Table 42, Page 211) showed a parent peak at m/e 268 and the general breakdown pattern was consistent with the proposed structure.

The second component was identified as threo-2,3-dibromo-1,1,1-trifluorobutane $\text{CF}_3 \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{CH}_3$ (0.45g., 1.68 mmoles, 90% of cis-olefin) (Found: C, 17.8; H, 1.7%. $\text{C}_4\text{H}_5\text{Br}_2\text{F}_3$ requires C, 17.8; H, 1.8%) b.p. (Siwoloboff) 138° .

The i.r spectrum showed bands at 3.33(w), 3.40(w), 6.84(w), 6.92(w), 7.20(m), 7.28(m), 7.40(m), 7.65(m), 7.81(s), 7.92(s), 8.10(m), 8.23(m), 8.47(s), 8.90(s), 9.51(m), 9.93(w), 10.52(m), 11.73(m), 12.20(w), 12.51(w), 13.36(m), and 14.60(w) μ .

The ^{19}F and ^1H n.m.r. spectra (see Page 167) were consistent with the proposed structure. The ^{19}F spectrum showed one region of absorption at 9.9 (doublet of quartets) p.p.m. to low field from external trifluoroacetic acid. The ^1H spectrum showed two regions of absorption at 5.67 (complex AB pattern, intensity 2) and 8.22 (doublet of quartets, intensity 3) τ .

The mass spectrum (Table 42, Page 211) showed a parent peak at m/e 268 and the general breakdown pattern was consistent with the proposed structure.

Material Balance: 77% of the trans-olefin was consumed during the reaction; 98% reacted to give the erythro-butane. 98% of the cis-olefin was consumed; 90% reacted to give the

three-butane. 75% of the 2-trifluoromethylpropene was consumed during the reaction; none of which was recovered as adducts. The products represent a 95% (molar)^{recovery} of input materials.

Addition of Hydrogen Bromide to Trifluorobutene.

I In the dark.

Hydrogen bromide (0.52g., 6.43 mmoles) and a mixture of the isomeric trifluorobutenes (0.48g., 4.33 mmoles) were sealed in a pyrex tube (capacity 100 ml.) together with aluminium bromide (1g.) and left in the dark (425 hr.); no reaction occurred.

II Photolytically.

Reaction 1.

Hydrogen bromide (4.05g., 50.0mmoles) and a mixture of the isomeric trifluorobutenes (2.94g., 26.72 mmoles) consisting of trans-1,1,1-trifluorobut-2-ene (2.33g., 21.09 mmoles), cis-1,1,1-trifluorobut-2-ene (0.50g., 4.55 mmoles), and 2-trifluoromethylpropene (0.11g., 1.04 mmoles) were sealed in a silica tube (capacity 350 ml.) and the vapour phase irradiated (6 hr.).

Fractional condensation of the products gave the following fractions.

i) Hydrogen (0.01g., 4.92 mmoles) (Found : M, 2.0. Calc. for H_2 : M, 2.0).

ii) Hydrogen bromide (2.79g., 34.50 mmoles, 69% recovered) (Found: M, 82. Calc. for HBr: M, 81) which was shown by i.r. spectroscopy to be contaminated with unchanged olefins.

iii) A -95° fraction (2.03g., 18.44 mmoles) (Found: M, 110) which was shown by i.r. spectroscopy and g.l.c. (4m. D.D.P. at 20°) to be a mixture of unchanged trans-1,1,1-trifluoro - but-2-ene (1.90g., 17.27 mmoles, 82% recovered), cis-1,1,1-trifluorobut-2-ene (0.08g., 0.77 mmole , 17% recovered), and 2-trifluoromethylpropene (0.04g., 0.40 mmole , 38% recovered).

iv) A -78° fraction (1.46g.) which was shaken with mercury to remove free bromine and shown by g.l.c. (2m. D.D.P. at 90°) to contain four components J,K,L,and M present in the ratio 35:26:5:34.

The three major components J,K, and M were separated by g.l.c. (2m. D.D.P. at 70°).

Component J was identified as 2-bromo-1,1,1-trifluorobutane $CF_3 \cdot CHBr \cdot CH_2 \cdot CH_3$ (0.51g., 2.67 mmoles, 35%) (Found: C, 25.4; H, 3.1%; M, 191. $C_4H_6BrF_3$ requires C, 25.2; H, 3.1%; M, 191) b.p. (isoteniscope) $72.9 \pm 0.2^\circ$.

