The preparation and reactions of some molyfliorobit-2-enes

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UNIVERSITY OF DURHAM

A THESIS

entitled

THE PREPARATION AND REACTIONS OF SOME POLYFLUOROBUT-2-ENES

by

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A candidate for the degree of Doctor of Philosophy

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I would like to thank my Supervisor, Dr. R.D. Chambers, for his continual interest, support and patience during the course of this work and also the many technical and laboratory staff of the Chemistry Department of the University of Durham for their help. Thanks are also due to Mrs. E. McGauley for the typing of this thesis and my wife, Shirl, for her help in its final preparation.

Finally, I would like to thank the Science Research Council for its' financial support.

To

My wife, Shirl, Mum and Dad

MEMORANDUM

The work embodied in this thesis was carried out during the period October 1970 to October 1973 in the Chemistry Department of the University of Durham under the supervision of Dr. R.D. Chambers and is the original work of the author unless otherwise acknowledged by reference.

This work has not been submitted for any other degree.

Part of this work has been the subject of a paper presented at the VIIth International Symposium on Fluorine Chemistry, Santa Cruz, California, U.S.A., July 1973.

SUMMARY

Several nucleophilic addition reactions to hexafluorobut-2-yne have been carried out. Fluoride ion-initiated reaction with tetrafluoropyrimidine at room temperature has been found to produce a *cis-trans* mixture of perfluoro-4-(2-butenyl)-pyrimidine, while at 100° a mixture of the mono-2-butenyl-pyrimidines and the 4,6-di-2-butenyl-derivative is formed. A similar reaction with cyanuric fluoride has been found to produce only tarry material. Trapping of the intermediate butenyl anion with halogens (Br_2 and I_2) has been found to produce *cis-trans* mixtures of the respective 2-halo-but-2-enes. It has been shown that under the conditions of the reaction, i.e. fluoride ion in sulpholan, the *cis-trans* isomers of these heptafluorobut-2-enes are in equilibrium and consequently the stereochemistry of fluoride ion addition to hexafluorobut-2-yne cannot be determined. From the isomer ratios in these systems a rough order of steric requirement of the various groups has been determined and has been found to be:

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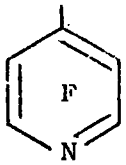


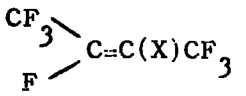
< Cl < Br < I

Reaction of hexafluorobut-2-yne with mercuric chloride in the presence of fluoride ion produces only the *trans* isomer of the bis-2-butenyl-mercury derivative which considering the previous results where *cis-trans* isomers are produced appears to be an anomolous result as the covalent radius of mercury would lead one to expect a mixture of geometrical isomers to be produced. It is thought that in the formation of this compound an *anti* addition of fluoride ion is the kinetically controlled route and that the

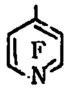
presence of the electropositive mercury atom then deactivates the heptafluoro-2-butenyl group towards further nucleophilic attack.

Base catalysed addition of methanol at room temperature is thought to proceed by an <u>anti</u> route to produce the <u>trans</u> olefin, however, at higher temperatures it is thought that an uncatalysed <u>syn</u> addition may occur. The stereochemical results of the addition of diethyl amine has been found to be critically dependent on the reaction medium and it is proposed that in solvents of low dielectric constant an intramolecular <u>syn</u> proton transfer is the preferred mechanism leading to a <u>cis</u> olefin. Reaction with sulphur has been found to proceed at low temperatures to produce tetrakis-trifluoromethylthiophene and again this reaction may proceed by a rapid <u>syn</u> addition step.

An extensive series of nucleophilic reactions with polyfluorobut-2-enes has been carried out, e.g.

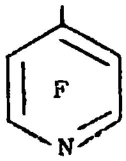


$CF_3(F)C=C(X)CF_3$

X = H, Cl, Br, 

With methanolic sodium methoxide, i.e. protic conditions, addition of methanol is found to compete with nucleophilic vinylic substitution of fluorine. No evidence for chlorine or bromine substitution or an allylic S_N2' reaction was observed.

Under aprotic conditions with sodium phenoxide vinylic substitution of fluorine occurs readily. It has been found however that the stereospecificity of these reactions is critically dependent on the solvent, the higher the dielectric constant the lower the stereospecificity. Results of competition reactions to determine the relative reactivity of these olefins have shown an order

X = H << Cl < Br < 

the reactivity of the cis and trans isomers of the 2-chloro and 2-bromo olefins have been found to be very similar.

These results in which preferential retention of stereochemistry is generally observed are thought to be a consequence of an anti addition of phenoxide followed by a syn elimination of fluoride ion. The solvent effects observed in these reactions are thought to be a direct result of the differences in lifetime of the various carbanionic intermediates in the various reaction media.

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INTRODUCTION

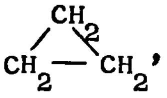
CHAPTER I

Properties Of Carbanions

I.A Thermodynamic Stability Of Carbanions

I.A.1 Introduction

Measurement of kinetic and thermodynamic acidities of various hydrocarbons indicate that the greater the 2s character of the orbital containing the two paired electrons the greater will be the stability of the carbanion.[1] Thus in the series

$HC \equiv CH$, $CH_2=CH_2$, , CH_3-CH_3

the pK_a values show a steady increase in going from acetylene to ethane. A plot of % 2s character against pK_a for these compounds gives a reasonable straight line.

Electrons in 2s orbitals are closer to the nucleus than electrons in 2p orbitals and are therefore more stabilised by the nuclear positive charge which accounts for increased acidity with increasing s orbital character.

I.A.2 α Halogen substituents

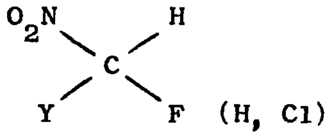
The ability of α halogen substituents to stabilise carbanions has been shown by Hine to depend critically upon their conformation.[2]

Kinetic acidity measurements (rate of deuterium-hydrogen exchange) of various haloforms (for example CDI_3, $CDBr_3$, $CDBr_2Cl$, $CDBrCl_2$ etc.) have been carried out by Hine[3] and co-workers to investigate the effect of structure on reactivity towards carbanion formation. Results of this work show that α halogen substituents in these compounds facilitate carbanion formation in the order

$$I \approx Br > Cl > F$$

which is the opposite of what would be predicted from consideration of the inductive effect alone. Similar results have been obtained for kinetic acidity studies on compounds of the type CF_3CXYH (X and Y are Cl, Br, I).[4]

An α fluorine has been found to be less acidifying than an α hydrogen in a series of nitromethanes (1) studied by Adolph and Kamlet.[5] For example:-

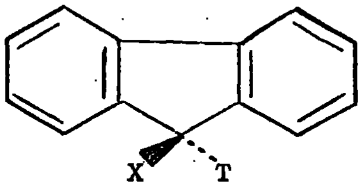


(1)

The application of ionisation constants (pK_a) in this work eliminates uncertainties concerning the transition state. Observed pK_a values were in the order

$$F > H > Cl$$

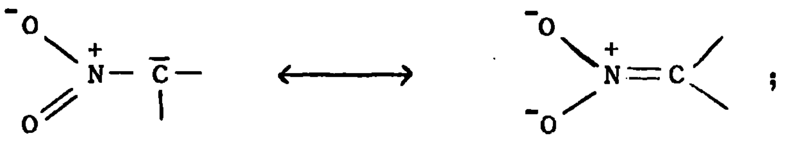
for a given Y group, (except for Y = NO_2, where Cl ~ H) which indicates that whilst an α chlorine leads to an increase in C-H acidity relative to hydrogen the effect of fluorine is in the opposite direction. Comprehensive hydrogen isotope exchange studies carried out by Streitweiser[6,7] on 9-substituted, 9-tritiated fluorene derivatives show that whilst a 9-trifluoromethyl substituent (3) increases the exchange rate by a factor of 2 x 10^4 relative to hydrogen (2) a 9-fluorine substituent (4) actually decreases the rate by a factor of eight relative to hydrogen.



(2), X = H
(3), X = CF_3
(4), X = F
(5), X = Cl
(6), X = Br

9-Chloro (5) and 9-bromo (6) fluorenes were found to be 4 x 10^2 and 7 x 10^2 times more reactive than fluorene (2) respectively. The authors propose that the carbanions generated from these fluorene systems are planar.

According to available data α fluorine substituents either decrease rates or equilibrium constants for formation of carbanions believed to be sp^2 hybridised (or increase them to a much smaller extent than would be expected from the electronegativity of fluorine). Thus in carbanions which are substituted with groups which can interact by a mesomeric effect (for example $-NO_2$ and phenyl) their geometry will tend towards planarity due to resonance contribution from (7) and (8) and in compounds of this type (for example the nitromethane and fluorene series) fluorine has a destabilising effect.



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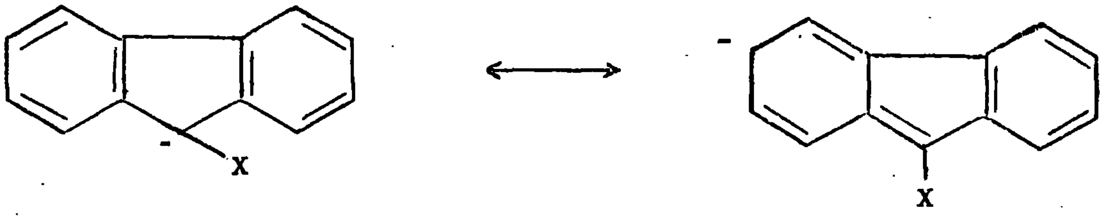
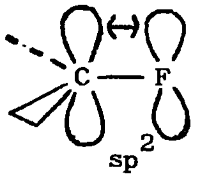


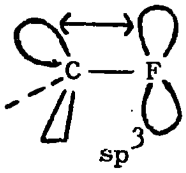
(8)

In carbanions which tend towards tetrahedral geometry (i.e. sp^3), for example at the bridgeheads of bicyclic ring systems,[8] α fluoro substituents increase the stability (relative to α hydrogen substituents). In many of these cases the magnitude of the stabilising effect correlates well with predictions based on the inductive effect of fluorine.

Several suggestions have been made to explain the behaviour of fluorine relative to hydrogen and the other halogens; the overall effect is probably a combination of several factors.

In a planar (sp^2 hybridised) carbanion the electron pair is localised within a 2p orbital. Unfavourable overlap of this orbital with a filled 2p orbital on fluorine, or simple coulombic repulsion will tend to destabilise the carbanion (I_π effect).[9] For a carbanion with tetrahedral geometry this effect will be reduced both by increased distance (i.e. reduced coulombic repulsion) and also by a reduction in overlap of the orbitals.





The order of I_π repulsion has been shown to be

$$F > Cl > Br > I$$

as would be expected from size consideration of the outer p orbitals of the heavier halogens.

A bond weakening electronegativity effect has been suggested by Hine[2] to be a contributing factor in the effect of fluorine on carbanion stability. It has been suggested that sp^2 carbon is more electronegative than sp^3 carbon and as the strength of covalent bonds is proportional to the square of the electronegativity difference between the atoms concerned the sp^3 carbon-halogen bond will be stronger than the sp^2 halogen bond. The electronegativities of the halogens are, (Pauling values)

F, 3·98; Cl, 3·16; Br, 2·96; I, 2·66.

Therefore on the formation of an sp^2 carbanion from an sp^3 substrate there will be an unfavourable energy factor (ΔH^*) in the overall free energy of the change resulting from bond weakening of the carbon-halogen bond. This effect will obviously be greater for fluorine than for the other halogens and will decrease as the carbanion becomes more tetrahedral.

Polarisability[3] and "d orbital effects"[10] have been proposed by other workers to be important factors which must be considered when attempting to explain the ability of α halogens to stabilise carbanions.

I.A.3 β Halogen substituents

Only the effect of β fluorine substituents has received full investigation. Andreades[11] has measured the rate of hydrogen-deuterium exchange for a series of monohydro-fluorocarbons, for example

$$R_FH + CH_3OD \rightleftharpoons R_FD + CH_3OH$$

$$(R_F = CF_3-,\ CF_3(CF_2)_5CF_2-,\ (CF_3)_2CF-\text{ and }(CF_3)_3C-)$$

and concluded that a β fluorine has a strong stabilising effect on carbanions and that the order of stability is,

tertiary > secondary > primary.

Polarographic studies on the electrochemical reduction of a series of compounds $(R_F)_2Hg$ afforded estimated pK_a values of the corresponding hydrides which were in reasonable agreement with those reported previously,[12] (Table 1).

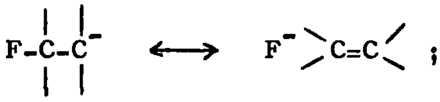
TABLE 1

Compound	Relative Reactivity	pK_a Value
CF_3H	1	25·5
$CF_3(CF_2)_5CF_2H$	6	-
$(CF_3)_2CFH$	2×10^5	22·5
$(CF_3)_3CH$	10^9	7

Knunyants[13] determined the acidity of some nitroethanes and found the k_A value of $CF_3CH_2NO_2$ to be $4{\cdot}0 \times 10^{-8}$ and that of $CH_3CH_2NO_2$ $6{\cdot}1 \times 10^{-11}$. Analogous results were observed by Hine[4] who found the kinetic acidity of

CF_3CCl_2H to be ~40 times that of $CFCl_2H$.

Negative hyperconjugation (9) (analogous to stabilisation of carbonium ions by positive hyperconjugation (10)) has been attributed by Andreades[11] to be responsible for the stabilising effect of β fluorine.



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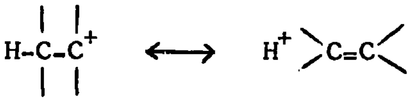
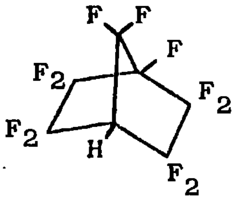


(10)

Exchange studies on 1-H-undecafluorobicyclo(2.2.1)-heptane (11) and (tris-trifluoromethyl)methane (12) show the latter to be less reactive.[14] This however should not be the case if negative hyperconjugation is a contributing factor in the stabilisation of carbanions. The intermediate carbanion from (11) will have a fixed pyramidal structure and will be



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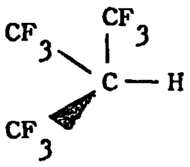
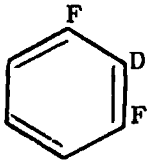
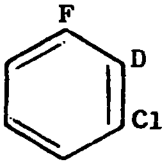


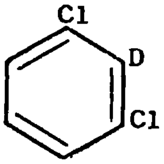
(12)

incapable of negative hyperconjugation. Thus stabilisation of a carbanion by a β fluorine atom is probably due to an inductive effect.

There is only a very limited amount of information available on the ability of other β halogens to stabilise a carbanion. Exchange reactions of m-dihalobenzenes[15] indicate that replacement of a β chlorine by a β fluorine increases the kinetic acidity by a factor of about 7.







10^6 k (100°)	978	151	20·2

These results have been attributed to an inductive effect.

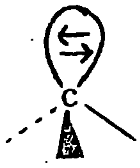
I.B Stereochemistry Of Carbanions

I.B.1 Alkyl carbanions

A complete spectrum of structures is possible for alkyl carbanions which varies from planar (sp^2) to tetrahedral (sp^3).

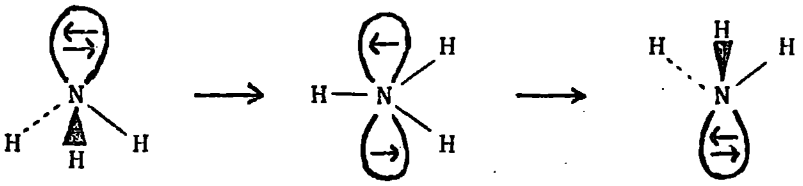
If the carbanion is stabilised by groups which exert a strong mesomeric effect then planarity is essential for significant delocalisation via overlapping p orbitals to occur.

In simple carbanions not stabilised by resonance a pyramidal configuration is assumed as the methide ion (13) is isoelectronic with ammonia which is known to be pyramidal and undergo rapid inversion.



(13)

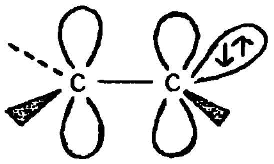
cf.



Although a planar sp^2 hybridised configuration is reasonable for the six bonding electrons of a carbonium ion it is not acceptable for a carbanion; it is expected that the additional electron pair will be localised in an orbital having s character and not be in a pure p orbital thus leading to a pyramidal configuration.

I.B.2 Vinyl anions

Vinyl anions are predicted to have a configuration in which the carbon-carbon double bond and the atom (or group) attached to the carbanionic centre are non-linear. For example:



Such an anion has the non-bonded pair of electrons in an orbital of maximum s character (sp^2). The isoelectronic species containing carbon-nitrogen double bonds are well known to assume this geometry and vinyl organometallic compounds are known to have a non-linear configuration.[16,17]

I.C Configurational Stability Of Carbanions

I.C.1 Alkyl carbanions

Carbanions which are thought to be planar or near planar (i.e. stabilised by aryl, nitro substituents etc.) have been shown by Cram[16] to be capable of retention, racemisation or inversion in isotopic exchange reactions depending upon the detailed structure of the substrate, base and solvent.

Measurements of the relative rates of base catalysed hydrogen-deuterium exchange of optically active starting materials have been used to give information on the stereochemical fate of the intermediate carbanion. Four limiting ratios of k_e (rate constant for isotopic exchange) and k_α (rate constant for racemisation) are envisaged.

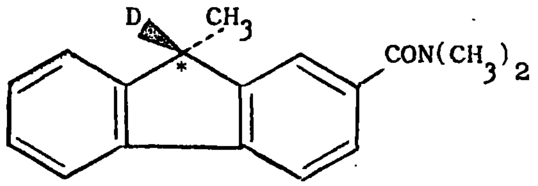
$k_e/k_\alpha \longrightarrow \infty$, stereochemistry ⟶ 100% retention

$k_e/k_\alpha \longrightarrow 1$, stereochemistry ⟶ 100% racemisation

$k_e/k_\alpha \longrightarrow 0{\cdot}5$, stereochemistry ⟶ 100% inversion

$k_e/k_\alpha \longrightarrow 0$, stereochemistry ⟶ 100% isoracemisation

The effect of reaction conditions upon the rate ratio can be seen when the fluorene derivative (<u>14</u>) is subjected to hydrogen isotope exchange. By varying the solvent and base a complete spectrum of stereochemistries from retention to inversion was observed (Table 2).



(14)

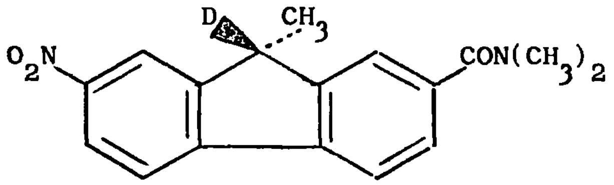
$pK_a \sim 21$

TABLE 2

Hydrogen-Deuterium Exchange Reactions Of 9-Deutero-9-methyl Fluorene

Solvent	Base	T (^oC)	k_e/k_α
$(CH_2)_4O$	NH_3	145	148
$(CH_3)_2SO$	NH_3	25	1·0
CH_3OH	Pr_3N	75	0·65

Comparison of (14) with the similar fluorene derivative (15) illustrates



(15)

$pK_a = 18$

the effect of lifetime of carbanionic intermediates on the stereochemical outcome of reactions. Introduction of the nitro group which can stabilise a carbanion on the 9-position by mesomeric interaction decreases the pK_a by 3 units. Reaction of (14) in tetrahydrofuran/propylamine proceeded with complete retention ($k_e/k_\alpha > 56$) whilst (15) under the same conditions showed racemisation (k_e/k_α, 1).

Similar dependence of configurational stability on solvent and base has been found in exchange reactions of compounds which are thought to produce non-planar carbanions. 2-Methyl-3-phenyl-1,1,1-trifluoropropane in t-BuOH/t-BuOK underwent exchange with racemisation whilst in MeOH/MeOK reaction proceeded with inversion. Optically active 2-octyl-phenylsulphone[16,18] underwent base catalysed hydrogen-deuterium exchange with high retention although the degree of retention was critically dependent on solvent and base, see Table 3.

TABLE 3

Exchange Reactions Of 2-Octyl-phenylsulphone

Solvent	Base	T (^{o}C)	k_e/k_α
t-BuOD	t-BuOK	25	73-1200
$(CH_2OD)_2$	$DOCH_2CH_2OK$	100	15

I.C.2 Vinyl anions

Work on the configurational stability of vinyl anions has centred around hydrogen isotope exchange reactions and the stereo-chemical stability of vinyl organometallic compounds.

Isotopic exchange reactions of cis- and trans-1,2-dichloroethylene[19] in D_2O (with CH_3ONa) show that significant isomerisation does not occur at moderate temperatures (3-70^{o}). Lower limits to the activation energy for isomerisation of 1,2-dihalovinyl anions have been calculated to be in the range 25 $\gg$ 35 kcal/mol.

Curtin and co-workers[20] have studied the geometrical stability of cis- and trans-vinyl-lithium compounds as structure and solvent were varied. Cis- and trans-propenyl-lithium were found to be configurationally stable for periods of 1 hr. in refluxing ether.

Work carried out on aryl-vinyl organometallic derivatives however, show that these compounds have considerably less configurational stability. Cis-1,2-diphenyl-vinyl-lithium readily isomerises to the trans-isomer above -40° in benzene[21] and cis- and trans-2-p-chlorophenyl-1,2-diphenyl-vinyl-lithium undergo interconversion at 0° [22] or above. Comprehensive studies on configurational stability of cis-stilbenyl-lithium have shown a critical dependence on solvent,[21] see Table 4. (Trapping of the lithio derivatives was carried out using CO_2 or benzophenone).

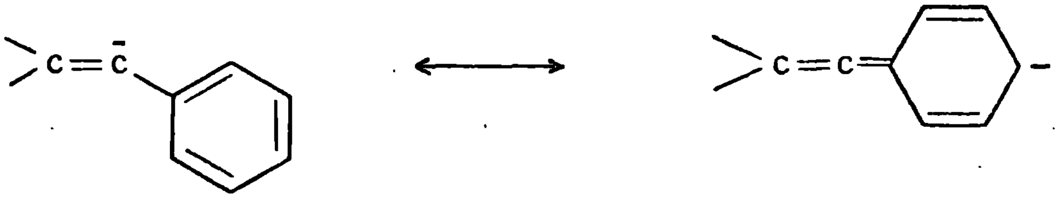
TABLE 4

Configurational Stability Of Cis-stilbenyl-Lithium

Solvent	T (°C)	% Cis-olefin	% Trans-olefin
Ether:Benzene, 3:1	-54	100	0
T.H.F.	-45	0	100
Benzene:Pentane, 1:1	3	~ 85	~ 15
Benzene	27	29	71

The conclusions drawn are that aryl-vinyl-lithium compounds isomerise much more readily than alkyl-vinyl derivatives and that the rates vary markedly with solvent polarity.

In a cis-trans isomerisation of a vinyl anion the transition state must possess a linear geometry, thus placing the pair of electrons in a p orbital which will increase the activation energy. The presence of α aryl groups is expected to stabilise the transition state due to mesomeric interaction which will lower the energy for the linear geometry. For example



CHAPTER II

Acetylenes

Introduction

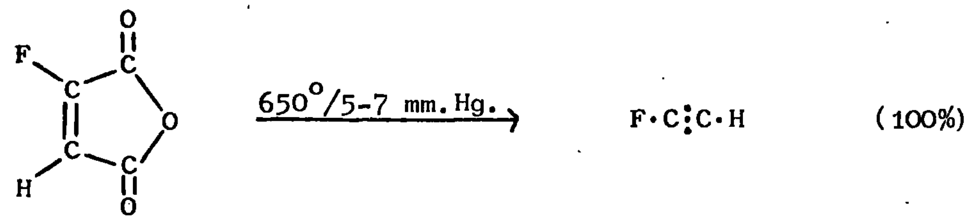
Hydrocarbon acetylenes have for many years been some of the most important and versatile starting materials for the synthesis of complex organic molecules. Production of acetylene, $H{\cdot}C{\equiv}C{\cdot}H$, was originally limited to the hydrolysis of calcium carbide but is now being supplemented by the "cracking" of fossil fuels. (Recently, however, ethylene has superceded acetylene as the main starting material for the production of organic compounds on an industrial scale). The versatility of acetylenes is due, in part, to the ease with which both ionic and radical addition reactions take place. Hydrogen attached to a carbon-carbon triple bond is relatively acidic due to the electronegativity of sp hybridised carbon. Substitution occurs with alkali metals, alkali metal amides, hydrides, Grignard reagents and many other metals. These compounds in turn lead to many other useful products. The chemistry of hydrocarbon acetylenes has been extensively reviewed.[23,24]

The chemistry of fluorinated acetylenes has been effectively limited to the study of 3,3,3-trifluoropropyne and hexafluorobut-2-yne because these two are the most readily available fluoroacetylenes. A review of the chemistry of fluorinated acetylenes has recently appeared.[25]

II.A Methods Of Preparation Of Fluorocarbon Acetylenes

II.A.1 Mono- and di-fluoroacetylenes

Monofluoroacetylene, $F{\cdot}C{\equiv}C{\cdot}H$, can be prepared from the pyrolysis of fluoromaleic anhydride[26] or by dehalogenation reactions of $F{\cdot}CBr_2{\cdot}CBr_2H$[27] or $HCBrC{=}CF{\cdot}Br$[28] using magnesium in tetrahydrofuran.



Difluoroacetylene, $F\cdot C\equiv C\cdot F$, although never isolated has been suggested as a product in several pyrolytic,[29,30] photolytic,[31] and radiolytic[32] reactions of fluorocarbons. For example, pyrolysis of difluoromaleic anhydride at 650° is thought to produce difluoroacetylene.[33]

II.A.2 Fluoroalkyl acetylenes

Elimination of hydrogen halides or halogen (the latter being preferred[34]) is usually used to prepare polyfluoroalkynes. Dehalogenation can be carried out using zinc in ethanol although acetic anhydride or benzonitrile appear to be better solvents for some reactions.[35] The dichloro olefins used in these reactions can be conveniently obtained by reaction of an acid chloride with 1,1-dichloro-2,2-difluoroethylene in the presence of nickel carbonyl. For example:

$$R_FCOCl \;+\; NiCO_4 \;+\; CF_2{=}CCl_2 \longrightarrow R_FCF_2\cdot C\cdot Cl{=}CCl\cdot CF_2R_F \;+\; NiCl_2 \;+\; CO$$

Hexafluorobut-2-yne is generally prepared from hexachlorobutadiene; for example:

$$CCl_2{:}CCl\cdot CCl{:}CCl_2 \xrightarrow[SbF_3/Cl_2]{SbF_3/155^\circ} CF_3\cdot CCl{:}CCl\cdot CF_3 \qquad (85\%)$$

$$CF_3\cdot CCl{:}CCl\cdot CF_3 \xrightarrow[Heat]{Zn/C_2H_5OH} CF_3\cdot C{\vdots}C\cdot CF_3 \qquad (50\%)$$

This compound is also readily prepared from acetylene dicarboxylic acid with sulphur tetrafluoride in an autoclave.[36] (Sulphur tetrafluoride is a specific reagent for converting carbonyl and carboxyl groups to difluoromethylene and trifluoromethyl groups respectively).

$$HO_2C\cdot C\ C\cdot CO_2H \xrightarrow[\text{Autoclave}\\ \text{TiF}_4\text{ catalyst}]{SF_4/170^\circ} CF_3\cdot C{\vdots}C\cdot CF_3 \qquad (80\%)$$

3,3,3-Trifluoropropyne is most conveniently prepared from a zinc acetylide which is readily decomposed by water to produce the alkyne.[37,38]

$$CF_3{\cdot}CCl{:}CCl_2 \ + \ Zn \longrightarrow ((CF_3C{\equiv}C)_2Zn) \xrightarrow{H_2O} CF_3{\cdot}C{\equiv}C{\cdot}H$$

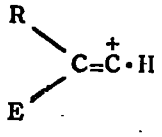
Perfluoropropyne is conveniently prepared from 2,3-dibromo-1,1,3,3-tetrafluoropropene which is isomerised almost quantitatively by $AlBr_3$ to 1,2-dibromo-1,3,3,3-tetrafluoropropene which can be debrominated with zinc in dioxane.[39]

$$CF_2{:}CBr{\cdot}CF_2Br \xrightarrow{AlBr_3} CF_3{\cdot}CBr{:}CFBr \xrightarrow{\text{Zinc/dioxane}} CF_3{\cdot}C{\equiv}C{\cdot}F$$

II.B <u>Nucleophilic Reactions Of Acetylenes</u>

II.B.1 <u>Introduction</u>

Simple hydrocarbon acetylenes are less susceptible to electrophilic attack but are more susceptible to nucleophilic attack than similar olefins. For example, acetylene, unlike ethylene, reacts with alkoxide ions in alcoholic solution at high temperatures and pressures. The difference in reactivity is attributed to the fact that unsaturated carbon is more electronegative than saturated carbon. Electrophilic attack on an acetylene will produce the intermediate (16) whilst electrophilic attack on an olefin will give (17), the latter being preferred due to the differences in electronegativity of the carbon atoms.



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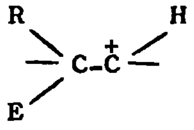

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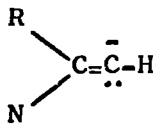
Nucleophilic attack on an acetylene however will produce the intermediate (18) whilst attack on an olefin will give (19). In this case the former is preferred due to electronegativity differences.



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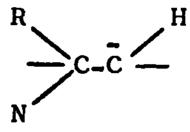
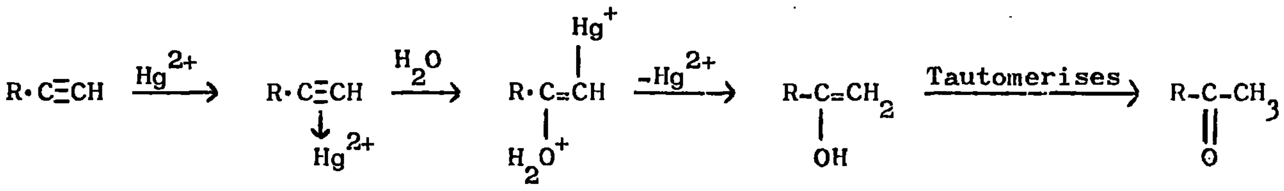


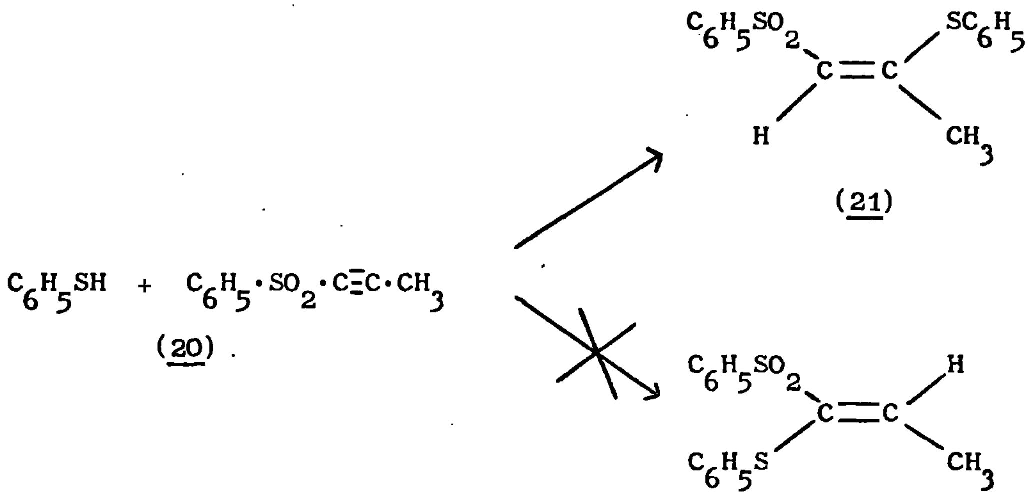
(19)

Substituted acetylenes undergo nucleophilic attack under mild conditions with strong nucleophiles (for example alkoxides in alcoholic solution). Less powerful nucleophiles require catalysts; mercuric ion is often used as it readily complexes with and withdraws charge from the triple bond. Water reacts in the presence of mercuric sulphate to give a vinyl alcohol which tautomerises to the ketone, (acetylene itself gives acetaldehyde).



II.B.2 Direction of nucleophilic addition to acetylenes

With unsymmetrical acetylenes, nucleophilic addition can in principle lead to two different products. For example, addition of thiophenol to phenyl-1-propynylsulphone (20) may lead to (21) or (22) (or a mixture of the two isomers). In practice only (21) is isolated[40] which exemplifies the increased ability of sulphone over methyl for stabilising negative charge.

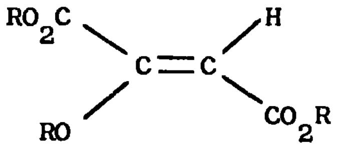


(20) (21) (22)

II.B.3 Hydrocarbon acetylenes

II.B.3.a Addition of alcohols and phenols

Additions of alcohols and phenols to acetylenes are base catalysed (usually alkoxides[41] or t-amines[42]) and generally proceed in an anti manner. In the case of dimethyl acetylene-dicarboxylate reaction leads to enol ether formation of the type (23).



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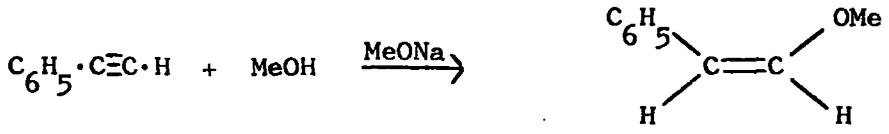
Similarly phenyl-acetylene adds methanol to produce the methoxy styrene (24).[43]



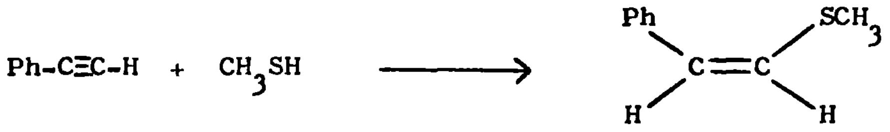
(24)

Reported additions of alcohols and phenols are seen to produce olefins by an overall anti route.

II.B.3.b Addition of thiols

Fundamental work by Truce et al. carried out on the addition of thiols to phenyl-acetylene[44] and but-2-yne[45] showed that "base catalysed addition of thiols to acetylenes proceeded in an anti fashion". Similar observations were made independently by Miller.[46]

Thus in the case of addition of methane thiol to phenyl-acetylene the substituted cis styrene derivative (25) is produced by an overall anti addition.[44]



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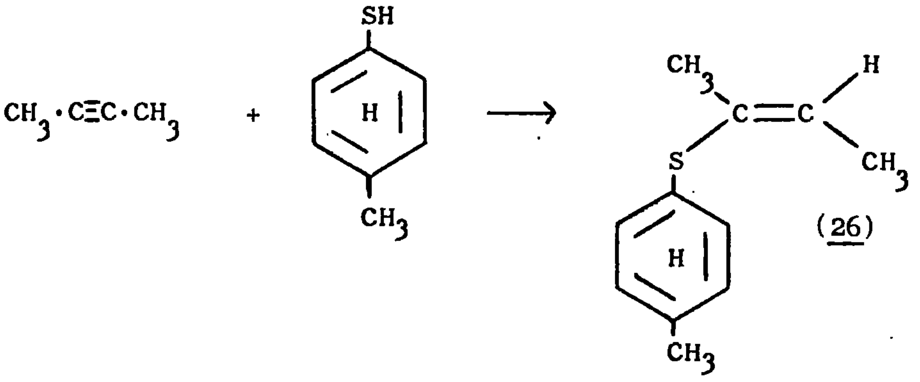
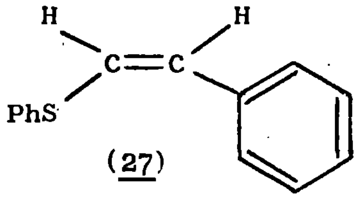
Similarly, reaction of but-2-yne with p-toluene thiolate[44] produces the 2-p-tolylmercapto-trans-but-2-ene (26).



(26)

The kinetic data of Truce and Heine[47] on the reaction between phenyl acetylene and p-toluenethiolate to produce cis-1-phenyl-2-p-tolylmercapto-ethylene (27) by an overall anti addition suggests that the reaction proceeds in a synchronous manner in protic solvents. Comparison of the rate of



(27)

reaction in ethanol and N,N-dimethylformamide/ethanol solutions showed the rate to be greater in the latter. Kinetic data for the reaction showed that the activation energy was greatest in D.M.F./ethanol but the entropy loss in formation of the activated complex is much lower in the mixed solvent system. The results are contained in Table 5.

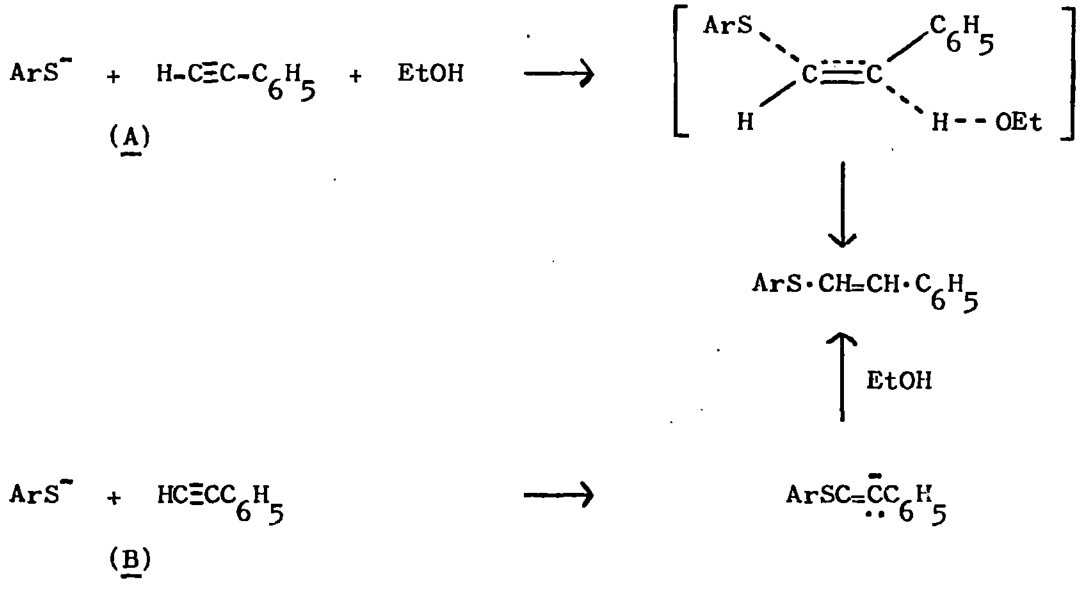
TABLE 5

Kinetic Data For The Reaction Of Phenyl Acetylene And p-Toluenethiolate With Variation Of Solvent

Solvent	k $l.m^{-1}sec^{-1}$	Temp ^{o}C	ΔH* kcal/mol	ΔS* e.u.
D.M.F.[a]	$2{\cdot}35 \times 10^{-4}$	59	18·8	-10·3
EtOH	$1{\cdot}48 \times 10^{-5}$	59	14·2	-30·0

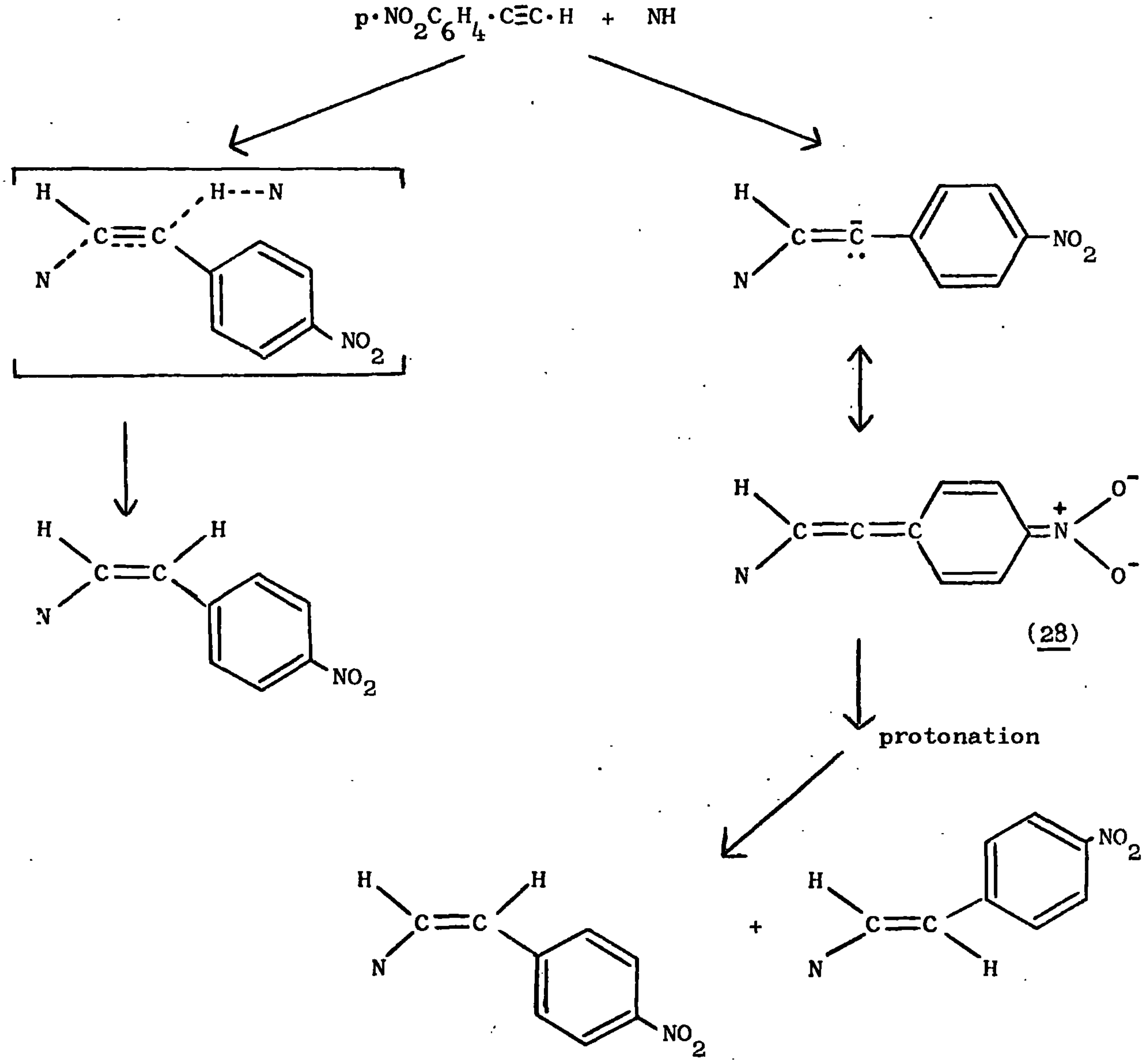
[a] As a solution with ethanol

Three possibilities were considered to explain the observed results, the favoured one being that two competing reactions, concerted and stepwise, were proceeding at the same time and that the latter was preferred in D.M.F./ethanol mixtures. For example:



The synchronous process (A) is therefore termolecular and is expected to exhibit a larger negative entropy of activation than the simple bimolecular process (B). In D.M.F./ethanol solutions, process (A) is not favoured on entropy grounds, and the reaction is expected to revert to the bimolecular process (B) to produce a carbanion which rapidly extracts a proton from the solvent. In ethanol alone, however, the termolecular mechanism (A) is expected to be much more favourable. Indeed reactions in ethanol show small isotope effect which suggests a synchronous reaction path is being followed. Unfortunately, the authors give no information regarding the stereochemistry of the olefins produced in either of the solvent systems. If the reaction in D.M.F./ethanol proceeds by a stepwise process then it seems likely that a mixture of cis- and trans-isomers should be produced.

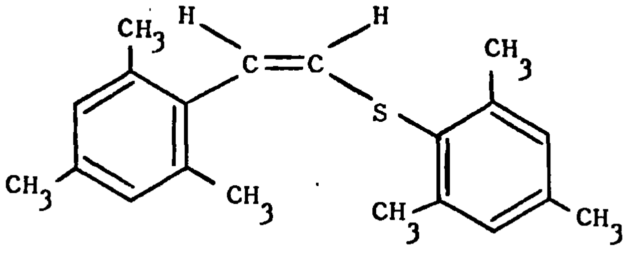
The fact that p-nitrophenyl-acetylene fails to undergo any syn-addition with thiols has been suggested to be due to the operation of a synchronous mechanism.[48,49] The authors propose that a stepwise carbanionic process would involve a delocalised intermediate (28) which would be expected to protonate to give a mixture of isomers. For example:



(28)

Ethynyl-p-tolylsulphone adds thiolate with 100% anti stereospecificity whereas the corresponding t-butyl derivative is reported to give some syn-addition probably by a stepwise process.[49]

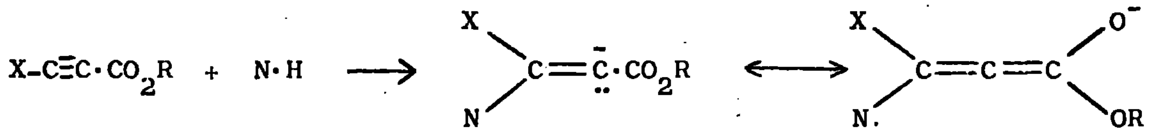
Steric requirements of the acetylene and thiol seem to have very little effect on the overall trans course of these additions as work by Truce has shown.[50] Reaction of mesitylacetylene with mesitylenethiol was shown to yield only the product derived from an anti addition (29), indicating that



(29)

steric hindrance between the bulky mesityl groups is insufficient to force the reaction to proceed via a syn-addition.

Acetylenes substituted with groups which contain a carbonyl function capable of mesomeric interaction with the intermediate vinyl anion are found to yield a mixture of both cis- and trans-olefins.[51] This has been explained in terms of an enolate anion (30) which can be protonated to yield either of the vinyl isomers, (see Table 6). For example:



(30)

TABLE 6

Reaction Of p-Toluene Thiolate With $HC\equiv C\cdot Y$

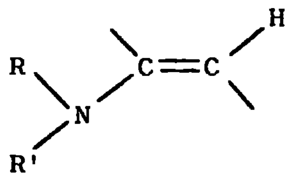
Y	% trans-addition	% cis-addition
$C\equiv N$	100	0
$SO_2\cdot C_7H_7$-p	100	0
$C_6H_4NO_2$-p	100	0
CO_2CH_3	92	8
$CONH_2$	87	13
$COCH_3$	82	18

As with alcohols and phenols addition of thiols proceeds almost exclusively to yield products via an overall anti route. The major exceptions involve acetylenes containing a carbonyl function capable of mesomeric interaction with the olefinic double bond.

II.B.3.c Addition of amines

Although several workers have proposed a general rule of anti base catalysed nucleophilic addition to acetylenes, it appears that in the case of addition of primary and secondary amines there is a substantial contribution from a syn-addition pathway.

Addition of amines produces enamines of the type (31) and (32).



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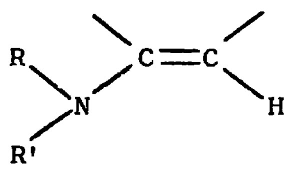
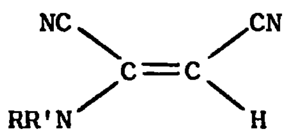


(32)

(R = H, R' = aryl or alkyl or R and R' = aryl or alkyl)

The steric course of the reaction depends on several factors including the nature of the acetylene and amine, the mixing process and the solvent.^{52}

The dinitrile (33) is produced exclusively when the amine is added very



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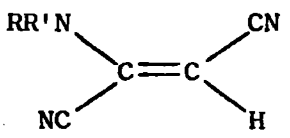
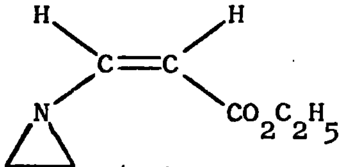


(34)

slowly to a solution of the acetylene. If, however, the reactants are brought together rapidly then a mixture of the dinitriles (33) and (34) is produced. This has been explained in terms of an intramolecular syn proton transfer at low amine concentrations (i.e. when addition is slow) due to the lack of a second amine molecule from which a proton can be abstracted by an intermolecular process.

The influence of solvent on the stereochemical outcome of these reactions can be seen in the results of work carried out by Dolfini and Winterfeldt.[53] Reaction of aziridine with dimethyl acetylene-dicarboxylate and ethylpropiolate was carried out in methanol and dimethylsulphoxide. In methanol a mixture of cis (35) and trans (36) isomers in the ratio 42:58 was produced from equimolar amounts of the amine and propiolate.



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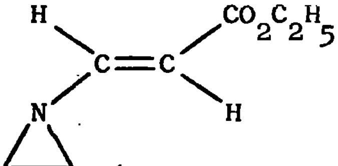


(36)

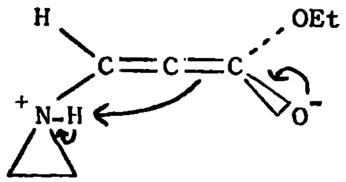
In dimethylsulphoxide however, only the trans ester was observed and it was found that the isomers did not interconvert under the conditions of their formation. Similar results were observed with dimethyl acetylene-dicarboxylate (Table 7).

TABLE 7

Reaction Of Ethylpropiolate And Dimethyl Acetylene-Dicarboxylate With Aziridine

Acetylene	Solvent	% cis-addition	% trans-addition
$Me{\cdot}O_2CC{\equiv}CCO_2Me$	MeOH	33	67
	D.M.S.O.	95	5
$H{\cdot}C{\equiv}CCO_2C_2H_5$	MeOH	42	58
	D.M.S.O.	100	0

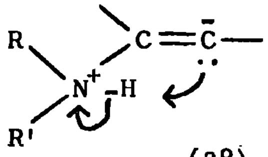
It was proposed that a zwitterionic intermediate (37) undergoes a stereospecific collapse via intramolecular proton transfer to yield an overall syn-addition in an aprotic solvent.



(37)

Other examples of syn-addition of amines to acetylenes are available.[54]

It has been proposed that direct uncatalysed addition of amines (and alcohols) probably proceeds by an intramolecular cyclic proton shift from an intermediate of the type (38).



(38)

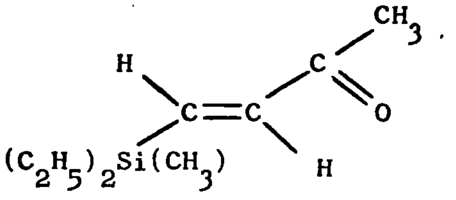
This has been confirmed by kinetic studies on the addition of ethylene-imine to dimethyl acetylene-dicarboxylate.[55]

II.B.3.d Addition of other compounds of the type HX

Nucleophilic additions of HBr and HI have been reported and are known to proceed in an anti manner.[56]

Reaction of methylpropiolate with deuterated trialkyl stannates ($DSn(R)_3$) proceeds via an anti-addition; kinetic studies have shown that addition of hydride ion is the rate determining step in the rate determining step in the reaction.[57]

Reaction of butynone with trialkyl silanes (R_3SiH)[58] yields a mixture of the isomeric cis- (39) and trans-olefins (40).



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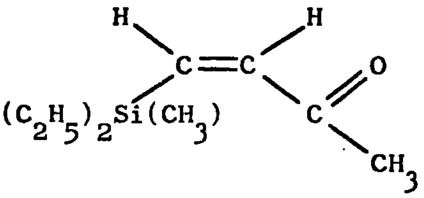

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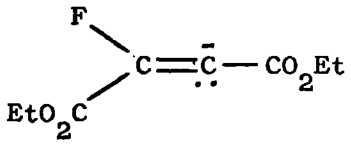
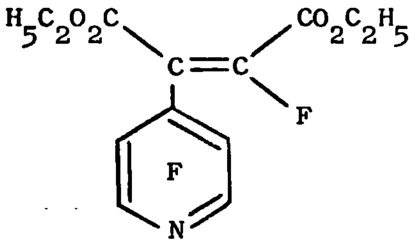
II.B.3.e Other nucleophiles

Fluoride ion generated from caesium fluoride in sulpholane reacts with acetylene dicarboxylate to produce the anion (41) which can be trapped by



(41)

pentafluoropyridine.[59] In this reaction a mixture of both cis- (42) and trans-isomers (43) was isolated on the ratio 50:50.



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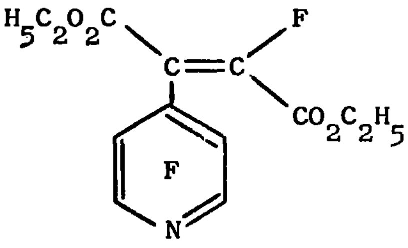
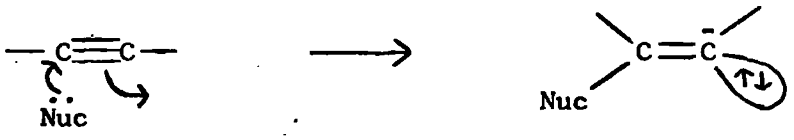


(43)

II.B.3.f Cyclisation reactions

The fact that cyclic products can be isolated from nucleophilic reactions of acetylenes indicates that syn-additions not influenced by intramolecular factors (i.e. proton transfer) are possible. This may take place by a true synchronous syn-addition (44) or by an "apparent" syn-addition in which anti addition occurs followed by inversion of the vinyl anion (45).