The i.r. spectrum showed bands ^{at} 3.33(m), 3.38(m),

3.45(m), 3.61(w), 4.45(w), 4.71(w), 5.05(w), 6.00(w),
 6.52(w), 6.82(m), 6.90(m), 7.16(m), 7.18(m), 7.28(s),
 7.57(s), 7.69(s), 7.88(vs), 8.24(s), 8.41(vs), ^{8.88 (vs),} 9.34(m),
 9.61(m), 9.66(m), 10.76(m), 10.82(m), 11.66(m), 11.72(m),
 11.77(m), 12.28(m), 12.87(w), 13.37(w), 14.65(m),
 14.74(m), and 14.86(m) *M* .

The ^{19}F and ^1H n.m.r. spectra (see Page 153) were consistent with the proposed structure. The ^{19}F spectrum showed one region of absorption at 4.9 (doublet of quartets) p.p.m. to low field from external trifluoroacetic acid. The ^1H spectrum showed three regions of absorption at 6.00 (doublet of quartets of doublets, intensity 1.0), 7.98 (a complex AB pattern, intensity 2.2), and 8.88 (distorted triplet of quartets, intensity 3.4) τ .

The mass spectrum (Table 40, Page 209) showed a strong parent peak at m/e 190 and the general breakdown pattern was consistent with the proposed structure.

Component K was identified as 3-bromo-1,1,1-trifluorobutane $\text{CF}_3 \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{CH}_3$ (0.38g., 1.99 mmoles, 26%) (Found: C, 25.3; H, 3.1%; \underline{M} , 190. Calc. for $\text{C}_4\text{H}_6\text{BrF}_3$: C, 25.2; H, 3.1%; \underline{M} , 191) b.p. (isoteniscope) $82.5 \pm 0.2^\circ$ (lit. ¹²⁸ b.p. 84°).

The i.r. spectrum showed bands at 3.33(m),

3.38(m), 3.45(m), 6.80(m), 6.92(m), 7.16(m), 7.18(m),
 7.28(s), 7.44(s), 7.57(s), 7.90(vs), 8.41(vs), 8.53(vs),
 8.74(vs), 8.89(vs), 9.34(m), 9.65(m), 9.84(m), 10.47(w),
 10.84(m), 11.38(w), 11.44(w), 11.66(m), 11.72(m), 11.78(m),
 11.96(m), 12.28(m), 13.37(broad, w), 14.14(broad, m),
 14.65(m), 14.74(m), 14.85(m), and 15.05(m) \mathcal{M} .

The ^{19}F and ^1H n.m.r. ^{spectra} (see Page 155) were consistent with the proposed structure. The ^{19}F spectrum showed one region of absorption at 13.0 (triplet) p.p.m. to low field from external trifluoroacetic acid. The ^1H spectrum showed three regions of absorption at 5.82 (septet, intensity 1), 7.05 (complex AB pattern, intensity 2), and 8.23 (doublet, intensity 3) τ . The spectra also showed the presence of an impurity (ca. 20%) which, in the ^{19}F spectrum, gave a region of absorption at 4.7 (doublet) p.p.m. to low field from the reference, and in the ^1H spectrum a region of absorption at 8.72 (doublet) τ .

The mass spectrum (Table 40, Page 209) showed a strong parent peak at m/e 190 and the general breakdown pattern was consistent with the proposed structure.

Component M was identified as trans-4-bromo-1,1,1-trifluorobut-2-ene $\text{CF}_3\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\text{Br}$ (0.50g., 2.64 mmoles, 34%) (Found: C, 25.4; H, 2.1%; $\underline{\text{M}}$, 190. $\text{C}_4\text{H}_4\text{BrF}_3$ requires C, 25.4; H, 2.2%; $\underline{\text{M}}$, 189) b.p. (isoteniscope) $100.0 \pm 0.2^\circ$.

The i.r. spectrum showed bands at 3.34(m), 3.46(w), 5.92(m), 6.84(m), 6.92(m), 6.96(m), 7.18(m), 7.27(m), 7.50(vs), 7.80(vs), 7.99(s), 8.24(s), 8.42(vs), 8.68(vs), 8.92(s), 9.45(m), 9.88(m), 10.86(s), 11.05(m), 11.15(m), 11.36(m), 11.42(m), 11.71(m), 12.31(w), 14.15(m), 14.30(m), 14.61(m), 14.74(m), and 14.85(m) μ .

The ^{19}F and ^1H n.m.r. spectra (see Page 157) were consistent with the proposed structure. The ^{19}F spectrum showed one region of absorption at 12.98(doublet of quartets) p.p.m. to low field from external trifluoroacetic acid. The ^1H spectrum showed three regions of absorption at 3.40 (doublet of triplets of quartets, intensity 1), 4.10 (doublet of quartets of triplets, intensity 1), and 6.04 (doublet of quartets of doublets, intensity 2) τ .