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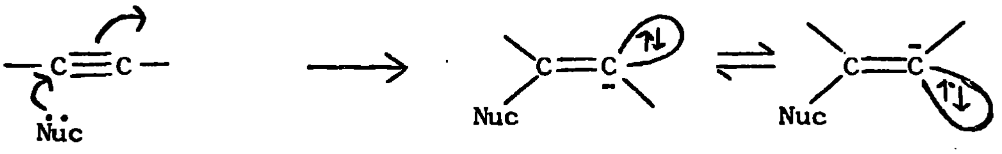
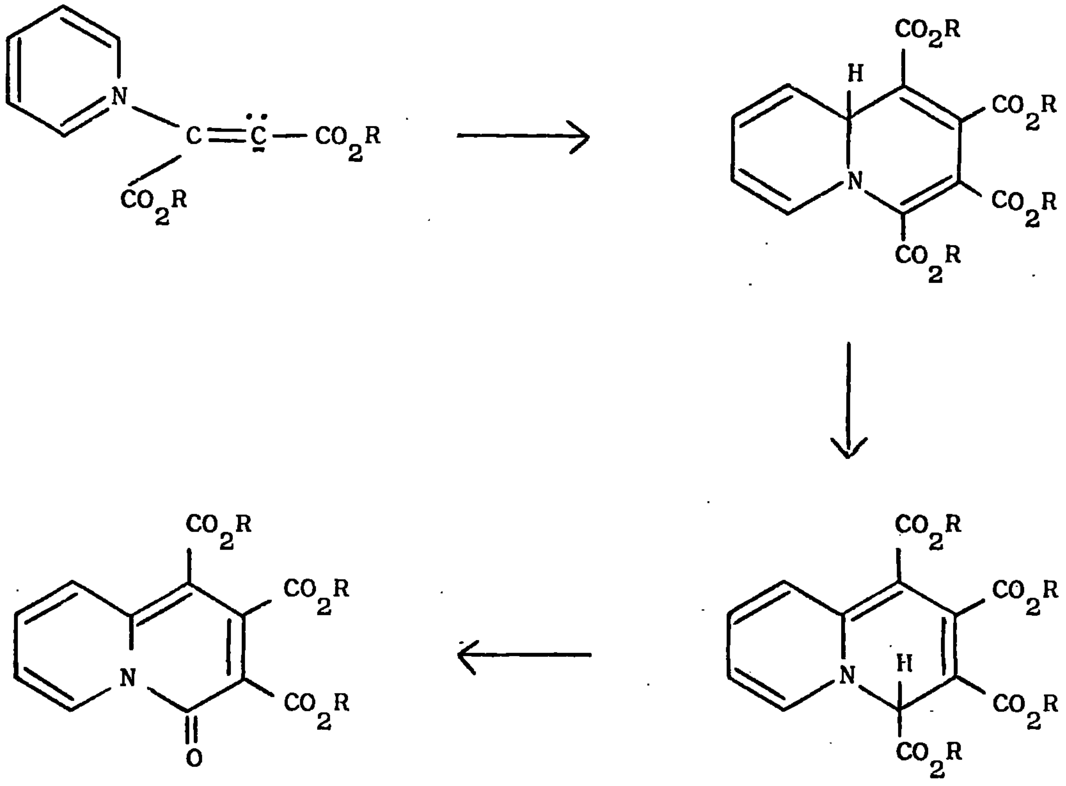


(45)

Aromatic amines, for example pyridine, were shown by Diels and Alder[60] to react readily with diethylacetylene-dicarboxylate to give adducts. The structure and mechanism of formation of these compounds were only established relatively recently. Thus in the case of pyridine (46) is the final product.



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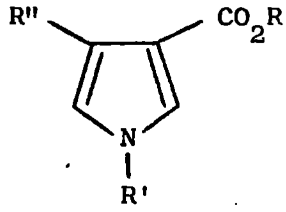
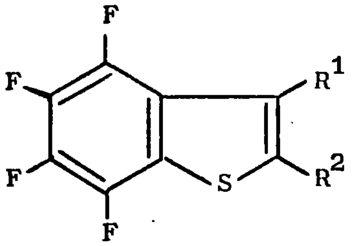
Methylpropiolate reacts readily with α amino ketones[61] in dimethylsulphoxide to produce pyrrole derivatives (47). Analogous products are



(47)

obtained from dimethylacetylene-dicarboxylate which produces pyrrole derivatives.[62]

Diethyl-4,5,6,7-tetrafluorobenzo[b]thiophene-2,3-dicarboxylate (48a) is produced in good yield from lithium pentafluorobenzenethiolate and diethylacetylene dicarboxylate in tetrahydrofuran at reflux temperature.[63] Analogous results are obtained with ethylphenylpropiolate[64] under the same conditions, in this case the benzo[b]thiophene (48b) is produced.



(48)

a; $R^1 = R^2 = CO_2Et$

b; $R^1 = CO_2Et$, $R^2 = Ph$

II.B.4 Fluorocarbon Acetylenes

II.B.4.a Introduction

Substitution of acetylene with fluorine or polyfluoroalkyl groups reduces electron density within the π system and renders these compounds resistant to electrophilic attack but very susceptible to attack by nucleophiles.

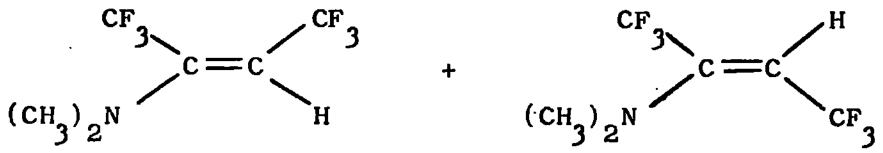
II.B.4.b Addition of alcohols

Haszeldine first reported the addition reactions of alcohols to hexafluorobut-2-yne and 1,1,1-trifluoropropyne[64] although no information regarding the stereochemical course of the reactions was given. It was found that 1:1 adducts were formed but under stringent conditions 2:1 adducts could be isolated. The sodium methoxide catalysed addition of methanol to 1,1,1-trifluoropropyne and hexafluorobut-2-yne have been reported to be predominantly anti addition (> 97%).[65]

II.B.4.c Addition of amines

Dimethylamine reacts with hexafluorobut-2-yne[66] in the absence of a solvent at room temperature to give a mixture of cis- (49) and trans-addition

(<u>50</u>) products in the ratio 1:6.

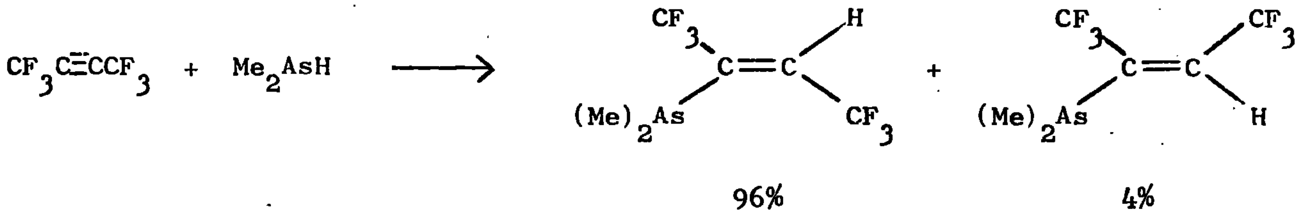


(<u>49</u>) (<u>50</u>)

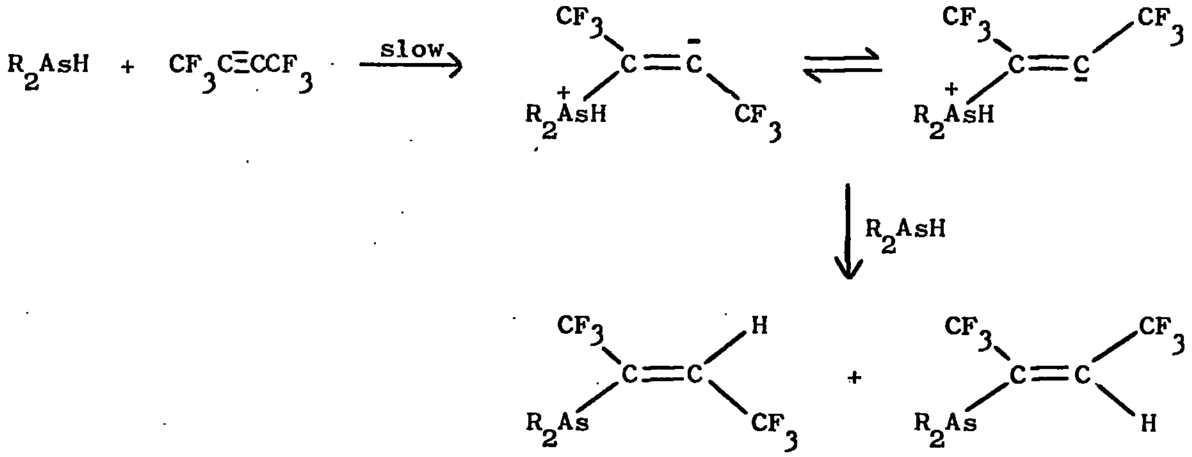
Similar reaction occurs with trifluoropropyne in which only the <u>trans</u>-isomer is isolated.

II.B.4.d <u>Addition of metalloidal and metal hydrides</u>

In an attempt to explain the results of the additions of amines and arsines etc. Cullen and Leeder[68] have studied the reaction of hexafluorobut-2-yne with dimethyl-arsine and dimethyl-arsenic-deuteride from which a 96:4 <u>trans</u>:<u>cis</u> product ratio is obtained. For example:



The reaction was found to be first order in both the acetylene and arsine; competition reactions indicated that reaction did not proceed via an intramolecular proton transfer. Several mechanisms were considered but the following was proposed.



Cis-trans interconversion is postulated to proceed through a hyperconjugated intermediate and at low concentration of the arsine syn-addition occurs due to the absence of another arsine molecule which is able to donate a proton.

A summary of the results of some addition reactions of hexafluorobut-2-yne and 1,1,1-trifluoropropyne appears in Tables 8 and 9.

TABLE 8

Isomer Distribution Of 1:1 Hexafluorobut-2-yne Adducts

Reactant	Trans-isomer %	Conditions
$(CH_3)_2PH$	100	Dark reaction 20^o
$(C_6H_5)_2PH$	80	Dark reaction 20^o
$CH_3(C_6H_5)AsH$	92	Dark reaction 20^o
$(CH_3)_3SnH$	100	Dark reaction 20^o
$(CO)_5MnH$	100	Dark reaction 20^o

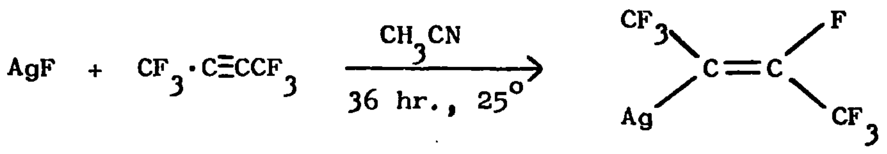
TABLE 9

Isomer Distribution Of 1:1 Trifluoropropyne Adducts

Reactant	Trans-isomer %	Conditions
$(CH_3)_2AsH$	50	Dark reaction 20^o
$(CH_3)_3SnH$	83	Dark reaction 20^o

II.B.4.e Other nucleophiles

Silver fluoride (AgF) was added to hexafluorobut-2-yne by Miller[67] to produce the first reported perfluorovinyl silver compound (51). Only the



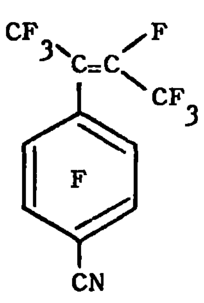
(51)

trans-isomer was observed which was found to have high thermal stability in contrast to the perhydro analogues (cis and trans) which are unstable at room temperature.[68]

Haszeldine has reported the reaction of the perfluorovinyl (52) and alkadienyl anions (53) generated from hexafluorobut-2-yne and fluoride ion (from CsF) with perfluoroaromatic and heterocyclic compounds.[69]

$$CF_3C{\equiv}CCF_3 + F^- \longrightarrow \underset{(52)}{CF_3FC{=}\overset{-}{C}CF_3} \xrightarrow{CF_3C\equiv CCF_3} \underset{(53)}{CF_3{\cdot}FC{=}C(CF_3){\cdot}C(CF_3){=}\overset{-}{C}{\cdot}CF_3}$$

Thus with pentafluorobenzonitrile in D.M.F at 120°, four major products were isolated (54), (55), (56) and (57).



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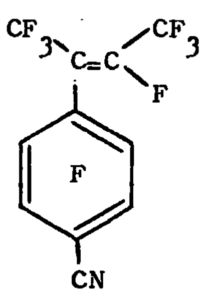

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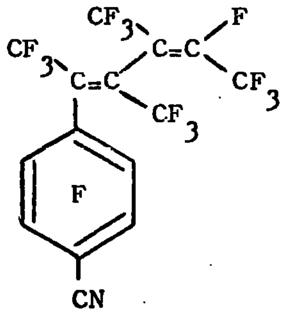

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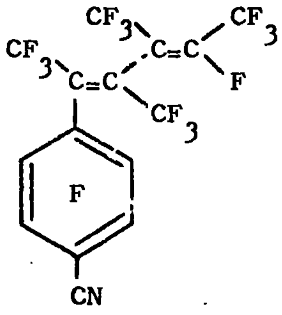
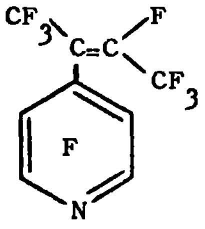


(54) (55) (56) (57)

Subsequent reactions showed that (54) was in equilibrium with (55) (5:1) and (56) was in equilibrium with (57) (5:1).

Chambers et al.[70] have reported similar reactions with pentafluoropyridine at 110° in sulpholane. Compounds (58) - (60) were isolated in moderate yield.



(58)

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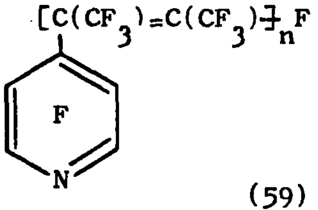
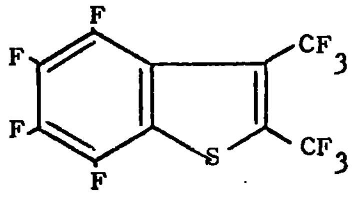


(59) n = 2

(60) n = 3

II.B.4.f Cyclisation reactions

Reaction of hexafluorobut-2-yne with lithium pentafluorobenzenethiolate at -70° in tetrahydrofuran[71] produces 4,5,6,7-tetrafluoro-2,3-bis-trifluoromethylbenzo[b]thiophene (61, 11%) and trans-1-pentafluorophenylthio-1,2,3,4-tetrakistrifluoromethylbutadiene (62, 2%).



(61)

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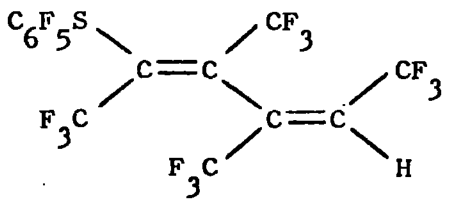
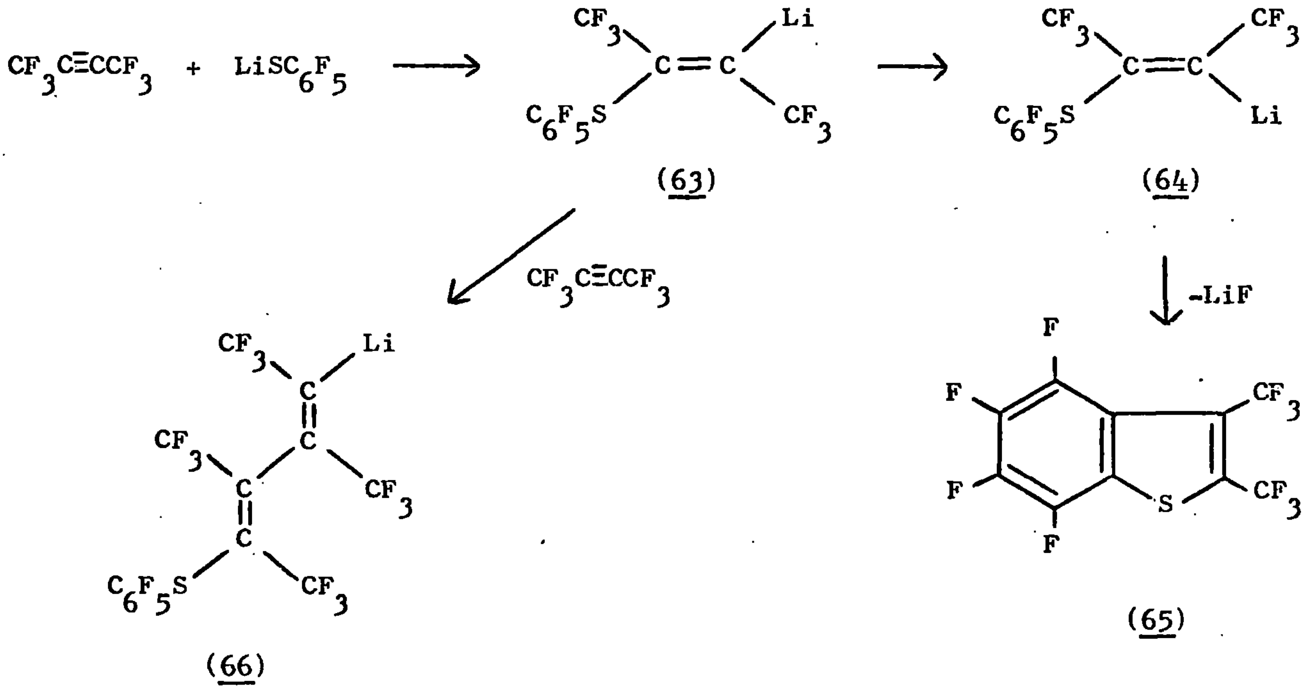


(62)

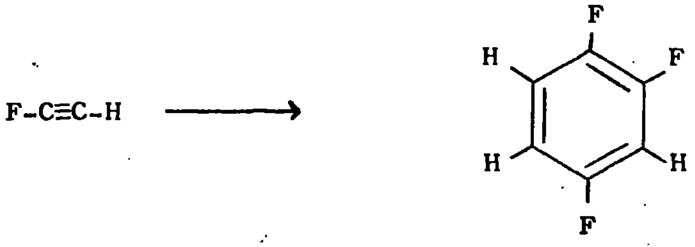
The reaction is proposed to proceed via the lithio derivative (63); isomerisation follows to give (64) which cyclises to (65). (63) can also react with a further molecule of hexafluorobut-2-yne to produce the butadiene derivative (66).



II.C Other Reactions of Fluorocarbon Acetylenes

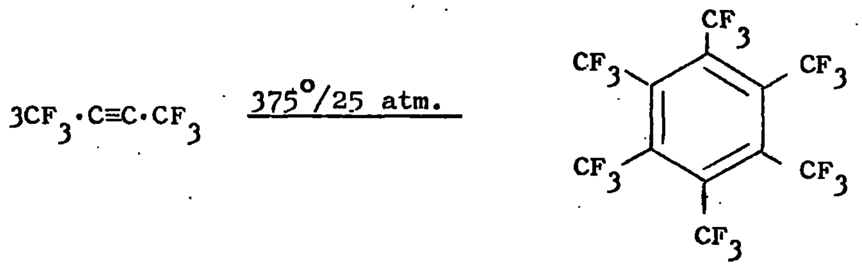
II.C.1 Oligomerisation and polymerisation

Mono- and di-fluoroacetylenes polymerise spontaneously at room temperature[72] although under suitable conditions monofluoroacetylene will undergo condensation to 1,2,4-trifluorobenzene (67).



(67)

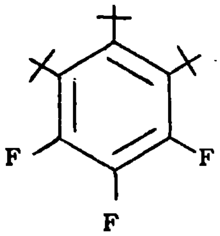
1,1,1-Trifluoropropyne is readily polymerised to an oil[73] and hexafluorobut-2-yne trimerises at 375° to hexakis(trifluoromethyl)benzene (68).[74-76]



(69%)

(68)

t-Butylfluoroacetylene trimerises spontaneously to give mixtures of 1,2,3-tris(t-butyl)trifluorobenzene (69) and its Dewar (70), and benzvalene (71) tautomers.[77]



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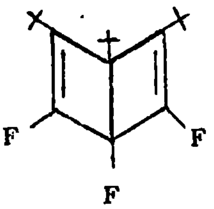
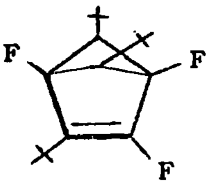


(70)



(71)

II.C.2 Free radical reactions of fluoroacetylenes

Chlorine and bromine are readily added to hexafluorobut-2-yne in the presence of u.v. radiation whilst the addition of iodine requires elevated temperatures. *Cis-*, *trans*-mixtures of the 1,2-dihalobutenes are produced.[78,34]

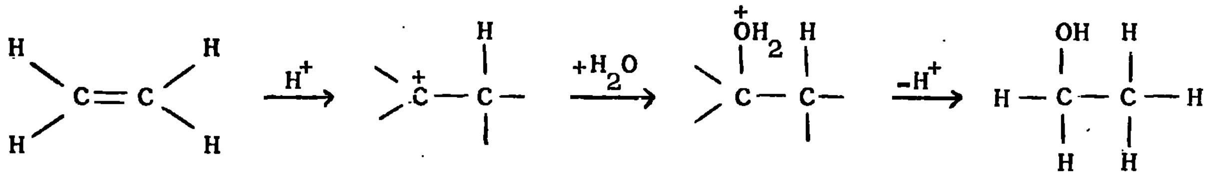
Monofluoroacetylene reacts with bromine to produce 1-fluoro-1,1,2,2-tetrabromoethane.[72] 1,1,1-Trifluoropropyne on heating with chlorine produces $CF_3 \cdot CCl_2CCl_2H$, whilst on irradiation with u.v. light, perchloropropane is the major product.[79]

CHAPTER III

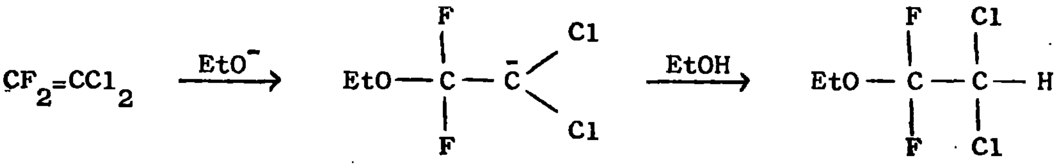
Nucleophilic Vinylic Substitution

Introduction

Ionic attack on olefins whether it be electrophilic or nucleophilic[80] is proposed to take place in a direction perpendicular to the plane of the double bond. In simple hydrocarbon olefins the presence of high electron density due to the π electrons renders these compounds susceptible to electrophilic rather than nucleophilic attack. Groups which can reduce the electron density and change the polarisation of the double bond by either mesomeric (-M) or inductive effects (-I) cause olefins to react in a nucleophilic rather than electrophilic mode. Thus, whereas ethylene undergoes acid catalysed hydration to the alcohol (73), 1,1-difluoro-2,2-dichloroethylene adds ethanol only in the presence of base (74).

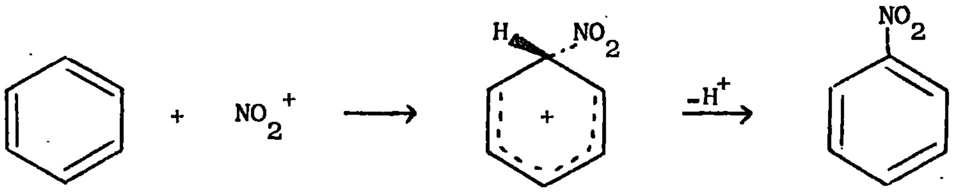


(73)



(74)

Similar trends are observed in aromatic systems; benzene is characterised by its electrophilic substitution reactions i.e. nitration (75), whereas nitrobenzene undergoes attack by hydroxide ion to produce σ-nitro phenol (76).



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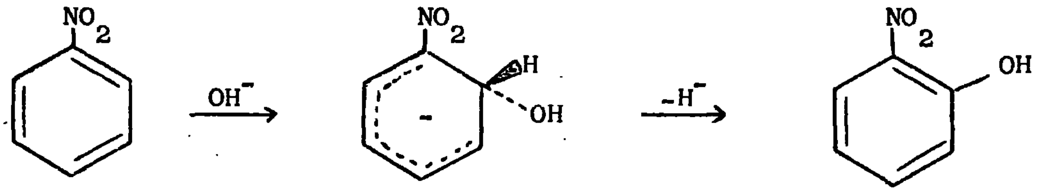
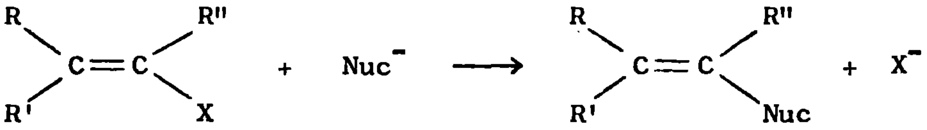


(76)

Polyhalo-olefins provide model compounds for the study of nucleophilic vinylic substitution due to the low π electron density in the double bond and the ease with which halide ion can be replaced by nucleophiles (77).



(77)

(R, R', R'' = halogen or polyhalo-alkyl; X = halogen).

III.A Nucleophilic Addition Reactions

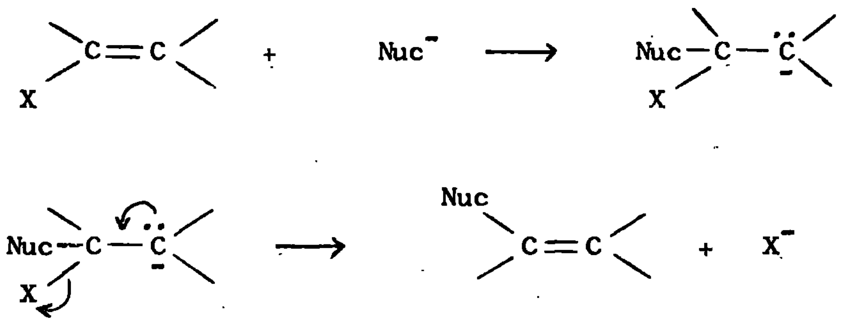
Nucleophilic vinylic substitution is known to proceed in certain cases via an addition-elimination process. Therefore in examining the overall stereochemistry, information on the addition step can in principle be obtained from the stereochemistry of nucleophilic vinylic addition reactions. Unfortunately little information is available on the stereochemistry of nucleophilic addition in acyclic systems and interpretation of results is complicated by equilibration of the kinetically controlled product.[81]

Reports of addition to cyclic olefins have proposed both *syn* and *anti* routes,[82,83] conformational requirements in these systems, however, are probably responsible for the stereochemical results.

III.B Mechanisms Of Nucleophilic Vinylic Substitution

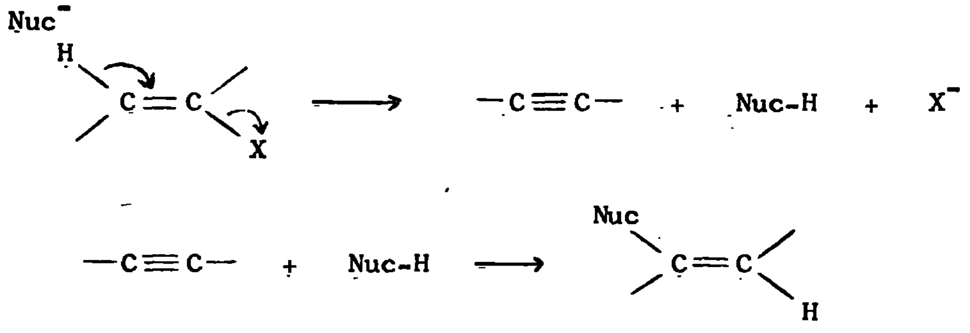
The two most common mechanisms encountered in vinylic substitution reactions are addition-elimination (78) and elimination-addition (79) although other mechanisms have been proposed.[84]

In the addition-elimination mechanism the primary step is addition of the attacking nucleophile to the vinylic carbon atom followed by elimination of the anionic leaving group from the carbanion to regenerate the double bond.



(78)

The elimination-addition pathway involves elimination of HX from the olefin to generate an acetylene followed by addition of the nucleophile and a proton to yield an olefin by overall substitution.

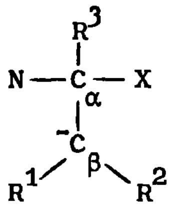


(79)

In suitable hydrogen containing substrates these two routes can proceed side by side, the former (78) being preferred when nucleophiles of high carbon nucleophilicity and low hydrogen basicity are used. In contrast the latter route (79) is preferred with nucleophiles of high proton basicity and low carbon nucleophilicity.

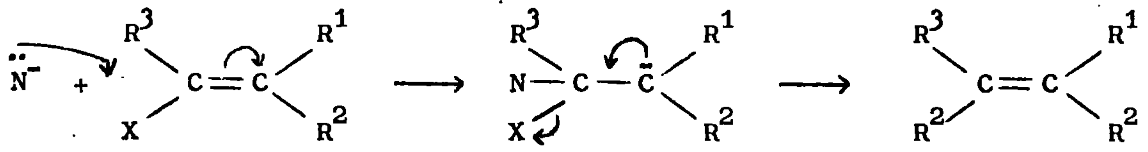
Comprehensive studies have been carried out by several workers on the addition-elimination mechanism.[84] Kinetic studies show the reaction to be first order in both substrate and nucleophile.[85-89,95]

Two alternatives have been proposed for the structure of the addition-elimination intermediate.[90] In the first (80) C_α has a tetrahedral configuration, the C_α-C_β bond has single bond character and C_β has sp^3 hybridisation, i.e. this intermediate corresponds to a true stepwise addition-elimination process. The second intermediate is visualised as having sp hybridisation of the co-linear R^3-C_α-C_β σ bonds whilst one of the valence electrons of C_α is involved in formation of the π bond between C_α and C_β and the other is involved in weak binding of the entering and leaving groups, i.e. this intermediate corresponds to a more synchronous mechanism analogous to aliphatic S_N2 reactions (81).

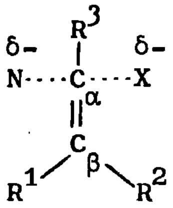


(80)

i.e.

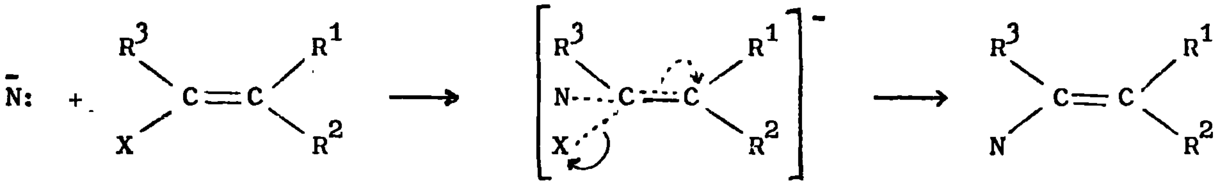


Alternatively

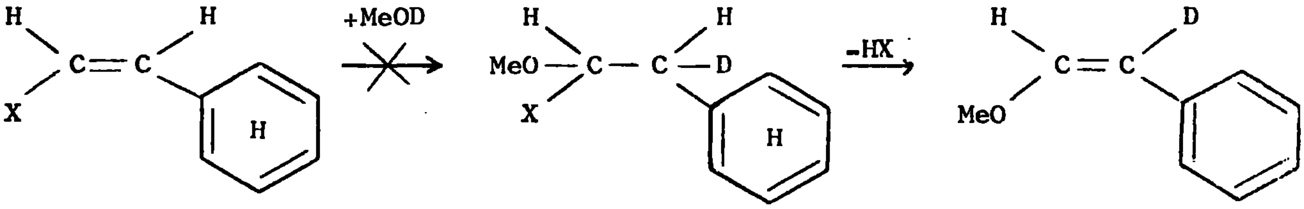


(81)

i.e.

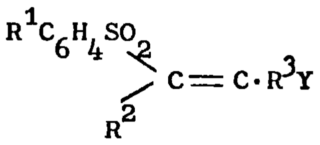


Reactions of β-halostyrenes with methoxide in deuterated methanol showed that protonation of the intermediate carbanion in the stepwise process (80) (i.e. formal addition of $\ddot{N}$H) followed by elimination of HX did not occur.[85,86] No incorporation of deuterium was observed in the product olefin.



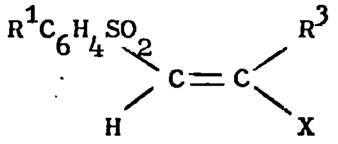
If some bond breaking occurs in the transition state i.e. the synchronous mechanism (81) is operative, then the rate of reaction will depend critically upon the leaving group. This criterion, the so called "element effect" has been used in both vinylic[91] and aromatic[92,93] substitution reactions to determine which of the two processes, synchronous (81) or stepwise (80) is occurring. Thus the synchronous process (81) will show an element effect on varying the leaving group whereas the stepwise mechanism (80) will not. (This of course assumes that the ground states of the molecules under consideration are similar).

Reactions with haloethylenes of the type[91]:



R^3 = Me or H

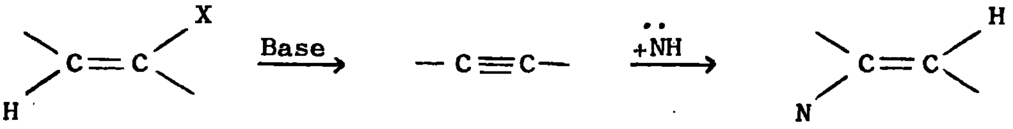
have shown that for the trans compounds i.e.



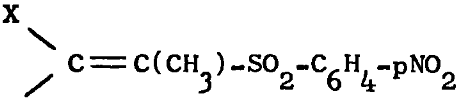
X = Cl, Br

R^3 = H

the rates for substitution of halide ion are very similar and the reactions are thought to proceed via a stepwise addition-elimination process. Complications arise however in the reactions of the cis compounds when a β hydrogen is present where it is found that the bromo derivative reacts much more rapidly than the analogous chloro compound. The results have been rationalised by proposing a facile elimination-addition reaction for the cis compound the first step of which can proceed readily by an anti route.



It has been shown by Modena and co-workers that in olefins without a β hydrogen where the elimination-addition mechanism is impossible, no element effect is observed, this again indicates a stepwise addition-elimination process.[94] Kinetics of halogen substitution in 1-halo-2-methylethylene-p-nitrophenyl sulphones (82) have been studied.



$$\overset{X}{\underset{H}{>}}C{=}C(CH_3)\text{-}SO_2\text{-}C_6H_4\text{-}pNO_2$$

(82)

X = Cl or Br

cis and trans isomers

A summary of the results appears in Table 9.

TABLE 9

Kinetics Of Reactions Of 1-Halo-2-methylethylene-p-nitrophenyl Sulphones With Methoxide And Thiophenoxide

(a) Substitution by methoxide

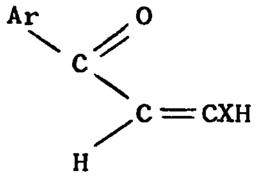
Chloro sulphone	Bromo sulphone
1. cis-olefin	1. cis-olefin
k = 54	k = 50·5
E = 19·2 kcals/mol	E = 17·9 kcals/mol
2. trans-olefin	2. trans-olefin
k = 62·2	k = 52·6
E = 16·8 kcals/mol	E = 18·5 kcals/mol

(b) Substitution by thiophenoxide

Chloro sulphone	Bromo sulphone
1. cis-olefin	1. cis-olefin
k = 1750	k = 4580
E = 14·7 kcals/mol	E = 15·8 kcals/mol
2. trans-olefin	2. trans-olefin
k = 630	k = 1430
E = 15·9 kcals/mol	E = 15·5 kcals/mol

With methoxide the rates for the chloro and bromo-olefins are very similar indicating a stepwise process, whereas with thiophenoxide the bromo-olefins react more rapidly which suggests that there may be a contribution from the synchronous mechanism.

Similar results have been observed in the reactions of cis- and trans-p-anisyl-2-halovinyl ketones (83) with thiophenoxide and methoxide.[95]

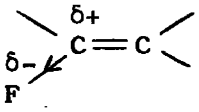


(83)

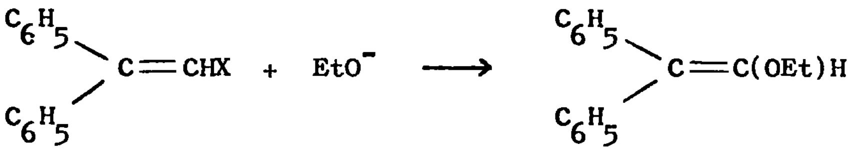
X = Cl and Br

cis and trans isomers

The high reactivity of vinylic fluorine towards nucleophilic displacement is due in part to its strong inductive effect which withdraws charge density from both the π and σ framework of the double bond and renders the attached carbon atom highly electrophilic[96] i.e.



Thus the effect of fluorine on the ground state is the predominant factor responsible for its higher rate of substitution compared to the other halogens. For example[97], 1,1-diphenyl-2-fluoroethylene (84a) undergoes substitution by ethoxide 270 times more rapidly than the analogous chloro compound (84b).



(84) a; X = F

b; X = Cl

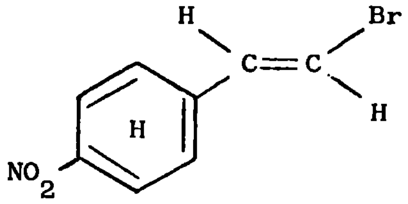
III.C Stereochemistry Of Substitution

Nucleophilic vinylic substitutions are characterised by their high stereospecificity i.e. the configuration of the starting material is retained in the product, the degree of retention is often greater than 95%.

Simple hydrocarbon olefins are extremely inert towards nucleophilic attack, however nucleophilic substitution occurs readily when electron withdrawing groups are substituted onto vinylic carbon. Olefins activated by groups such as sulphone,[98] carbonyl,[85,86,99] aromatic,[86-88,100] cyano[89] and perfluoroalkyl[101] have been investigated. A large variety of nucleophiles including alkoxide, azide, iodide, thiophenoxide and diphenyl arsine have also been used in numerous investigations.[101]

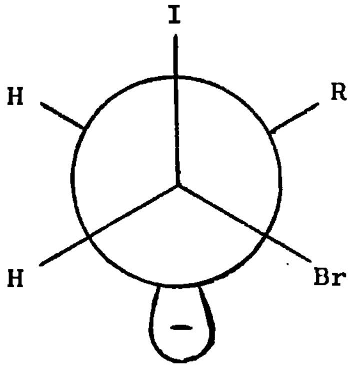
Some of the initial studies of this type of process were carried out by Jones and co-workers[85] who studied the reactions of β-chlorocrotonates with thioethoxide. A planar carbanion was proposed which eliminated chloride ion in a stereospecific manner due to steric factors.

Miller and Yonan[102] carried out halide ion exchange reactions with iodide ion and p-nitro-β-bromostyrene (85).

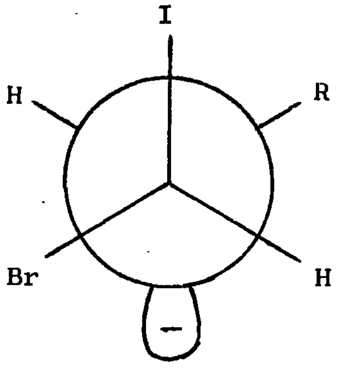


(85)

Almost complete retention of geometry occurred (> 95%) (i.e. cis ⟶ cis and trans ⟶ trans) although isomerisation of the products was observed after prolonged reaction times. It was assumed that the addition of the nucleophile takes place in an anti fashion and in a direction perpendicular to the plane of the double bond, to produce a tetrahedral carbanion. Only *anti* elimination of halide ion relative to the electron pair in one of the suitable conformations was assumed to complete the reaction. For the *cis*-isomer, *anti* addition of iodide ion produces the carbanion (86) which is one of a pair of D and L forms and one of a set of three threo rotamers.



(86)

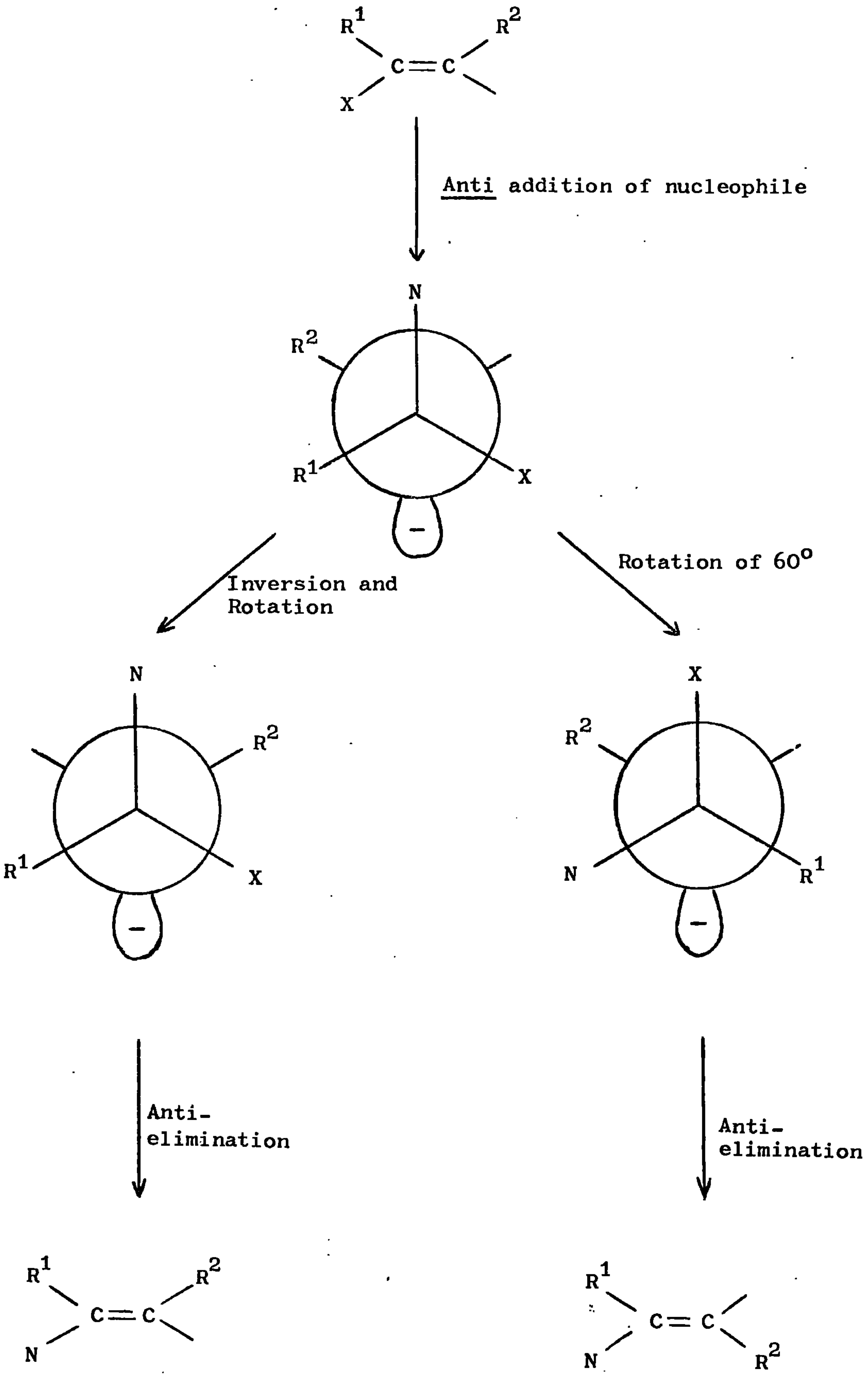


(87)

R = $pNO_2\text{-}C_6H_4$

Carbanion (87), however, is produced by *anti* addition to the *trans*-olefin and is one of the diastereoisomeric set of three erythro rotamers. It has been estimated that barriers to rotation of these carbanions are about 3 kcals/mol and that the threo and erythro isomers are separated by a barrier to inversion of c.a. 7 kcals/mol.

Although without foundation the authors propose in essence that inversion of the tetrahedral carbanion is much more rapid than rotation, this is however contradictory to the values given for the energy barriers for the two processes. *Anti* elimination of bromide ion after inversion is then proposed to generate the double bond with the same geometry as the starting olefin (88). Inversion of geometry is proposed to take place upon rotation of the intermediate carbanion followed by *anti* elimination (89). For example with the *cis*-olefin.



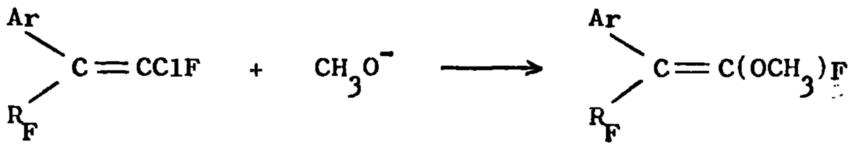
(88)
i.e. *cis*

(89)
i.e. *trans*

An analogous scheme can be visualised for the *trans* olefin.

More recent work by Park[103] on reactions of various alkoxides with cis- and trans-2,3-dichlorohexafluorobut-2-ene shows once again the high stereospecificity of nucleophilic vinylic substitution. It has been proposed that the reactions are governed by kinetic control in which the fate of the planar carbanion is determined by steric interactions in the various rotamers.

A tetrahedral carbanion produced by an irreversible anti addition of the attacking nucleophile to the double bond to produce a short lived carbanion has been proposed by Burton and Krutzsch[101] in the reactions of various β-substituted 1-chloroperfluoro olefins (90) with methoxide.



(90)

cis- and trans-isomers

In these systems chloride ion was found to be displaced 90 → 96% stereospecifically and the degree of retention was not affected by electron releasing or withdrawing groups in the aromatic ring (or by substitution of an aliphatic group in place of phenyl). Changing the size of the perfluoro alkyl group by using perfluoromethyl and perfluoroethyl similarly had no great effect on the stereospecificity of the reactions. A summary of the results of these reactions appears in Table 10.

The authors suggest that the stereochemical course of these reactions involves an irreversible anti addition of the nucleophile to the double bond followed by rapid syn elimination of the leaving group to retain the original geometry. For example with a cis-olefin.

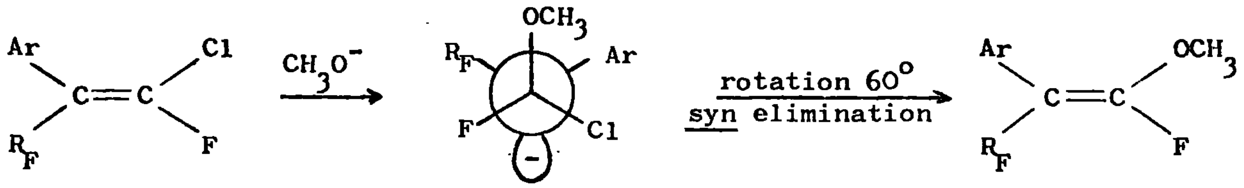
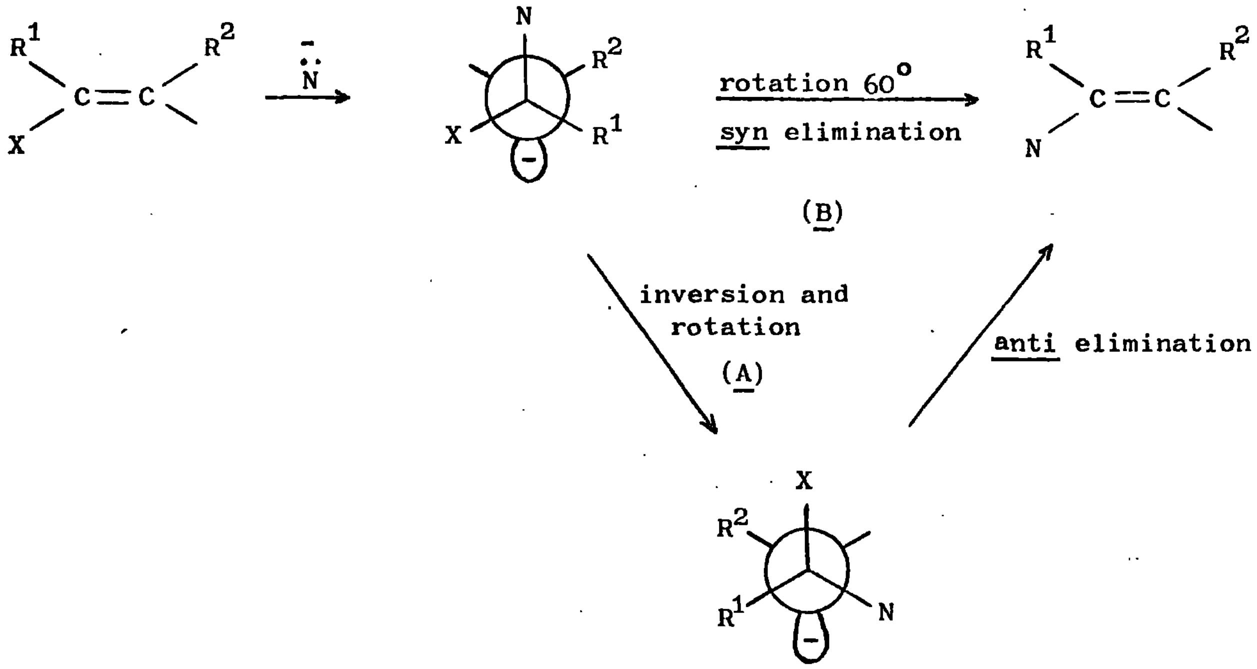


TABLE 10

Results Of Reaction Of Methoxide Ion With Various β-Substituted 1-Chloroperfluoro Olefins

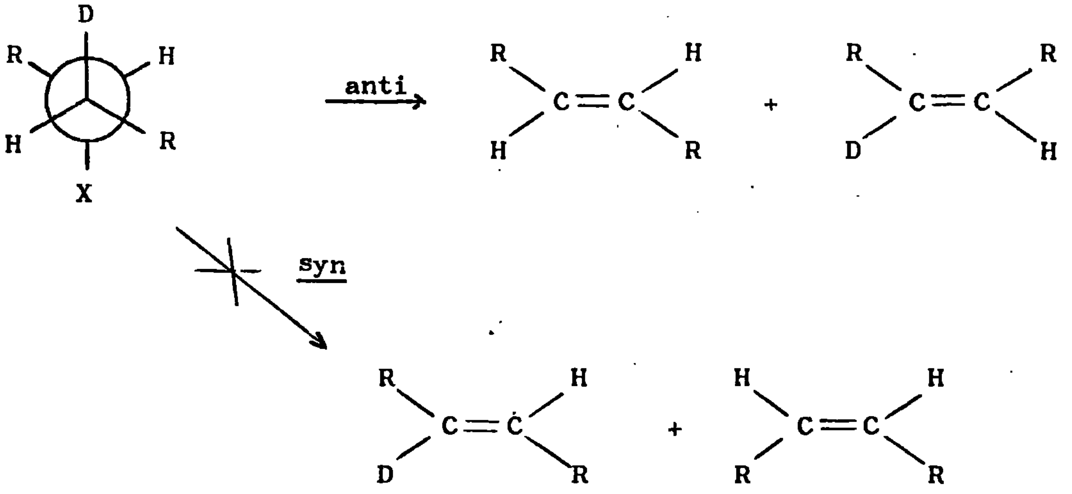
Ar	R_F	Isomer	% *cis*	% *trans*
C_6H_5	CF_3	*cis*	96	4
		trans	4	96
C_6H_5	C_2F_5	*cis*	90	10
		trans	9	91
$p\text{-}ClC_6H_4$	CF_3	*cis*	94	6
		trans	8	92
$p\text{-}CH_3OC_6H_4$	CF_3	*cis*	92	8
		trans	6	94
cyclohexyl C_6H_{11}	CF_3	*cis*	96	4
		trans	4	96

In conclusion the stereochemical results of vinylic substitution have been explained in two distinct ways. Both routes involve an *anti* addition of the nucleophile. In the first route (*A*) rapid inversion (in relation to rotation) of the tetrahedral carbanion is proposed to occur and the leaving group must then be eliminated in an *anti* manner for retention of geometry to occur. However there seems to be no basis for assuming that inversion is more rapid than rotation. The second more plausible route (*B*) involves rotation through 30° of the tetrahedral carbanion followed by a *syn* elimination of the leaving group.

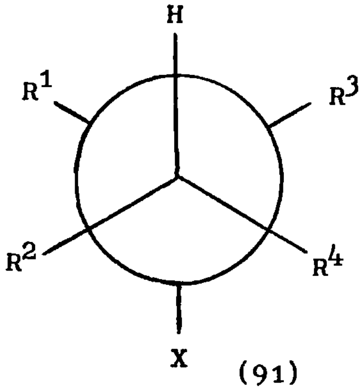


III.D Bimolecular Elimination Reactions

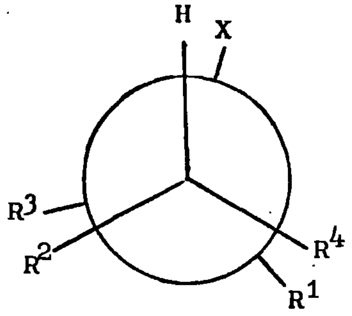
Although not directly related, E2 reactions in acyclic systems to produce olefins were shown by early work to proceed by an anti course.[104,105] For example, it was found that the elimination of both hydrogen bromide and toluenesulphonic acid from mono deuterated 2-butylbromide and 2-butyltosylate proceeded exclusively by an anti elimination. For example



The preference for anti over syn bimolecular eliminations is thought to be caused partially by steric effects i.e. in the anti route elimination can take place from a completely staggered conformation (91) whereas elimination via syn must proceed through a fully eclipsed conformer (92).