The mass spectrum (Table 41, Page 210) showed a strong parent peak at m/e 188 and the general breakdown pattern was reasonably consistent with the proposed structure.

Material Balance: 62% of the 2-trifluoromethylpropene was consumed during the reaction. 30% of the 1,1,1-trifluorobut-2-ene was consumed; 61% reacted to give the 1 : 1 adducts and 34% to give trans-4-bromo-1,1,1-trifluorobut-2-ene. The products represent a 90% (by weight) recovery of input material.

Reaction 2.

The -196° and -95° fractions of the previous experiment were combined and irradiated (19 hr.) to give 95% conversion of the olefins. The -78° fraction obtained from the fractional condensation of the products was shown by g.l.c. (2m. D.D.P. at 70°) to contain only the 1 : 1 adducts, $\text{CF}_3\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CH}_3$ and $\text{CF}_3\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CH}_3$, and trans-4-bromo-1,1,1-trifluorobut-2-ene in the ratio 46:16:38 respectively.

Reaction 3.

Hydrogen bromide (3.62g., 44.65 mmoles) and a mixture of the isomeric trifluorobutenes (2.46g., 22.30 mmoles) consisting of trans-1,1,1-trifluorobut-2-ene (1.94g., 17.62 mmoles), cis-1,1,1-trifluorobut-2-ene (0.42g., 3.79 mmoles), and 2-trifluoromethylpropene (0.10g., 0.89 mmole) were sealed in a silica tube (capacity 350 ml.), and the vapour phase was irradiated (3 hr.) to give products which, on fractional condensation, gave the following fractions:-

- i) hydrogen (1.16 mmoles),
- ii) hydrogen bromide (3.38g., 40.16 mmoles, 94% recovered) (Found: M, 81) condensing at -196° ,
- iii) a -95° fraction (2.02g., 19.22 mmoles) (Found: M, 110)

shown by i.r. spectroscopy and g.l.c. (4m. D.D.P. at 20°) to be a mixture of unchanged trans-1,1,1-trifluorobut-2-ene (1.86g., 16.92 mmoles, 97% recovered), cis-1,1,1-trifluorobut-2-ene (0.22g., 1.97 mmoles, 52% recovered), and 2-trifluoromethylpropene (0.03g., 0.31 mmole, 35% recovered), and

iv) a -64° fraction (0.49g.) shown by g.l.c. (2m. D.D.P. at 90°) to contain 2-bromo-1,1,1-trifluorobutane (0.11g., 0.57 mmole, 19%), trans-4-bromo-1,1,1-trifluorobut-2-ene (0.07g., 0.36 mmole, 12%), 3-bromo-1,1,1-trifluorobutane (0.14g., 0.72 mmole, 23%) which is probably contaminated with the unknown product previously observed, and an unknown component L, present in the ratio 22:14:28:32.

Component L was separated by g.l.c. (2m. D.D.P. at 70°) and was tentatively identified as 1-bromo-2-trifluoromethylpropane $\text{CH}_3\cdot\text{CH}(\text{CF}_3)\cdot\text{CH}_2\text{Br}$. Its i.r. spectrum contained bands at 7.36(m), 7.70(m), 7.92(s), 8.33(s), 8.43(m), 8.67(s), 8.88(s), 8.77(m), 10.50(m), 11.05(w), 11.75(w), 12.08(m), 12.30(w), and 14.23(m)/ μ .

The mass spectrum showed main peaks at m/e values

(assignments and relative abundances in parentheses) of 192 ($\text{C}_4\text{H}_6\text{F}_3^+\text{Br}^+$, 9), 190 ($\text{C}_4\text{H}_6\text{F}_3^+\text{Br}^+$, 13), 159 (-, 20), 111 ($\text{C}_4\text{H}_6\text{F}_3^+$, 84), 91 ($\text{C}_4\text{H}_5\text{F}_2^+$, 82), 69 (CF_3^+ , 68), 47 ($\text{C}_2\text{H}_4\text{F}^+$, 79), 41 (C_3H_5^+ , 69), 39 (C_3H_3^+ , 66), 31 (CF^+ , 63), 29 (C_2H_5^+ , 63), 28 (C_2H_4^+ , 100), and 27 (C_2H_3^+ , 56).

Material Balance: 14% of the trifluorobutenes were consumed during the reaction; 68% reacted to give the 1:1 adducts. The products represent a 97% recovery (by weight) of input material.

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