(91)

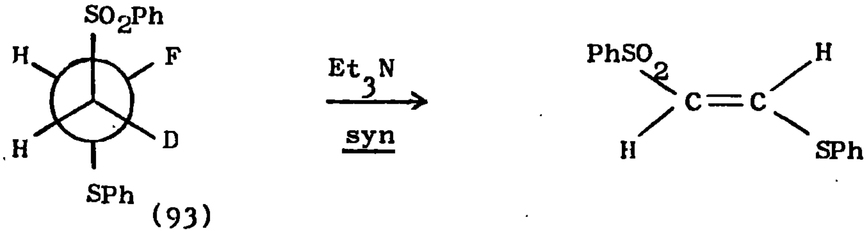


(92)

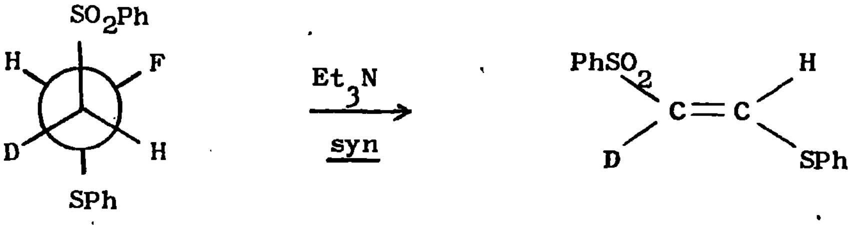
These conformational differences lead to an estimated factor of 10^2-10^3 in favour of anti elimination.[106] This of course pre-supposes that due to the principle of maximum orbital overlap, elimination can only take place from conformations which have torsional angles of 0° and 180°.

Recently, however, evidence has been produced which shows that in some common bimolecular elimination reactions syn and anti routes proceed side by side.[107] Separated as well as contact ions of the base are suggested to take part in these reactions and elimination from these species leads to different steric results depending on the nature of the leaving group.

Syn stereospecificity has also been observed in an E1cB elimination of sulphonyl fluoroethanes (93) and (94).

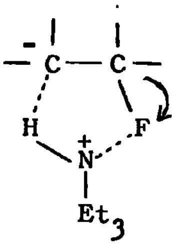


(93)



(94)

The mechanism suggested for the reaction involves an ion pair (95) which collapses to the products via an overall syn course due to attraction between the positive pole of the conjugate acid and the incipient negative charge on the leaving halogen.[108]



(95)

DISCUSSION

CHAPTER IV

Reactions of Hexafluorobut-2-yne with Nucleophiles

Introduction

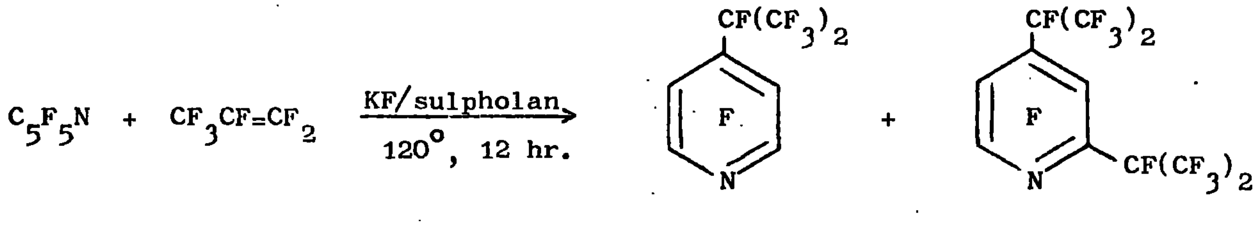
The aim of this work has been to prepare new polyfluoro-2-butene compounds derived from hexafluorobut-2-yne and also to gain a greater understanding of the factors which affect the stereochemistry of nucleophilic addition to activated acetylenes.

IV.A Fluoride Ion-Initiated Reactions

IV.A.1 Introduction

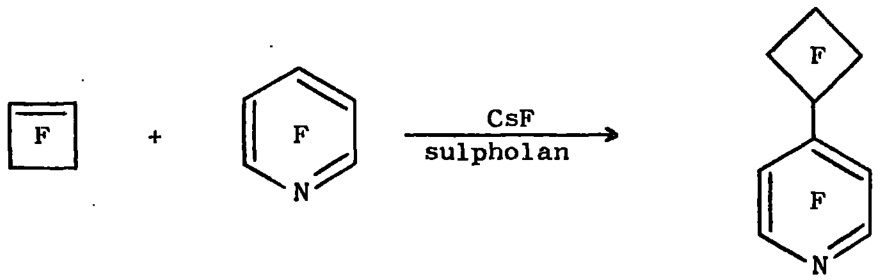
Polyfluoroalkylations of activated carbocyclic and heterocyclic aromatic compounds using polyfluoro-olefins in fluoride ion-initiated reactions are well documented. Many acyclic and cyclic olefins have been used in these processes under various reaction conditions with the fluoride ion being obtained from an inorganic salt, generally caesium or potassium fluoride.

For example, pentafluoropyridine, hexafluoropropene, potassium fluoride and sulpholan when heated in a sealed tube at 120° produce a 90% yield of perfluoro-(4-isopropylpyridine) (96) with a trace of perfluoro-(2,4-di-isopropylpyridine) (97).[109,110]



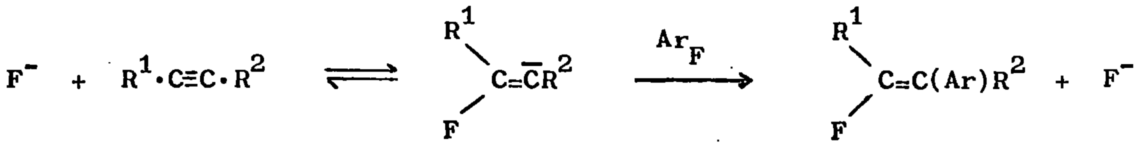
(96) (97)

Similarly under suitable conditions pentafluoropyridine reacts with perfluorocyclobutene to produce the perfluoro-4-cyclobutyl derivative (98).[11]



(98)

Polyfluoroalkenylations using fluorocarbon acetylenes in fluoride ion processes however are not nearly so numerous, e.g.



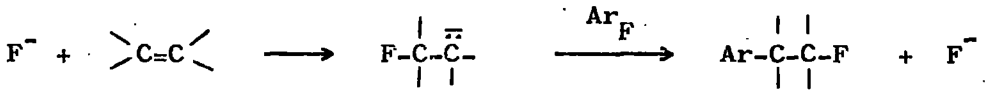
This is partially due to the inaccessibility of this type of acetylene and also due to problems associated with self condensation of these compounds under the conditions of the reactions.

Initial attempts to carry out perfluorovinylation of pentafluoropyridine using hexafluorobut-2-yne at elevated temperatures and pressures in Carius tubes produced only polymeric material derived from the acetylene with no sign of vinyl pyridines being present.[112]

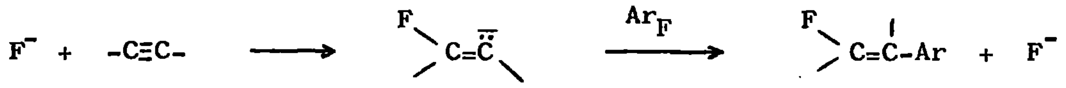
IV.A.2 Reaction Conditions

Extensive studies carried out in these laboratories to determine the most effective combination of solvent and source of fluoride ion have shown that sulpholan with caesium fluoride is commonly the most suitable system for initiation of fluoride ion reactions,[113] however, exceptions to this combination are known.[114]

In principle polyfluoroalkylations of fluorinated substrates requires only a catalytic quantity of fluoride ion to initiate the reaction, i.e. fluoride ion is being continuously replaced. For example with an activated olefin



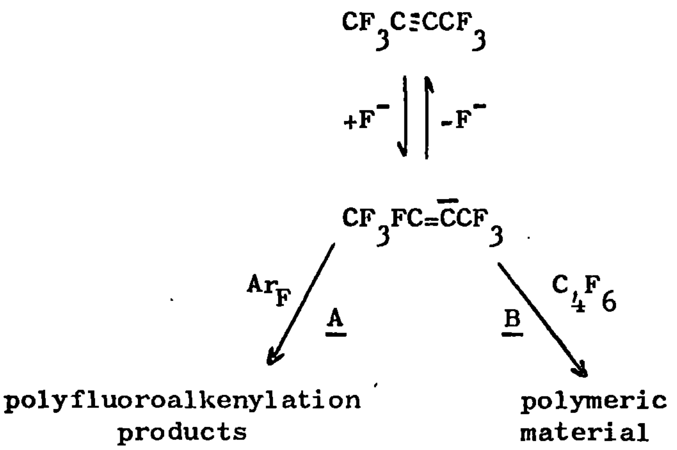
similarly with an activated acetylene,



However, studies have shown that reaction rates are critically dependant upon the quantity of initiator present and it has been suggested that reaction takes place on the surface of the salt.[114,115] Accordingly substantial quantities of metal fluoride are generally used in these reactions.

Original polyfluoroalkylation reactions were carried out in autoclaves at high temperatures (>120°) and pressures.[116] Unwanted side reactions particularly oligomerisation[111,114,115] and rearrangement, along with extensive solvent decomposition, however, complicated these processes.

The major problem associated with perfluoroalkenylation using hexafluorobut-2-yne was found to be that polymerisation of the acetylene occurred very readily in the presence of fluoride ion.[112] A competition therefore exists between self condensation of the acetylene to produce an unsaturated polymer and reaction of the perfluoroalkenyl anion with the substrate in perfluorovinylation reactions, e.g.



In principle the polyfluoroalkenylation reaction can be promoted in three distinct ways,

(i) the reaction temperature can be increased making the vinyl anion less selective,

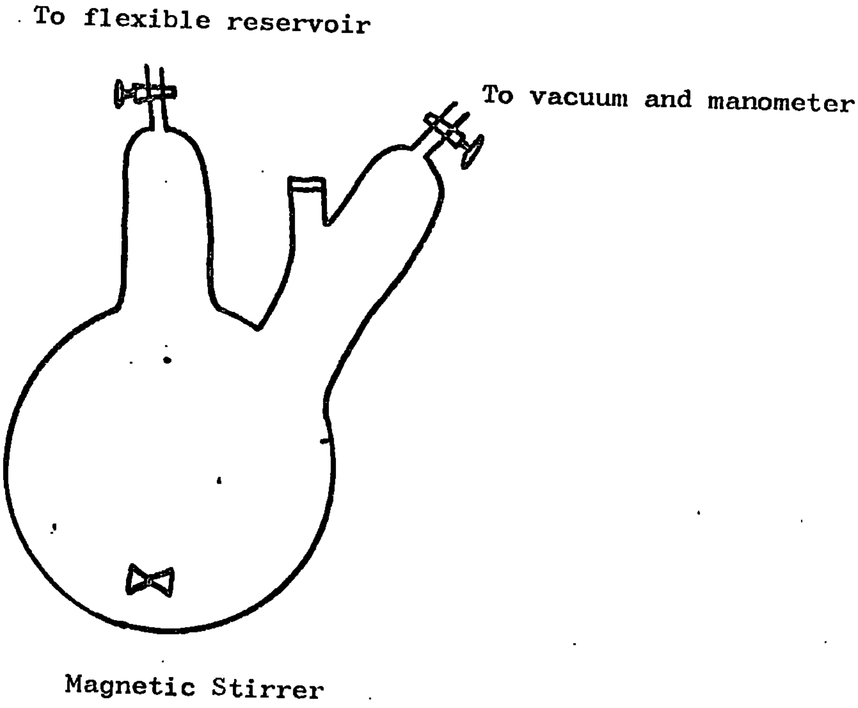

To flexible reservoir
To vacuum and manometer
Magnetic Stirrer

Figure 1

(ii) by reducing the concentration of acetylene relative to the substrate,

(iii) by increasing the reactivity of the substrate.

Techniques have been developed specifically within these laboratories to carry out fluoride ion-initiated reactions of hexafluorobut-2-yne under moderate reaction conditions with a variety of organic and inorganic substrates. A novel system whereby the concentration of the acetylene can be delicately controlled has meant that relatively unreactive substrates can be substituted with perfluoroalkenyl groups.

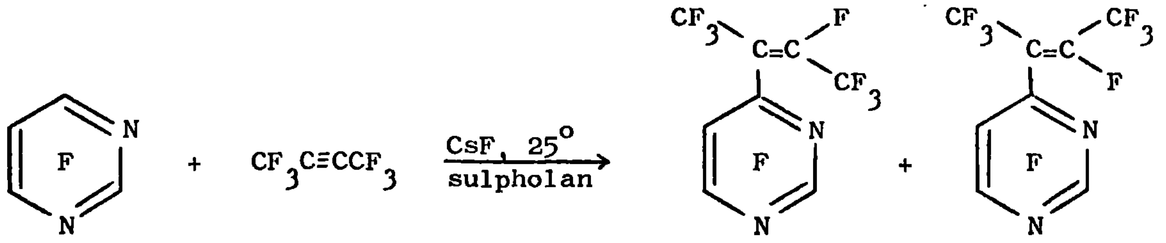
The apparatus used is shown in Figure 1. The solvent and metal fluoride are introduced into the conical flask which is then evacuated and degassed. The system is let down to almost atmospheric pressure (≈ 2 cm. of Hg.) with dry nitrogen and the substrate is introduced through the septum. The mixture is agitated by a magnetic stirrer and hexafluorobut-2-yne is then slowly introduced into the system from the flexible reservoir in small amounts (to approximately atmospheric pressure). The progress of the reaction can be followed by observing the development of a vacuum in the system as the acetylene reacts with the fluoride ion.

Using similar conditions pentafluoropyridine[112] and tetrafluoropyridazine[112] have been successfully polyfluoroalkenylated.

IV.A.3 Reaction of Hexafluorobut-2-yne with Tetrafluoropyrimidine

(a) Reaction at 20°

When hexafluorobut-2-yne was slowly introduced from a flexible reservoir into a rapidly stirred suspension of caesium fluoride, in sulpholan, containing tetrafluoropyrimidine in the apparatus shown in Figure 1, two perfluoroalkenyl pyrimidines (99) and (100) were obtained.

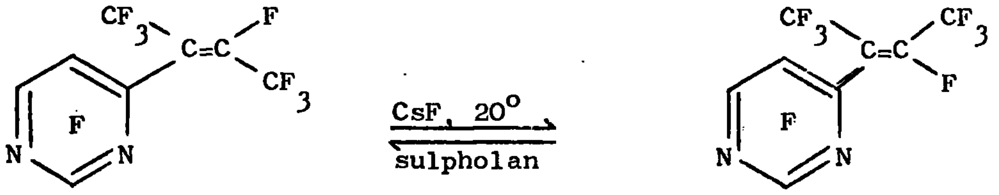


(99); 57% (100); 6%

(percentage yields based on 70% conversion)

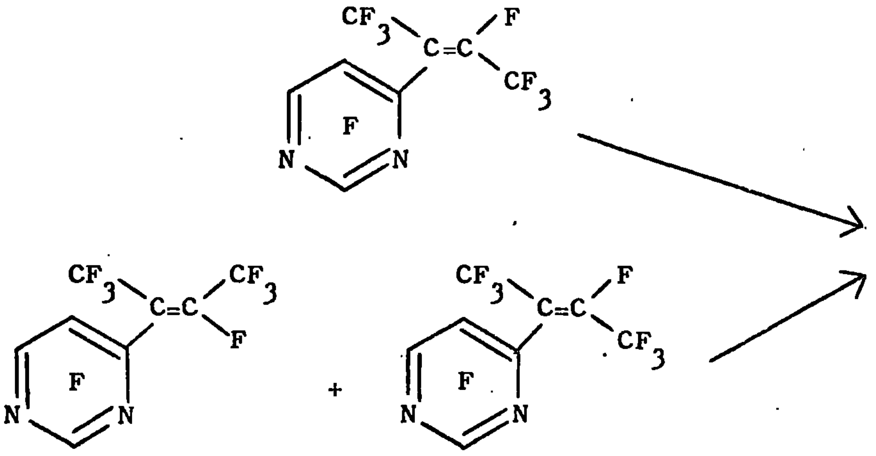
In the initial reaction the two substituted pyrimidines were isolated as a mixture containing unreacted starting material. However a subsequent reaction produced a pure sample of a mixture of the two butenyl pyrimidines (99) and (100).

Equilibration of the *cis* and *trans* isomers under the conditions of the reaction, i.e.



90% 10%

was shown to be operative by firstly reacting the pure *trans* isomer (99) with caesium fluoride in sulpholan and secondly by treating a *cis*:*trans* mixture of the butenyl pyridines (100) and (99) under the same conditions.



35% 65%

Equilibrium mixture

90% *trans*, 10% *cis*

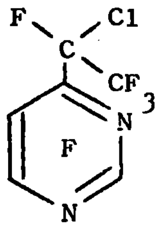
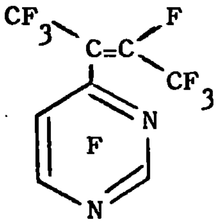
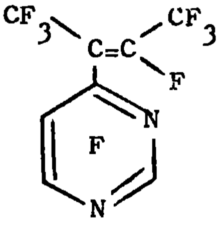
(99) and (100)

(i) Structure of the products

The two perfluoro-2-butenyl-pyrimidines (99) and (100) were characterised as a mixture which had satisfactory elemental analysis and showed a strong parent peak in the mass spectrum. N.m.r. spectroscopy was used to show that the compounds were perfluoro-4-substituted pyrimidines. These results completely resemble similar polyfluoromonoalkylations of tetrafluoropyrimidine,[117] the observed chemical shift values of the 2,5 and 6 ring fluorines atoms are in close agreement with those for similar compounds (Table 1).

Table 1

Chemical Shifts* in 4-substituted Trifluoropyrimidines

Compound	Chemical Shift, Ring Fluorines		
	2	5	6
	45·0	149·8	69·4
	48·2	154·4	74·0
	48·2	154·4	74·0

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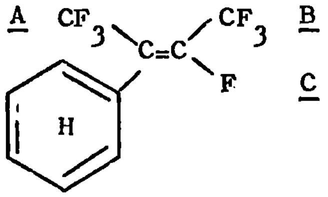
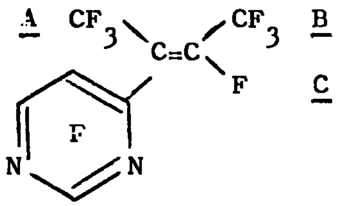
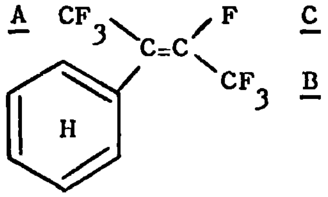
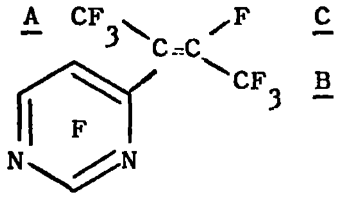
* From external $CFCl_3$

Comparison of coupling constants in cis and trans phenyl polyfluoro-olefins (prepared by the reaction of phenyl-lithium with octafluorobut-2-ene[118,119]) was used to determine the configuration of the olefinic side chains in the products derived from nucleophilic addition reactions of hexafluorobut-2-yne. For the butenyl pyrimidines good agreement was obtained for both the cis and trans compounds (Table 2).

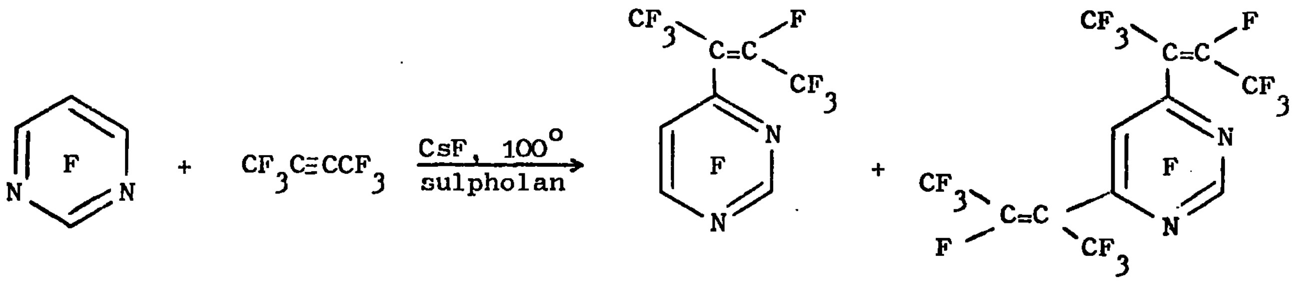
Table 2

Characteristic Coupling Constants (Hz) in Polyfluoro-2-substituted-but-2-enes

	J_{AB}	J_{BC}	J_{AC}
	12	7	12
	11	7	8·5
	1·5	7	28
	1·5	7·5	22

(b) Reaction at 100°

Identical apparatus and procedure were used as in the similar reaction of this heterocycle with hexafluorobut-2-yne (IV.A.3(a)) but here the reaction was carried out at 100°. The products of the reaction were transferred under vacuum from the apparatus, v.p.c. analysis showed the presence of two major components with a small amount of other material ($<$ 10%) of higher retention time. The two major products were separated by preparative scale v.p.c. and were identified as perfluoro-trans-4-(2-butenyl)-pyrimidine (99) and perfluoro trans-4,6-di-(2-butenyl)-pyrimidine (101).



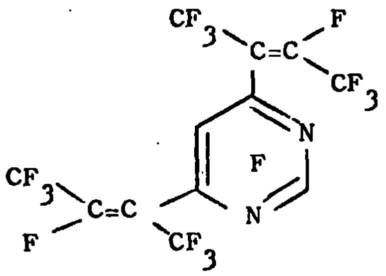
(99); 26% (101); 31%

(i) Structure of the products

The mono-2-butenylpyrimidine (99) was identified by comparison of its i.r. and n.m.r. spectra with those of an authentic sample (prepared from a similar reaction of the substrates at 25°). The second derivative (101) was characterised in the normal way, its mass spectrum showed a strong parent peak and elemental analysis of the compound was found to be satisfactory. ^{19}F n.m.r. spectroscopy was used to determine the substitution pattern of the pyrimidine nucleus and the configuration of the olefinic side chain. The absence of resonances in the 60 ⟶ 80 p.p.m. (from $CFCl_3$) region confirmed 4,6-disubstitution (Table 3).

Table 3

Chemical Shifts (p.p.m.) in Perfluoro-trans-4,6-di-(2-butenyl)-pyrimidine

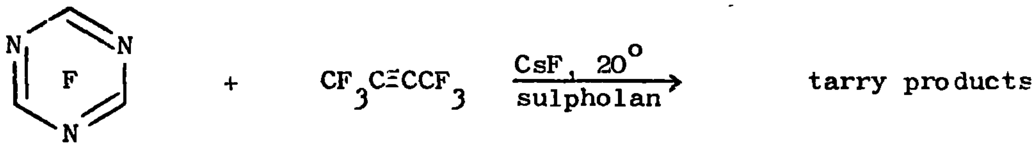
	Ring fluorines	
	2	5
	49·5	136·0

Inspection of the trifluoromethyl group resonances clearly showed that the olefinic side chains had a trans configuration. A small coupling of 1·5 Hz. characteristic of a trans CF_3-CF_3 grouping with a corresponding cis CF_3-F coupling of 20 Hz. can be clearly seen in the spectrum.

IV.A.4 Reaction of Hexafluorobut-2-yne with Cyanuric Fluoride at 20°

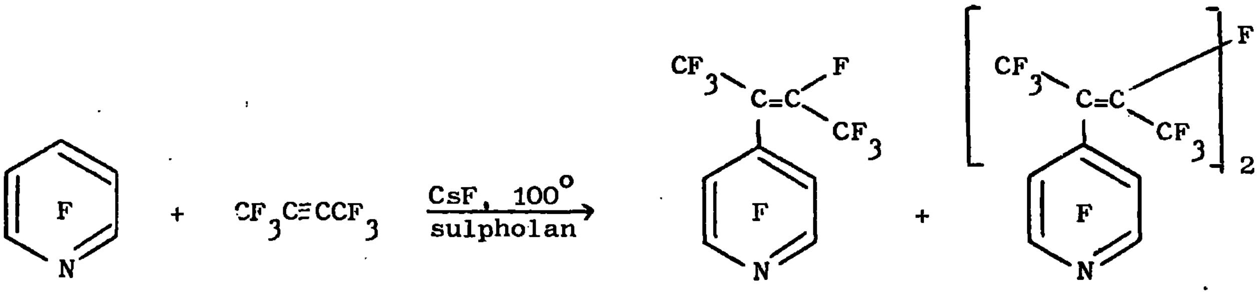
(a) Reaction conditions and products

Attempts to produce butenyl derivatives of this highly reactive heterocycle have met with failure. When hexafluorobut-2-yne was introduced into a rapidly stirred suspension of caesium fluoride in sulpholan containing cyanuric fluoride only intractable tars were recovered.

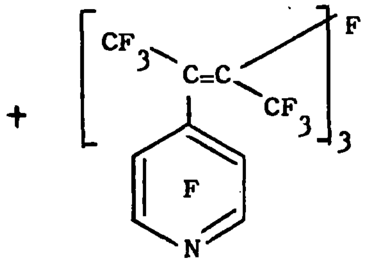


IV.A.5 Discussion of Perfluoroalkenylation of Perfluoroheterocyclic Compounds

Similar reactions of hexafluorobut-2-yne with pentafluoropyridine, previously carried out in these laboratories, have been shown to produce several substituted pyridine derivatives.[112]



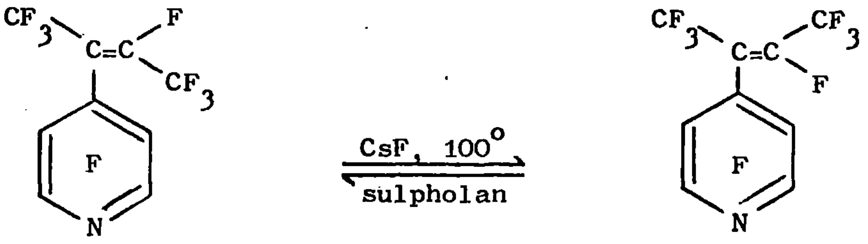
(102); 13% (103); 20%



(104); 10%

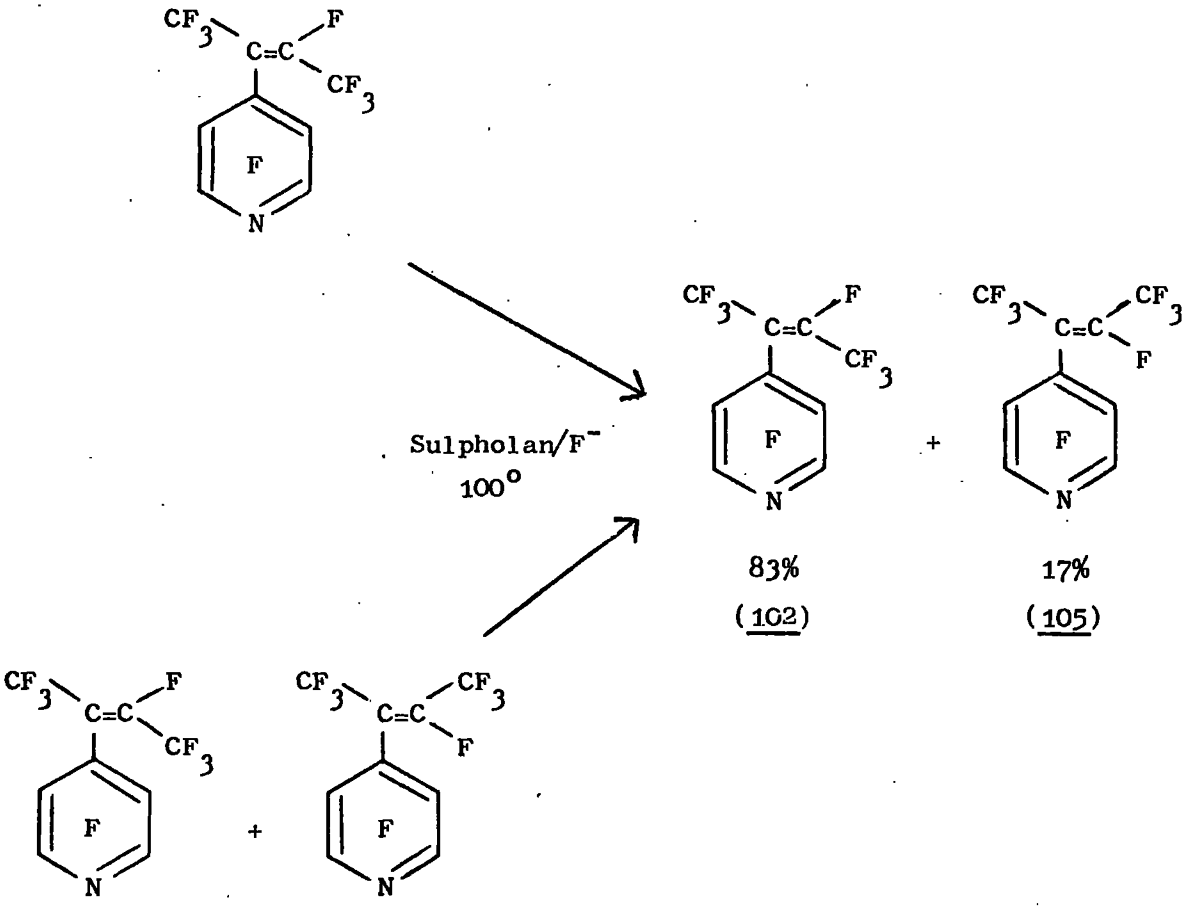
two isomers

Although only the trans isomer of the monoene (102) was originally reported, it has now been shown that under the conditions of the reaction this isomer is in equilibrium with the cis analogue (105).



(102); 83% (105); 17%

Thus when perfluoro-trans-4-(2-butenyl)pyridine was heated in sulpholan in the presence of fluoride ion a 17:83 cis:trans mixture of (105) and (102) was produced.

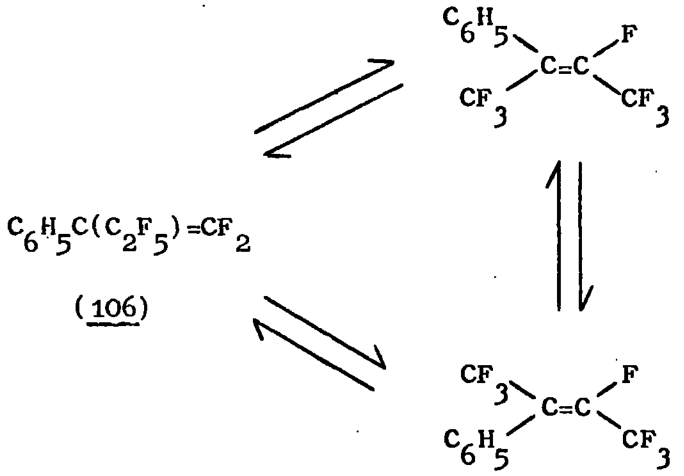


83% (102) 17% (105)

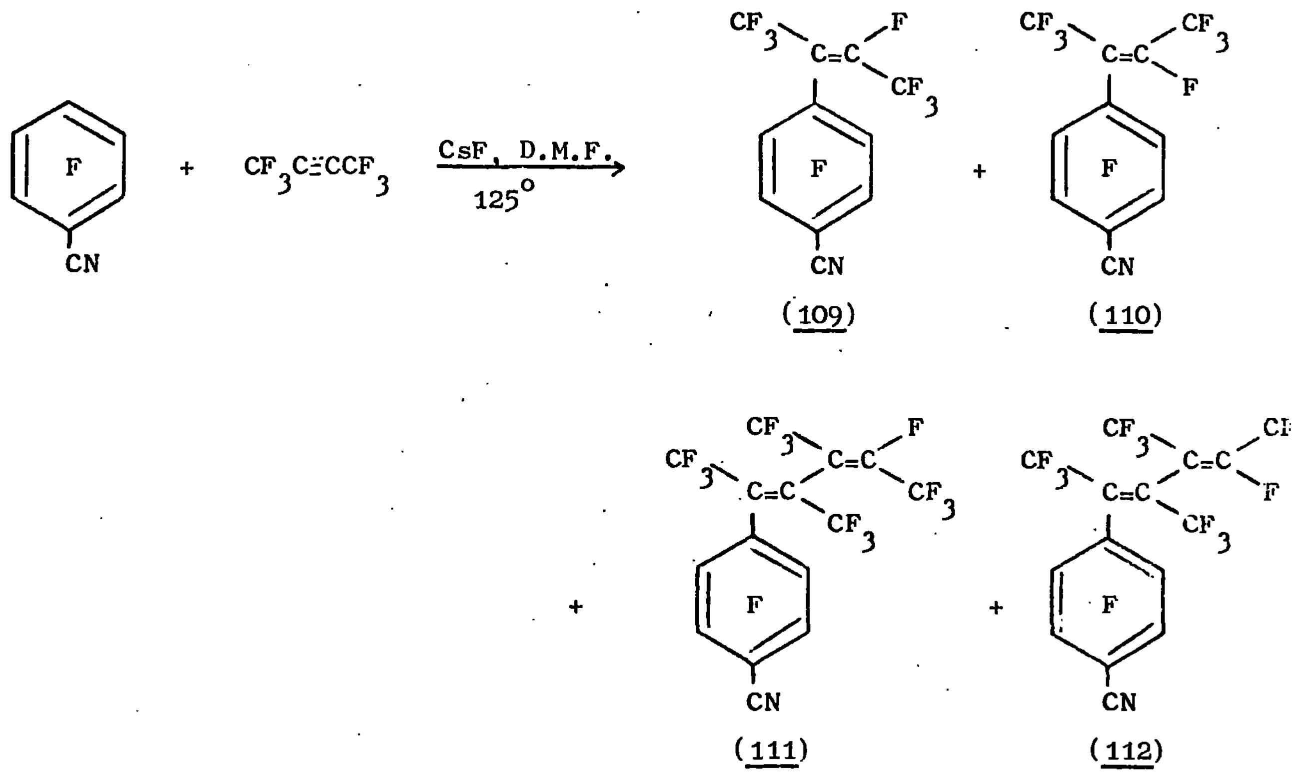
55% 45%

Similarly a 55:45, trans:cis mixture of the two butenes (102) and (105) when treated under similar conditions was again found to produce an equilibrium mixture consisting of 83% (102) and 17% (105). This is of course analogous to the equilibration of the cis and trans butenylpyrimidines (99) and (100); it can be seen that the position of equilibrium for the two systems is very similar.

Equilibrations of fluoro-olefins in the presence of fluoride ion have been reported by other workers. Burton and Herkes[120] have reported the preparation of 2-phenylheptafluoro-1-butene (106) and its subsequent rearrangement to cis and trans 2-phenylheptafluorobut-2-ene (107) and (108) in the presence of fluoride ion. Equilibration of the cis and trans 2-butenes was demonstrated by allowing pure cis and trans isomers to react with caesium fluoride under the conditions of the reaction (diglyme at 100°).



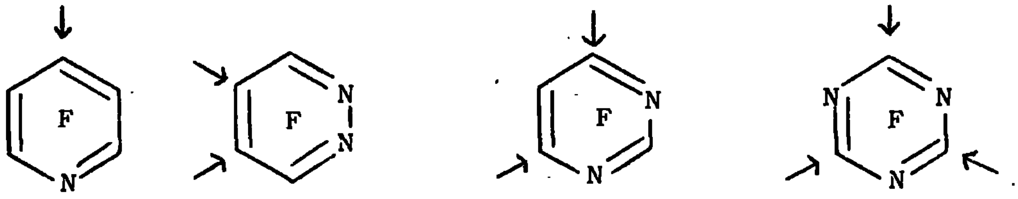
Cis:trans equilibration promoted by fluoride ion has been reported for a similar series of monoenes and dienes derived from reaction of hexafluorobut-2-yne and perfluorobenzonitrile with caesium fluoride.[69]



(109) (110) (111) (112)

Equilibration was shown to occur between the two monoenes (109) and (110); similarly, the dienes (111) and (112) were in equilibrium under the conditions of the reaction.

The fact that no substituted dienes and trienes analogous to (103) and (104) are isolated from the pyrimidine reaction can be rationalised when the reactivity of the two systems is considered. Kinetic studies to determine second order rate constants and relative reactivities towards nucleophilic substitution have been carried out in these laboratories on several perfluoroheterocyclic compounds.[121] (Reactions were carried out at 25° using ammonia as the nucleophile). The relative rates are as follows:

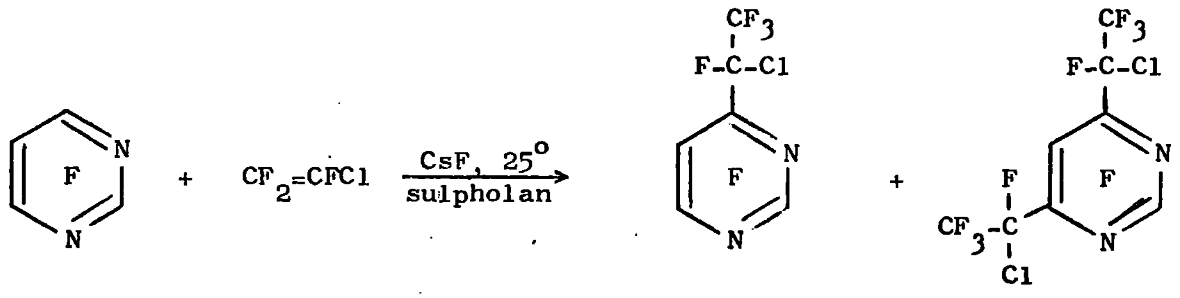


1 : 37·4 : 2000 : $> 10^5$

Tetrafluoropyrimidine is seen to be a much more highly reactive compound towards nucleophilic attack than is pentafluoropyridine. As mentioned previously (IV.A.2) a competition exists between polyfluoroalkenylation and polymer formation in the fluoride ion-initiated reactions of hexafluorobut-2-yne. Therefore, it must be assumed that because of the reactivity difference between the two heterocycles, reaction between the substrate and the butenyl anion is the more favoured process with tetrafluoropyrimidine (process <u>A</u>) whereas with pentafluoropyridine, the much less reactive compound, self condensation of the acetylene to produce dimers and trimers, which then react with pyridine, is the more predominant (processes <u>B</u> and <u>C</u>) i.e.

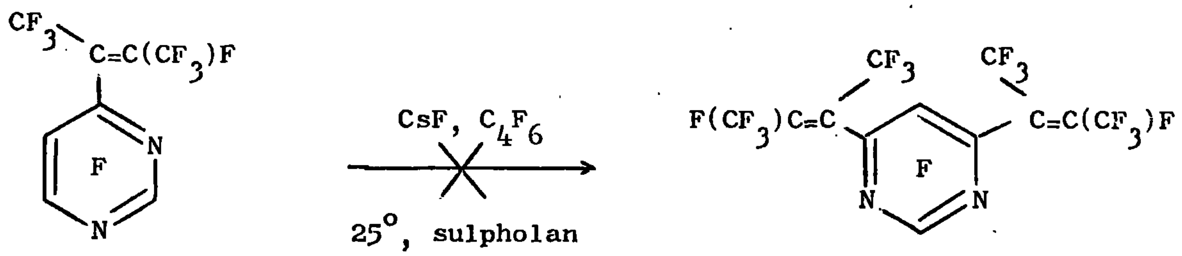
$$\begin{tikzcd}
CF_3FC{=}\bar{C}CF_3 \arrow[r, "C_4F_6"] \arrow[d, "Ar_F", "\underline{A}"'] & CF_3CF{=}C(CF_3)C(CF_3){=}\bar{C}CF_3 \arrow[r, "C_4F_6"] \arrow[d, "Ar_F", "\underline{B}"'] & CF_3CF[{=}C(CF_3)C(CF_3)]_2{=}\bar{C}CF_3 \arrow[r, "etc."] \arrow[d, "Ar_F", "\underline{C}"'] & {} \\
CF_3CF{=}C(CF_3)Ar & F(C(CF_3){=}C(CF_3))_2Ar & F(C(CF_3){=}C(CF_3))_3Ar &
\end{tikzcd}$$

Two equivalent positions, 4 and 6, exist within the tetrafluoropyrimidine molecule at which nucleophilic reaction can take place. Several reactions have been investigated in which disubstitution takes place.[117] In the case of polyfluoroalkylation with chlorotrifluoroethylene both the mono (<u>113</u>) and disubstituted (<u>114</u>) products have been isolated from a reaction at 25°.



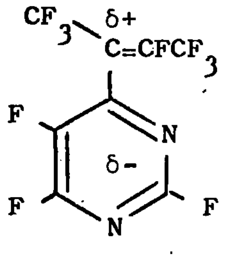
(<u>113</u>) (<u>114</u>)

However polyfluoroalkenylation with hexafluorobut-2-yne produces only the mono-2-butenyl derivatives (99) and (100) in room temperature reactions as shown previously. An attempt to prepare a disubstituted compound in a room temperature reaction using the cis- and trans-mono-butenyl compounds (99) and (100) was found to be unsuccessful. Thus only starting material was recovered when a mixture of cis- and trans-perfluoro-4-(2-butenyl)pyrimidines (99) and (100), caesium fluoride and sulpholan were vigorously agitated in the presence of hexafluorobut-2-yne at room temperature.

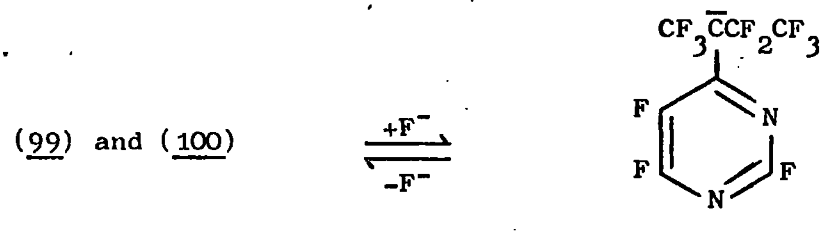


However preparation of a disubstituted compound (101) has been achieved from tetrafluoropyrimidine at 100°.

This apparent deactivation could be an indication that the aromatic ring in the mono-2-butenyl-pyrimidines (99) and (100) is deactivated towards further nucleophilic attack by an electronic effect caused by the olefinic side chain, i.e.

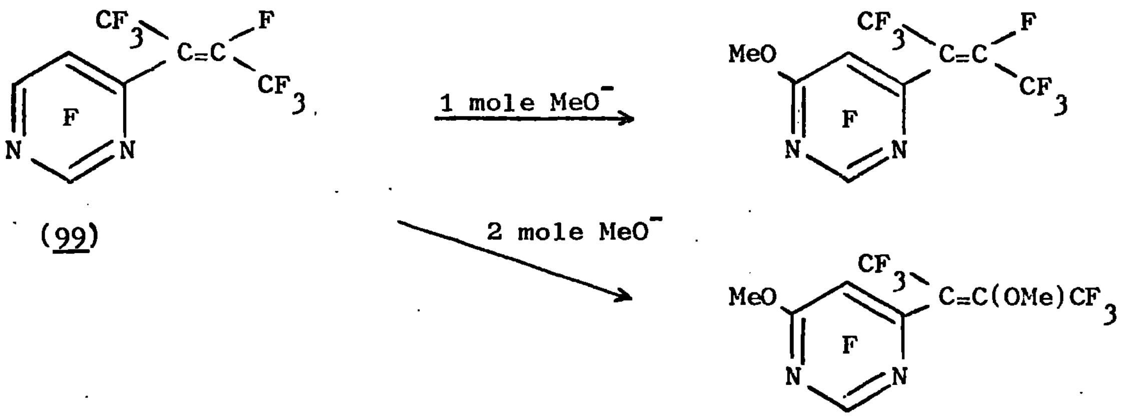


Alternatively these compounds may exist in solution largely as the anion (115) in the presence of fluoride ion, i.e.



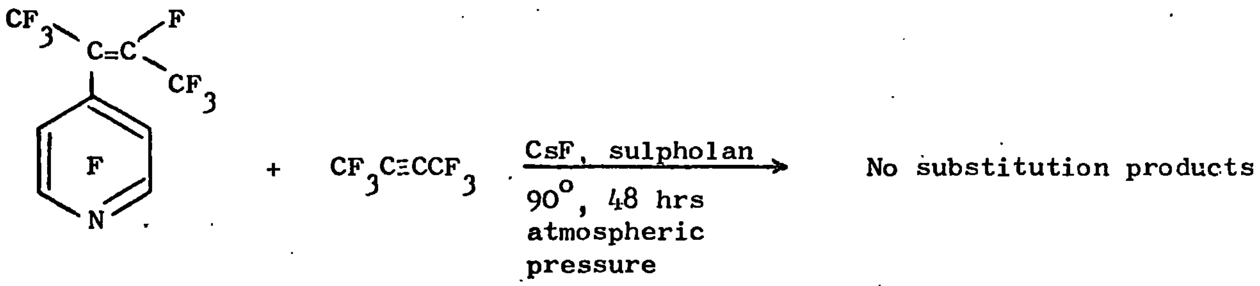
(115)

Support for the latter hypothesis comes from recent reactions carried out with this pyrimidine derivative and methoxide. It has been shown that using a 1:1 ratio of MeO^- to the butenyl pyrimidine (<u>99</u>) substitution occurs in the aromatic nucleus. However using a 2:1 ratio both nucleophilic aromatic and vinylic substitution are found to occur.[117]

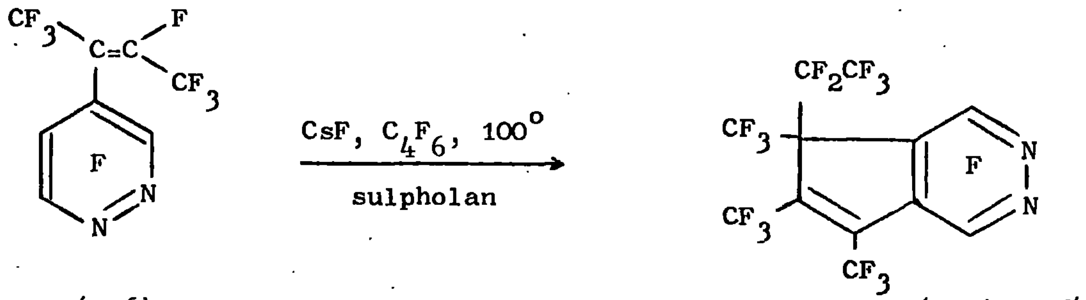

(<u>99</u>)

These results indicate that the aromatic nucleus is not deactivated towards nucleophilic attack and suggests that the compound may exist in solution as the anion in the presence of fluoride ion.

These polyfluoroalkenylation results are analogous to those obtained for perfluoro-<u>trans</u>-4-(2-butenyl)pyridine (<u>102</u>) which similarly does not undergo further reaction with hexafluorobut-2-yne in the presence of caesium fluoride.[11] Only polymeric material derived from the acetylene and fluoride ion, and starting material were recovered.



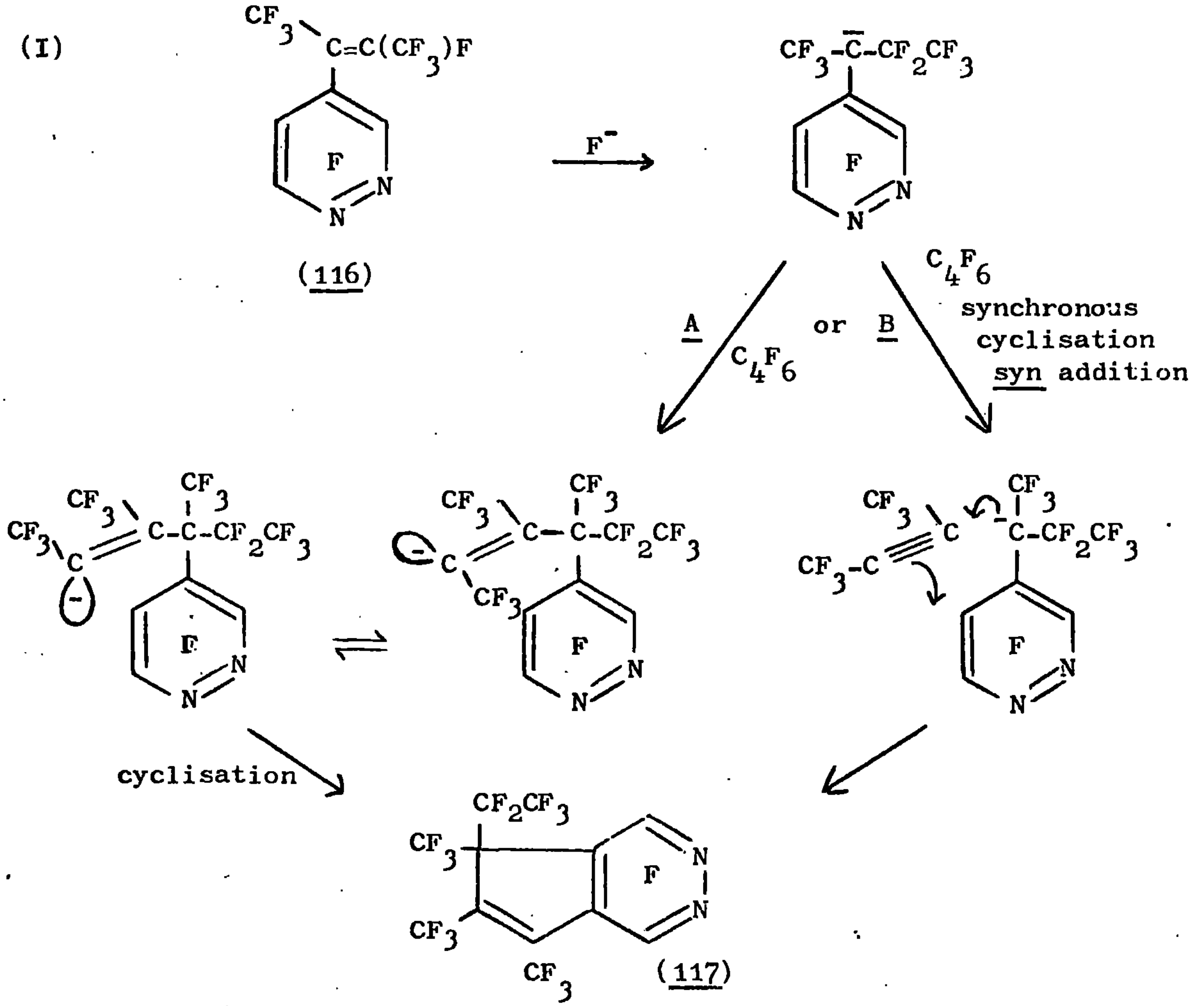
However, these results from the pyridine and pyrimidine systems clearly present a contrast to work carried out in these laboratories by S. Partington[112] who showed that the analogous pyridazine system (116) when reacted with hexafluorobut-2-yne and caesium fluoride at atmospheric pressure gave perfluoro-(1,2,3-trimethyl)-1-ethyl-5,6-diazaindene (117) in reasonable yield.[112]



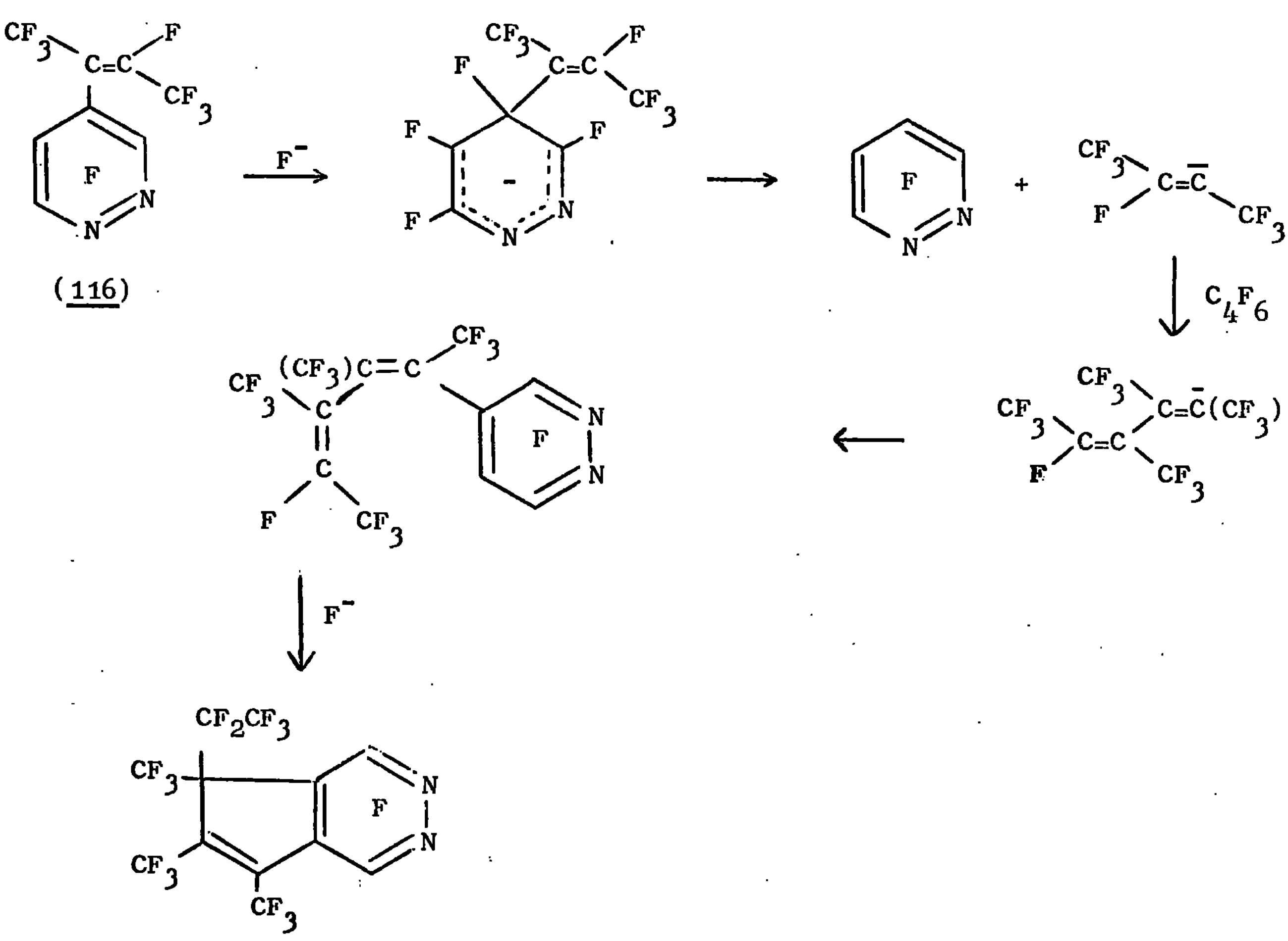
(116) (117); 50%

It can be seen that the pyridazine derivative (116) is unique when compared with the pyrimidine and pyridine derivatives (99), (100) and (102) in that it has a relatively reactive site towards nucleophilic attack which is ortho to the 2-butenyl substituent. Several mechanisms can be envisaged to explain the formation of the diazaindene derivative (117), the more plausible ones are as follows.

(I)



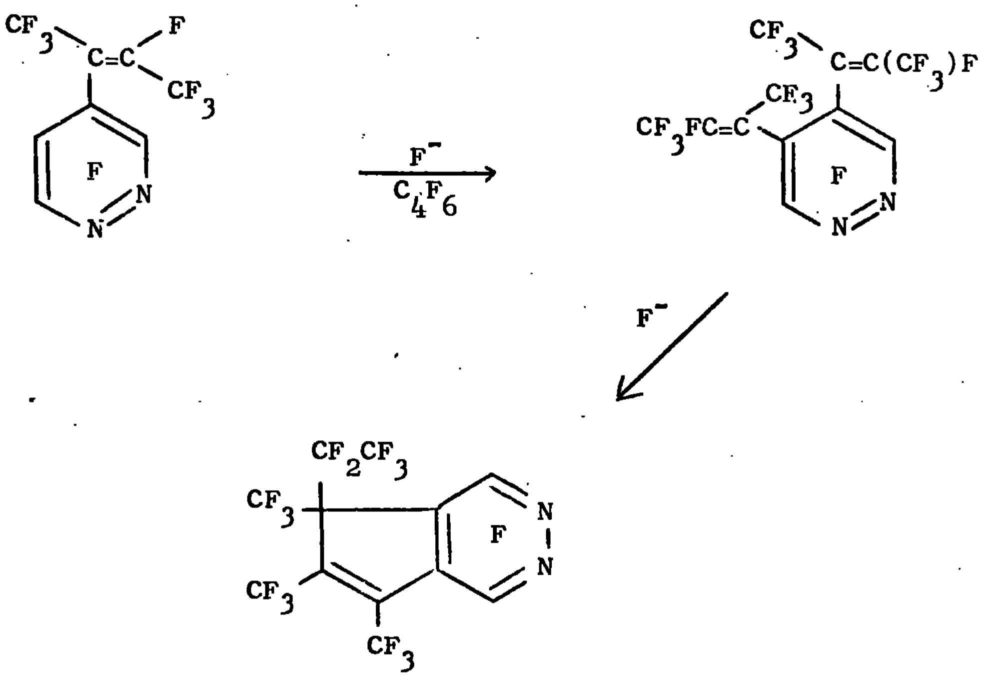
(II)



(116)

(117)

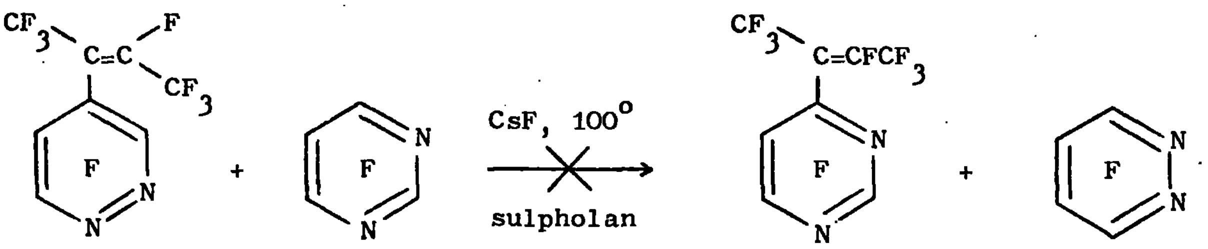
(III)



(117)

Reaction of tetrafluoropyrimidine with hexafluorobut-2-yne in the presence of fluoride ion at room temperature indicates that this type of compound may exist in solution mainly as an anion of the type (115) in the presence of fluoride ion thus deactivating the aromatic nucleus to further nucleophilic attack. From this evidence, and the fact that tetrafluoropyridazine is a much less reactive compound towards nucleophilic attack than is tetrafluoropyrimidine, mechanism (III) which involves a disubstituted pyridazine seems rather unlikely.

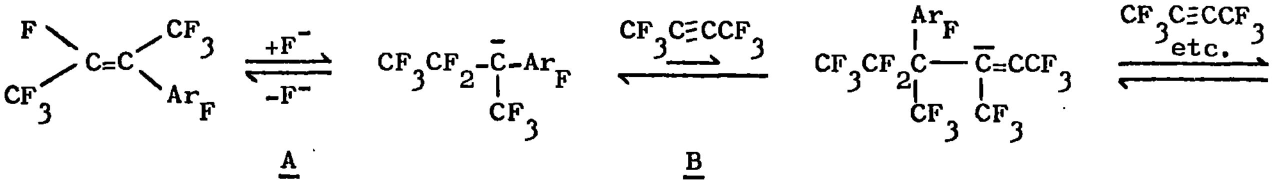
A second possibility, mechanism (II), which involves attack of the unsubstituted pyridazine by an alkadienyl anion has been shown to be unlikely. It has been shown that displacement of a butenyl anion from the 2-butenylpyridazine (116) does not occur in the presence of fluoride ion, by attempting to promote an intermolecular crossover of the anion. Thus when perfluoro-2-butenylpyridazine (116), tetrafluoropyrimidine and caesium fluoride were heated together at 100° for 6 hrs. in sulpholan only starting materials were recovered. If displacement of a butenyl anion had occurred from the pyridazine derivative (116) then substituted pyrimidine compounds (99 and 100) would be expected to be produced as it is known that the latter heterocycle is considerably more reactive towards nucleophiles than is the former.



(116)

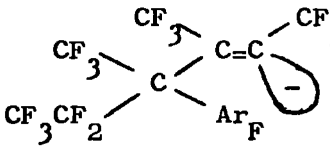
(99 and 100)

The third alternative, mechanism (I), appears to be the most suitable alternative which will account for all the facts available at the present time. The pyridazine system can be rationalised when the equilibria which must be set up during the reaction are considered. For example,

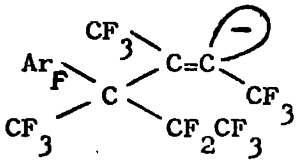


(118) (119)

The relative concentrations of the anions (118) and (119), i.e. the positions of equilibria A and B, can be estimated from consideration of the relative stabilities of the two carbanions. It is possible that equilibrium B lies well to the left, i.e. carbanion (118) is expected to be considerably more stable than carbanion (119). A relatively high concentration of (118) may therefore be present in the reaction mixture. However if the diazaindene (117) is produced by mechanism (I) then further reaction of anion (118) with hexafluorobut-2-yne must occur. This process can in principle take place in either of two ways, syn addition will give (120), whereas anti will produce (121).

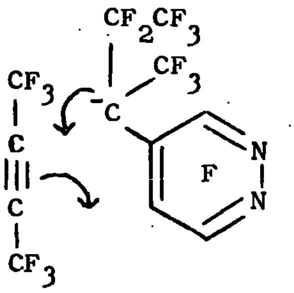


(120)



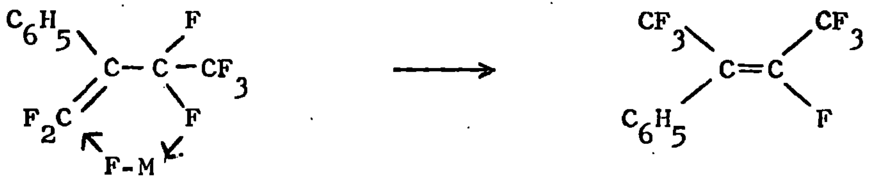
(121)

The cyclisation process, however, must be considerably more rapid than further condensation with the acetylene to produce polymeric material. It can be envisaged then that a rapid concerted cyclisation step which involves a syn addition to hexafluorobut-2-yne may take place to form the diazaindene (117) by attack at the 5-position of the pyridazine nucleus which is known to

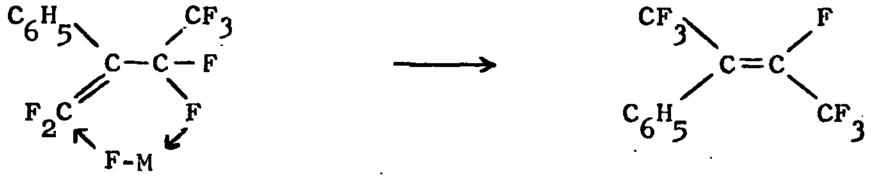


be reactive towards nucleophilic attack. If *anti* addition of the anion (118) to hexafluorobut-2-yne occurred then inversion of configuration would have to take place before the diazaindene could be produced as the trifluoromethyl groups in the product have a *cis* configuration. Polymerisation of the acetylene would then be expected to be more prevalent; a *syn* addition then seems to be the most suitable alternative which will account for the facts available at the present.

No *syn* additions of fluoride ion to acetylenes have been reported, and in the polyfluoroalkenylations discussed here the *cis* and *trans* olefinic products are in equilibrium under the conditions of the reaction. This eliminates any possibility of determining the stereochemistry of addition in these systems. However *syn* elimination of fluoride ion, which is brought about by interaction with the cationic metal ion has been proposed to account for the results of the rearrangement of 2-phenylheptafluoro-1-butene (122)[120] to *cis* and *trans*-2-phenylheptafluorobut-2-ene (123 and 124).

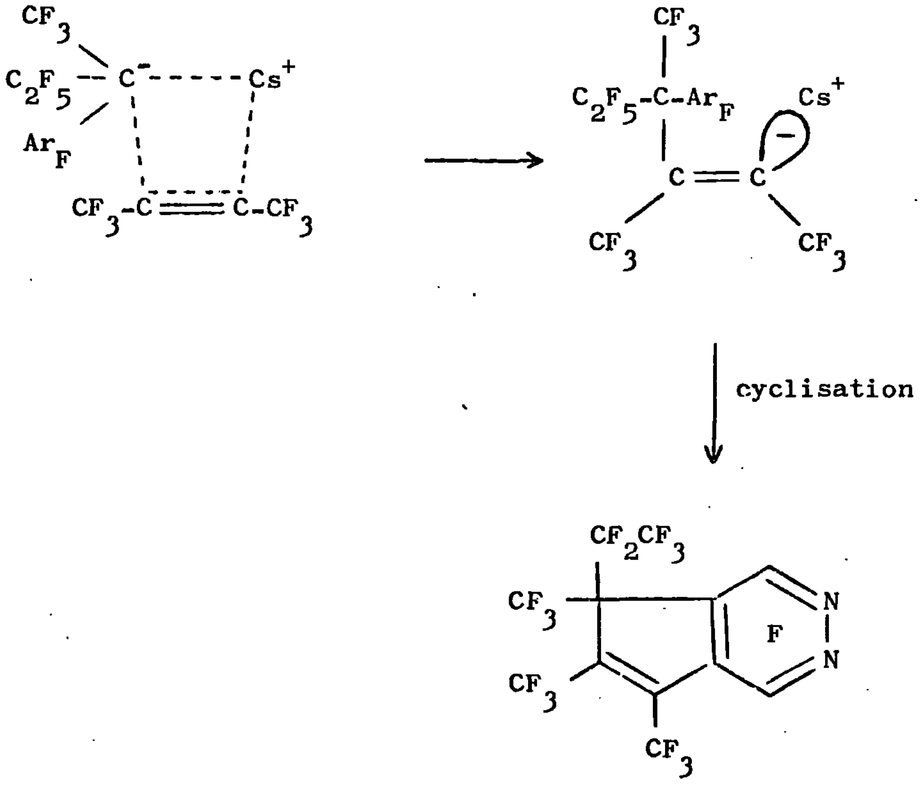


(122) (123)



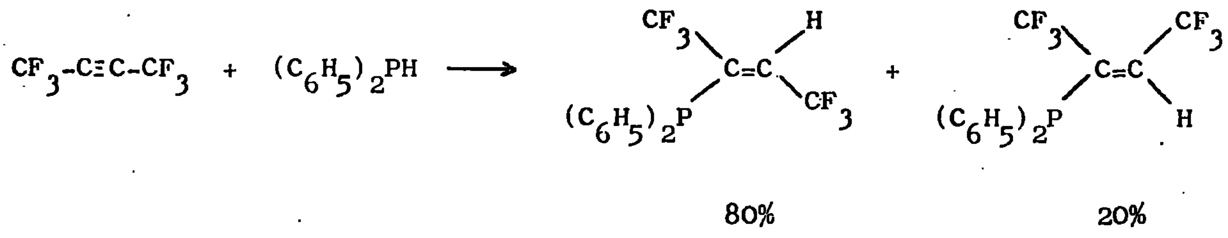
(122) (124)

It is not unreasonable then that in the case of hexafluorobut-2-yne a *syn* addition could occur through an intimate ion pair composed of the carbanion and the cationic metal atom, for example

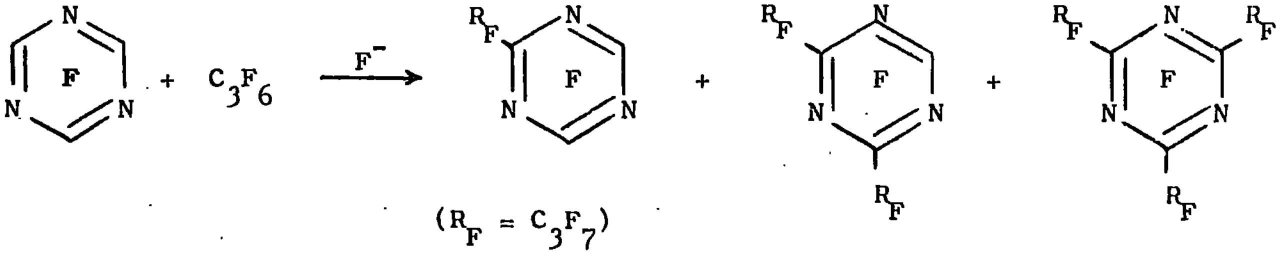


(117)

Syn additions to acetylenes however do appear in the literature and an example of this mode of reaction has been observed in the course of this research work. The syn reaction course is common with substrates containing a mobile hydrogen, i.e. phosphines and amines, which can migrate via an intramolecular proton shift[52] i.e.,

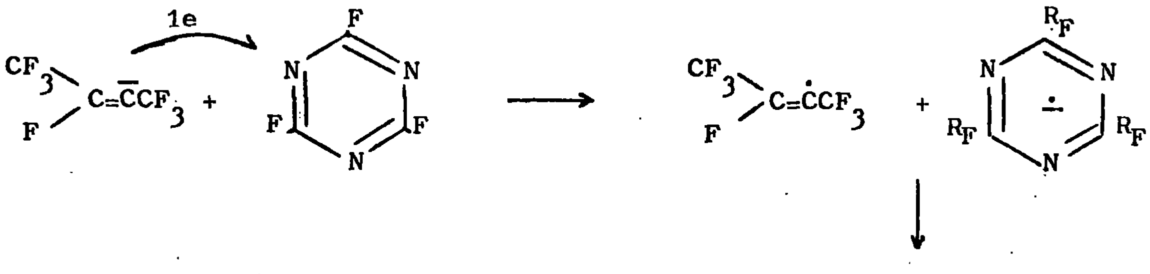


Kinetic studies to determine the susceptibility towards nucleophilic attack of the common perfluoroheterocycles have shown that cyanuric fluoride is by far the most reactive.[121] It would be expected therefore that this compound should readily produce the desired butenyl derivatives. Analogous polyfluoroalkylations carried out with a variety of perfluoro-olefins have produced mono-, di- and tri-substituted compounds. For example under autogeneous conditions in the absence of a solvent hexafluoropropene and caesium fluoride react with cyanuric fluoride (2,4,6-trifluoro-1,3,5-triazine) to give a mixture of mono-, bis- and tris-(heptafluoroisopropyl) derivatives.[122,123]



($R_F = C_3F_7$)

Similar results were obtained with fluoro-olefins (including perfluoroethylene, -propene and -butenes) and alkali metal fluorides in dipolar aprotic solvents at moderate temperatures and pressures.[124] However, in the reaction with hexafluorobut-2-yne no low molecular weight material was recovered. This may be an indication that with this highly reactive heterocycle a different reaction process takes place. The results can be best explained by postulating a ready one electron transfer from the butenyl anion to the triazine to produce a radical and an anion radical which then readily polymerise, e.g.



(R_F = F or C_4F_7)

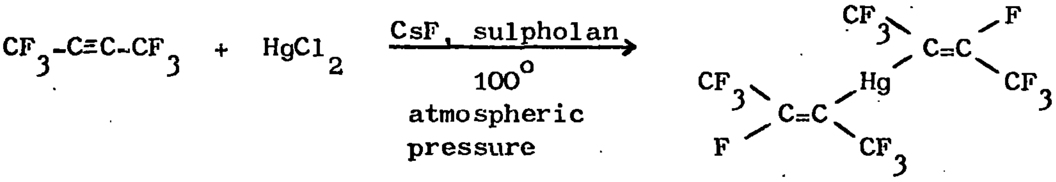
Tarry material

Consistent with such a process, we would expect the triazine to be the best electron acceptor of the heterocyclic systems which have been studied in these investigations.

IV.A.6 Fluoride Ion-Initiated Reaction of Hexafluorobut-2-yne with Mercuric Chloride ($HgCl_2$)

(a) Reaction conditions and products

Reaction of hexafluorobut-2-yne with freshly sublimed mercuric chloride and caesium fluoride at 100° in the usual atmospheric pressure apparatus was found to produce a highly volatile white crystalline solid which was isolated by sublimation at room temperature. The material was identified as perfluoro-trans-bis-(2-butenyl)mercury (125).



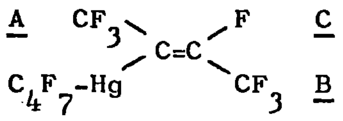
(125); 64%

A small amount of homo-polymer of the acetylene was isolated in this reaction.[112]

(b) Structure of the product

The perfluoro-organomercurial (125) after recrystallisation from carbon tetrachloride was found to have a satisfactory elemental analysis. Its mass spectrum was found to have a strong parent peak which showed the characteristic mercury isotope pattern. The detailed structure was determined by ^{19}F n.m.r. spectroscopy, (carried out on an ethereal solution) observed chemical shift values and relative intensities of the three components in the spectrum indicated that the compound contained a perfluoro-2-butenyl group. Resonances at 51·5 p.p.m. and 71·4 p.p.m. (from external $CFCl_3$) of relative intensity 3 were assigned to the two trifluoromethyl groups, similarly a resonance at 96·1 p.p.m., relative intensity 1, was attributed to the vinylic fluorine.

The trans configuration of the trifluoromethyl groups about the double bond was confirmed by comparison of the observed coupling constants with those found in cis- and trans-2-phenylheptafluorobut-2-ene (see Table 2, page 55).



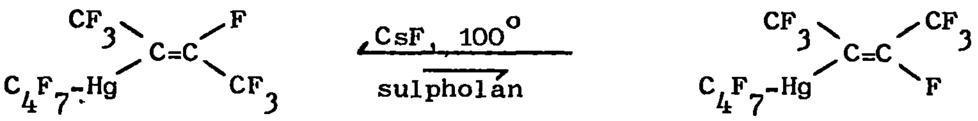
J_{AB} (Hz.)	J_{AC} (Hz.)	J_{BC} (Hz.)
1·5	18	9

Although the n.m.r. spectrum was carried out on an ethereal solution, no indication for the presence of the cis isomer was observed. Further confirmation of the trans structure came from the i.r. spectrum where a weak olefinic, C=C absorption at 5·9μ characteristic of a symmetrically substituted trans olefin was observed.[125]

An interesting feature of the ^{19}F n.m.r. spectrum is the presence of a large ^{199}Hg-F coupling of 136 Hz., which splits the low field trifluoromethyl group at 52·2 p.p.m. into a doublet of quartets of 16% relative intensity compared to the parent resonance.

(c) Discussion

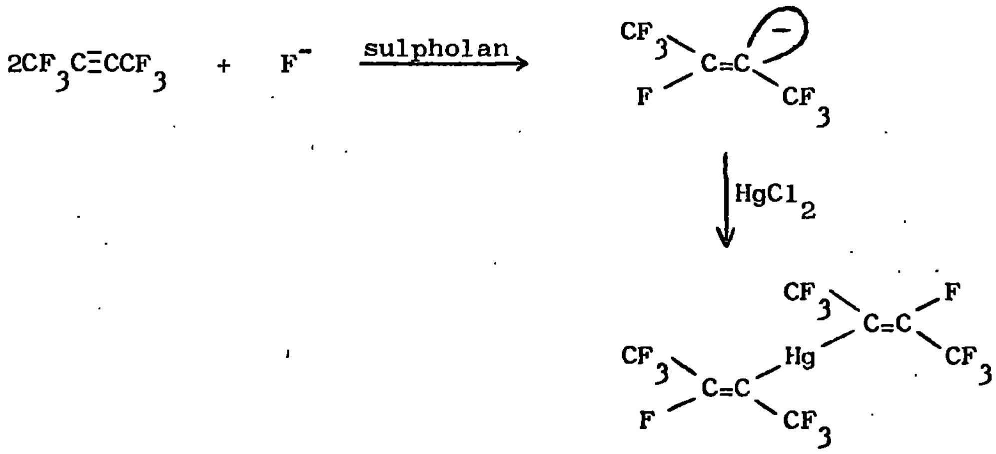
Unlike other polyfluoroalkenylations using hexafluorobut-2-yne where an equilibrium mixture of olefinic products has been isolated, in this case only the trans isomer is produced. This may be an indication that the trans isomer is considerably more thermodynamically stable than the cis analogue under the conditions of the reaction.



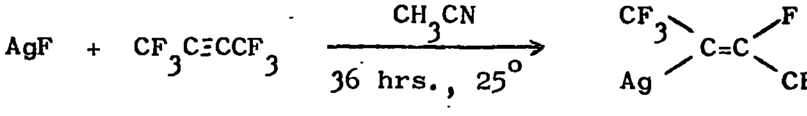
Alternatively, the result may indicate that addition of fluoride ion proceeds in an anti fashion to produce the trans mercurial (125) which is the kinetically controlled product. Deactivation towards further nucleophilic attack by the electropositive metal atom may then impose a kinetic barrier to equilibration.

Evidence to support the latter explanation comes from a qualitative experiment to determine the relative reactivity of the mercurial towards nucleophilic substitution by methoxide. The rate of substitution was compared to that of trans-2H-heptafluorobut-2-ene and the mercurial (125) was found to be less reactive. Relative rate studies carried out on cis- and trans-2-halo-heptafluorobut-2-enes have shown them to be considerably more reactive than the 2H-analogue (V.C.9).

It seems reasonable to propose then that formation of the trans mercurial (125) by an anti addition of fluoride ion is the kinetically preferred route. Equilibration of the trans compound promoted by fluoride ion does not occur due to deactivation by the presence of the metal atom (cf. the 2-chloro and 2-bromo-heptafluorobut-2-enes).



Preparation of the analogous silver derivative (51) has been reported and similarly only the trans isomer was observed.[67]

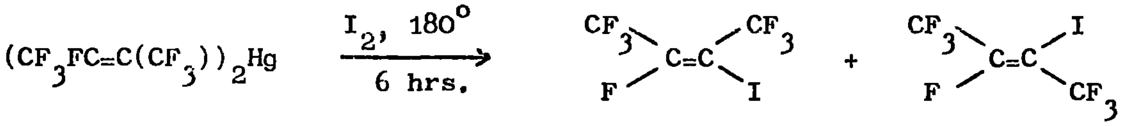


(51)

IV.A.7.a Cleavage of Perfluoro-trans-bis-2-butenylmercury with Iodine

(i) Reaction conditions and products

Perfluoro-trans-bis-2-butenylmercury (125) and iodine were heated together at 180° in a sealed evacuated Carius tube. A volatile liquid was transferred from the tube and was identified by i.r. and n.m.r. spectroscopy as a mixture of cis- and trans-2-iodo-heptafluorobut-2-ene (126) and (127) which had been formed in good yield (92%).

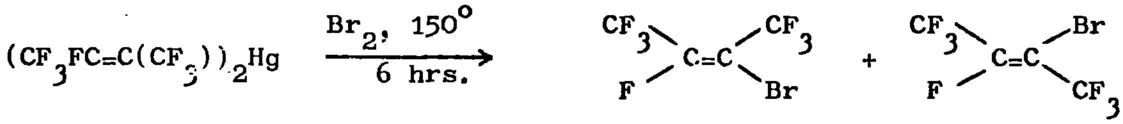


(125) (126); 19% (127); 72%

IV.A.7.b Cleavage of Perfluoro-trans-bis-2-butenylmercury with Bromine

(i) Reaction conditions and products

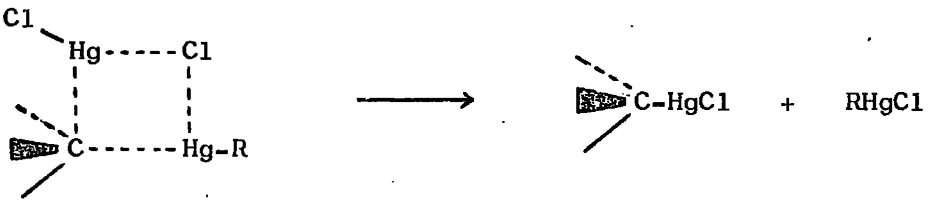
Perfluoro-trans-bis-2-butenylmercury (125) and bromine were heated together at 150° in a sealed evacuated Carius tube. A mixture of cis- and trans-2-bromo-heptafluorobut-2-ene (128) and (129) was isolated from the reaction in 90% yield. The products were identified by comparison of their i.r. and n.m.r. spectra with those of authentic samples prepared from trans-2H-heptafluorobut-2-ene.[126]

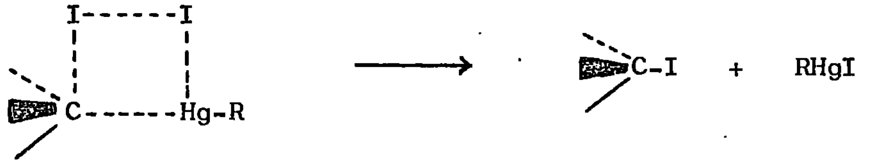


(125) (128); 45% (129); 45%

IV.A.7.c Discussion of Cleavage Reactions

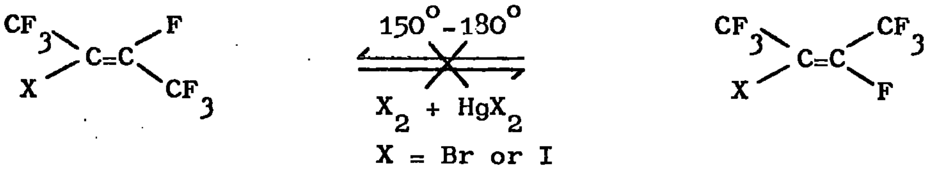
It has been shown by several workers that electrophilic substitution of saturated organomercurials generally proceeds with retention of configuration. Reactions with iodine and mercuric chloride are proposed to occur through cyclic transition states (S_Ei) which are expected to give retention of configuration.[127-129]



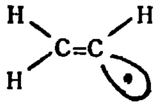
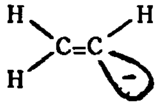


If the cleavage reactions of perfluoro-*trans*-bis-2-butenylmercury (125) proceed via cyclic mechanisms then it is to be expected that only the *trans*-2-halo-2-butenes will be produced in the reaction, however, it has been shown that this is not the case.

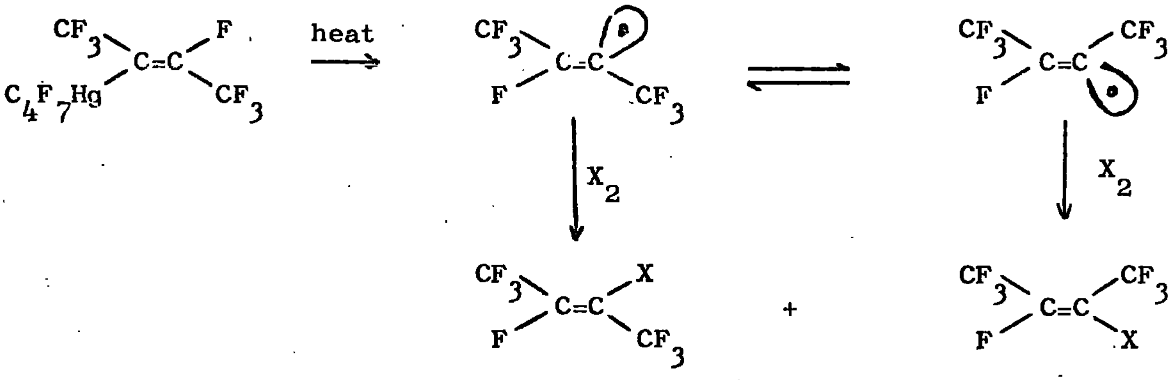
Attempts to equilibrate the *trans* iodo (127) and bromo (129) butenes with the *cis* analogues (126) and (128) under the conditions of the reactions proved unsuccessful. Thus when pure *cis* (128) and pure *trans* (129) bromo-butenes were heated at 150° in the presence of bromine and mercuric bromide no change in the isomer composition was found to occur. Similarly, heating a 68:32, *cis*:*trans* mixture of the iodo-butenes (126) and (127) in the presence of iodine and mercuric iodide at 180° produced no change in the isomer composition.



However, when the *trans* organomercurial (125) was heated in the presence of sulpholan a very small amount of 2H-heptafluorobut-2-ene was produced, however insufficient material was isolated to enable the isomeric composition to be determined. This result may indicate that these cleavage reactions proceed partially by a mechanism involving a butenyl radical. Theoretical calculations have shown that the barriers to inversion of vinyl radicals are relatively low compared to those for analogous anions.[130]

	Calculated barrier kcal.mol^{-1}
	7·97
	38·9

Thus if the trans butenyl radical is formed inversion may be expected to take place readily to the cis analogue and the stereochemical results may be interpreted as being due to a contribution from this mechanism which may occur alongside the normal S_Ei reaction, i.e.



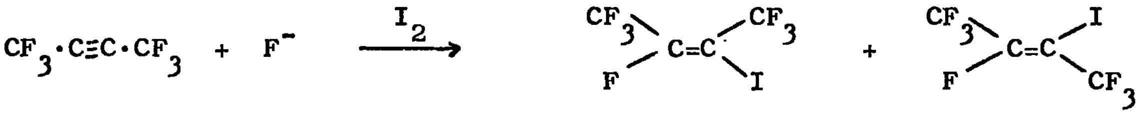
X = Br or I

IV.A.8 Reaction of Hexafluorobut-2-yne with Fluoride Ion in the Presence of Halogens

(a) In the presence of iodine

(i) Reaction conditions and products

When hexafluorobut-2-yne was slowly introduced from a flexible reservoir into a rapidly stirred suspension of caesium fluoride in sulpholan containing excess iodine at 20° in the apparatus shown in Figure 1, a 68:32, cis:trans mixture of the 2-iodo-heptafluorobut-2-enes (126) and (127) was obtained.



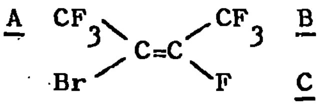
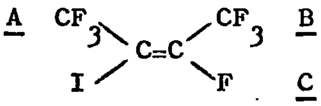
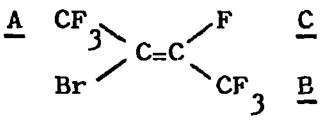
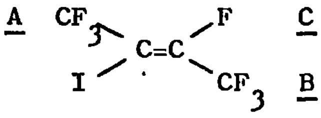
(126); 54%   (127); 25%

(ii) Structure of products

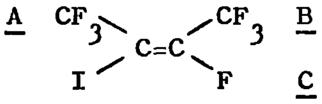
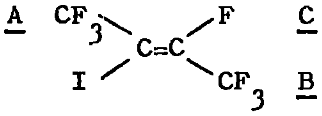
Analytical scale v.p.c. (di-n-decyl-phthalate, 70°) of the mixture of the iodobutenes (126) and (127) showed that the two compounds had very similar retention times and separation of the isomers by this method proved impossible. Characterisation was carried out on the mixture which was found to have satisfactory elemental analysis and an appropriate parent peak in the mass spectrum. ^{19}F n.m.r. spectroscopy was used to identify the perfluoro-2-butenyl grouping in these compounds. The chemical shifts of the trifluoromethyl groups and vinylic fluorines were in agreement with values obtained for similar heptafluorobut-2-enes (Table 4).

Table 4

Chemical Shifts in Heptafluoro-2-butene Compounds

Compound	Chemical Shift		
	A	B	C
	59·8	66·2	95·6
	57·5	67·4	78·5
	62·6	68·1	102·4
	60·3	68·5	87·9

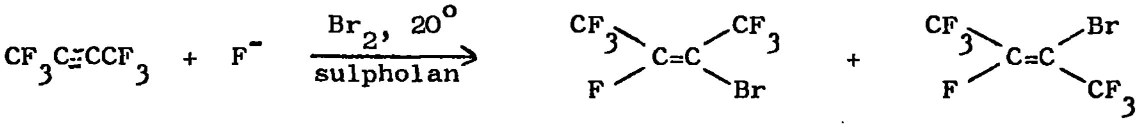
Detailed study of the coupling constants within the n.m.r. spectrum was used to assign the resonances in the individual isomers. Characteristic trifluoromethyl group couplings of 12·0 Hz., assigned to the cis isomer, and 1·5 Hz., assigned to the trans analogue, were observed.

	J_{AB} (Hz.)	J_{BC} (Hz.)	J_{AC} (Hz.)
	12·0	~ 8	9·0
	1·5	4·0	24·5

(b) In the presence of bromine

(i) Reaction conditions and products

When hexafluorobut-2-yne was slowly introduced from a flexible reservoir into a rapidly stirred suspension of caesium fluoride containing bromine in the apparatus shown in Figure 1 a cis-trans mixture of 2-bromo-heptafluorobut-2-enes (128) and (129) was produced in 73% yield.



(128); 40%   (129); 33%

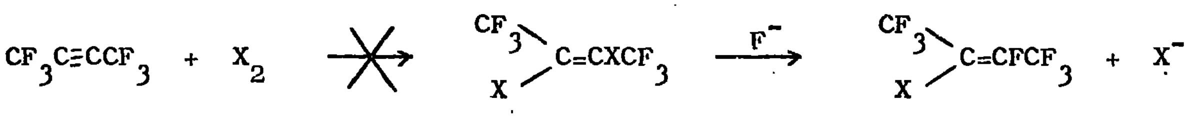
(ii) Structure of products

Analytical scale v.p.c. (di-n-decyl-phthalate, 45°) of the material isolated showed the presence of only two components which had very similar retention times. The mixture of the two bromobutenes (128) and (129) was characterised by comparison of its i.r. and ^{19}F n.m.r. spectra with those of authentic samples of cis- and trans-2-bromo-heptafluorobut-2-enes prepared by dehydrobromination of 2H-2,3-dibromo-heptafluorobutane.[126]

(c) Discussion

Attempts to react hexafluorobut-2-yne and the halogen (Br_2 or I_2) together in sulpholan without fluoride ion in an atmospheric pressure system proved unsuccessful. Thus it was shown that the mechanism of formation of the 2-halo-heptafluorobutenes (126), (127), (128) and (129) does not involve addition of halogen to produce 2,3-dihalo-olefins (130) which are then substituted by fluoride ion.

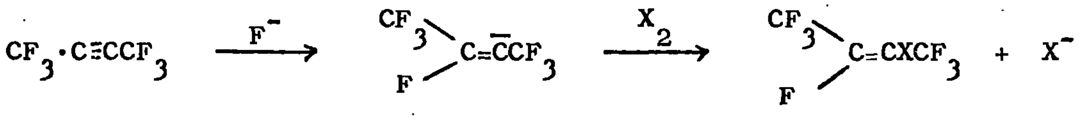
For example:



(130)

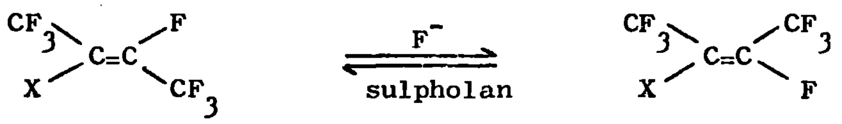
X = Br, I

Therefore the reactions must be assumed to proceed by an ionic addition mechanism in which the intermediate carbanion (131) is trapped by the halogen, i.e.



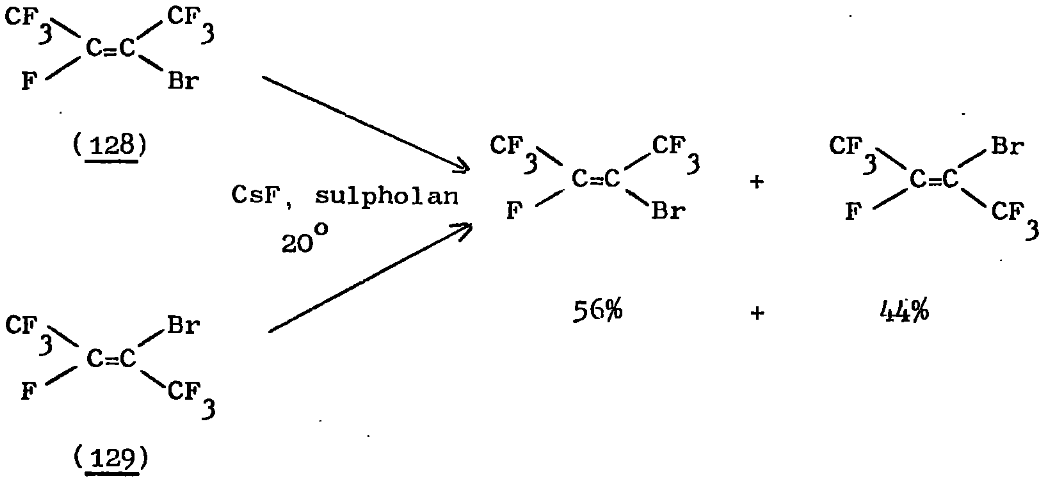
(131)

The stereochemistry of addition of fluoride ion cannot be ascertained from these reactions as it has been shown that under the conditions of the reaction the *cis* and *trans* isomers are in equilibrium.



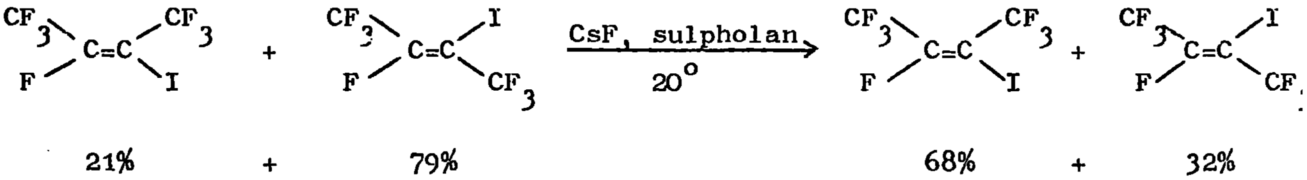
X = Br, I

Thus when pure *cis* and *trans* isomers of the 2-bromobutene (128) and (129) were stirred with caesium fluoride in sulpholan at room temperature the equilibrium mixture was produced from both isomers.

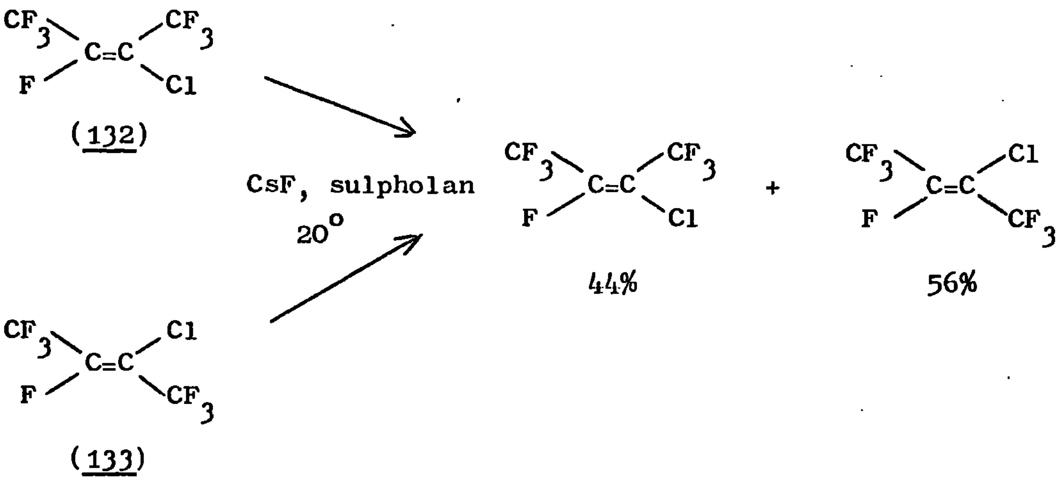

(128)

(129)

Similarly a 21:79, cis:trans mixture of the 2-iodobutenes (126) and (127) when stirred with caesium fluoride in sulpholan at 20° produced the equilibrium mixture containing 68% cis and 32% trans.

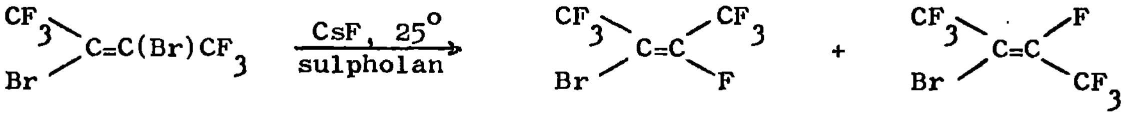


Although practical problems prohibited an analogous fluoride ion-initiated addition reaction with chlorine it was shown that in the presence of fluoride ion the cis- and trans-2-chloro-heptafluorobut-2-enes (132) and (133) were at equilibrium. Thus when the pure geometrical isomers (132) and (133) were stirred with caesium fluoride in sulpholan an equilibrium mixture containing 44% cis and 56% trans was produced.


(132)

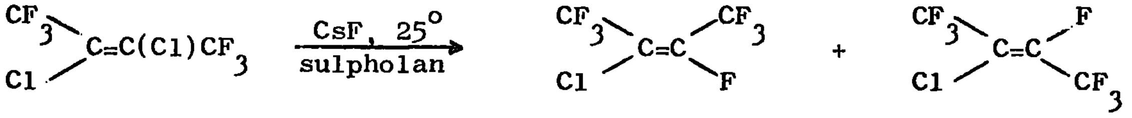
(133)

It was shown previously that these additions to hexafluorobut-2-yne to produce polyfluorobut-2-enes do not proceed by formation of a 2,3-dihalobutene (130), however, it has been found that the 2,3-dibromo- and 2,3-dichlorobutenes (134) and (135) readily undergo substitution by fluoride ion to give equilibrium mixtures of the respective 2-halo-heptafluorobut-2-enes.



(134)   56%   +   44%

cis and trans isomers



(135)   44%   +   56%

cis and trans isomers

Inspection of the ratio of cis:trans isomers present at equilibrium (Table 5) for the series of 2-halo-but-2-enes (halogen = Cl, Br, I) shows a steady increase in the amount of cis olefin present in the order,

$$Cl < Br < I$$

Table 5

Equilibrium Mixtures of Cis- and Trans-2-halo-2-butenes at 20° in Sulpholan

Olefin	% Cis	% Trans
Chloro	44	56
Bromo	56	44
Iodo	68	32

This of course is in the same order as the increase in covalent radii[131] of the three halogens and the results can be interpreted as being due to steric effects.

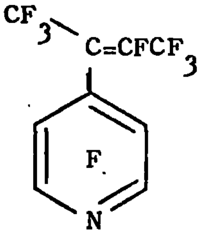
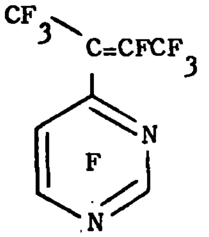
Covalent Radii (Å), Cl, 0·99; Br, 1·14; I, 1·33.

In 2-chloro-heptafluorobut-2-ene steric interactions between the trifluoromethyl groups in the cis olefin are presumably greater than those between trifluoromethyl and chlorine in the trans isomer rendering the latter more stable. However, in the iodo analogue steric interaction between the trifluoromethyl and halogen becomes predominant rendering the cis isomer more stable.

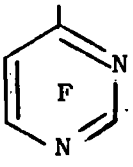
Comparison of these equilibria with those set up with the 2-butenylpyridines and -pyrimidines (102), (105), (99) and (100) in the presence of fluoride ion (Table 6) show that these two perfluoroheterocyclic groups have a smaller steric requirement than the halogens chlorine, bromine or iodine.

Table 6

Equilibrium Mixtures of Cis- and Trans-perfluoro-2-butenylpyridines and -pyrimidines

	% Cis	% Trans
	17	83
	10	90

Therefore, for the series of 2-butenes the proportion of cis isomer present at equilibrium increases in the order

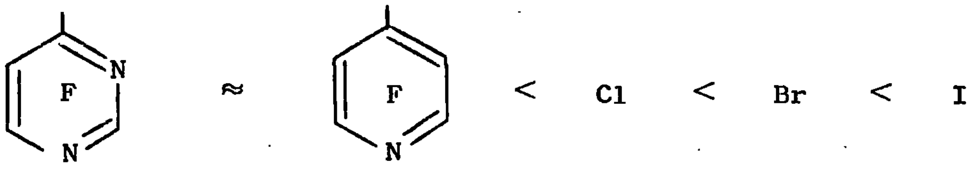


≈


< Cl < Br < I

IV.A.9 General Conclusions

The stereochemistry of fluoride ion-initiated reactions to hexafluorobut-2-yne cannot be determined from the results of several of the processes studied here. This is due to a ready *cis-trans* equilibration of the vinyl products which is promoted by fluoride ion. Comparison of the *cis:trans* equilibrium mixture for several polyfluoro-2-butenes has enabled a rough order of steric requirement to be determined which increases along the series



as would be expected.

Fluoride ion-initiated reaction of hexafluorobut-2-yne in the presence of mercuric chloride produces the perfluoro-bis-(2-butenyl)mercury derivative which has a *trans* configuration. This compound is thought to be relatively unreactive towards nucleophiles which indicates that *anti* addition of fluoride ion may be the kinetically controlled route. This organometallic compound is readily cleaved with bromine and iodine at elevated temperatures to produce the respective 2-halo-2-butenes, the reaction is thought to proceed partially by a free radical process brought about by homolytic fission of the C-Hg bond.

IV.B. Other Nucleophilic Additions to Hexafluorobut-2-yne

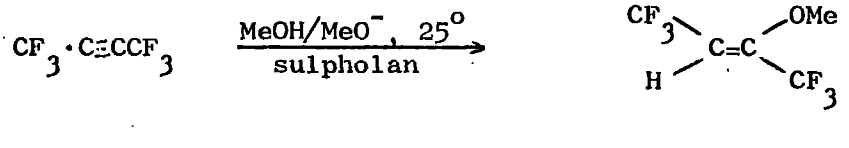
Introduction

As explained previously (II.B.1) nucleophilic additions to hydrocarbon acetylenes is considerably more facile than addition to the analogous olefins. Nucleophilic addition to hexafluorobut-2-yne proceeds very readily due to the reduced electron density within the π system caused by inductive electron withdrawal of the trifluoromethyl groups.

IV.B.1 Base-catalysed Addition of Methanol

(a) Reaction conditions and products

When hexafluorobut-2-yne was introduced from a flexible reservoir into a rapidly stirred solution of sulpholan containing methanol (with a small amount of sodium methoxide) in the apparatus shown in Figure 1, trans-2H-3-methoxy-hexafluorobut-2-ene (136) was produced.

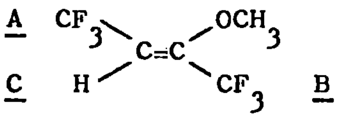


(136); 83%

A similar reaction carried out using methanol as solvent once again produced the trans butene (136).

(b) Structure of product

The product was characterised in the usual way, elemental analysis of the material proved difficult due to the high volatility of the compound, however, satisfactory results were obtained. The mass spectrum showed a parent peak, characteristic of an unsaturated fluorocarbon. ^{19}F n.m.r. spectroscopy was used to determine the configuration of the trifluoromethyl groups about the double bond. Presence of a 1·5 Hz. CF_3-CF_3 coupling, characteristic of trans trifluoromethyl groups, confirmed the structure of the compound.

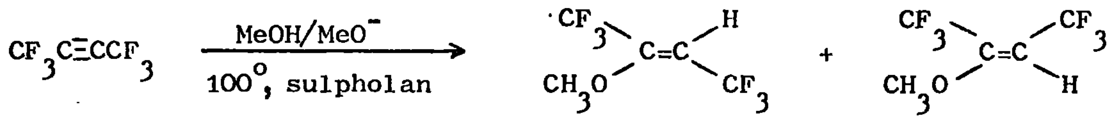


J_{AB} (Hz.)	J_{BC} (Hz.)	J_{AC}(Hz)
1·5	-	~ 7

(c) Discussion

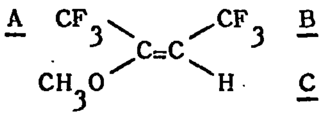
Numerous additions of alcohols (and phenols) to acetylenes have been reported, alkoxides[41] or t-amines[42] are usually used as basic catalysts. In this case a trace of sodium methoxide solution was added to the methanol.

Reaction in both methanol and sulpholan at room temperature produced only the trans isomer (136). However, reaction at 100° using sulpholan as the solvent produced a cis-trans mixture in 75% yield containing 11% of the former isomer (137).



(136); 67% (137); 8%

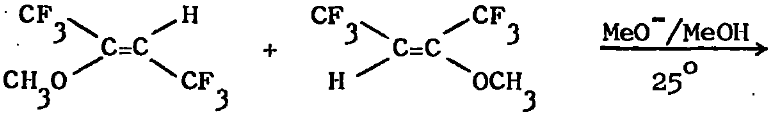
Coupling Constants (Hz.) in Cis-2H-3-methoxy-hexafluorobut-2-ene



J_{AB} (Hz.)	J_{BC} (Hz.)	J_{AC} (Hz.)
11	≈ 8	-

Attempts to produce the cis derivative (137) in an uncatalysed reaction at 100° proved unsuccessful, the process being too slow.

No change occurred in the cis-trans isomer ratio obtained from the 100° reaction after 17 hrs. in the presence of sodium methoxide solution.



89% 11%

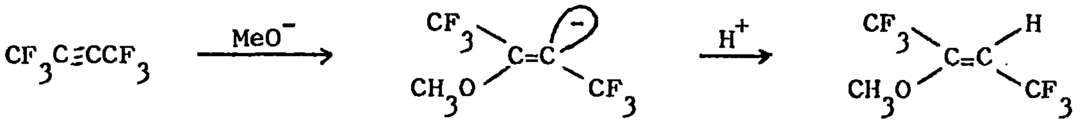
No change in isomer ratio

Similarly no equilibration of the trans isomer (136) occurred under the influence of sodium methoxide in sulphol an at 100°.

(136)

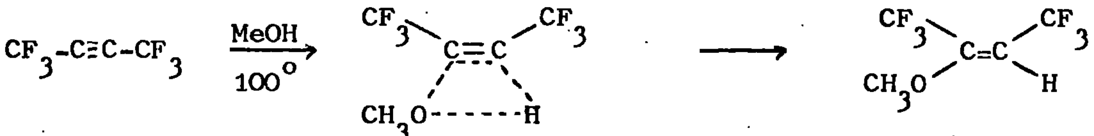
No equilibration

Therefore the results of the addition of methanol to hexafluorobut-2-yne may be interpreted as involving two distinct routes. Base catalysed addition, a rapid process, is thought to proceed in an *anti* manner to produce the *trans* olefin (136).



(136)

However, at higher temperatures a slow uncatalysed addition of methanol may occur via a *syn* route to produce the *cis* olefin (137) in what can be visualised as being a synchronous reaction.



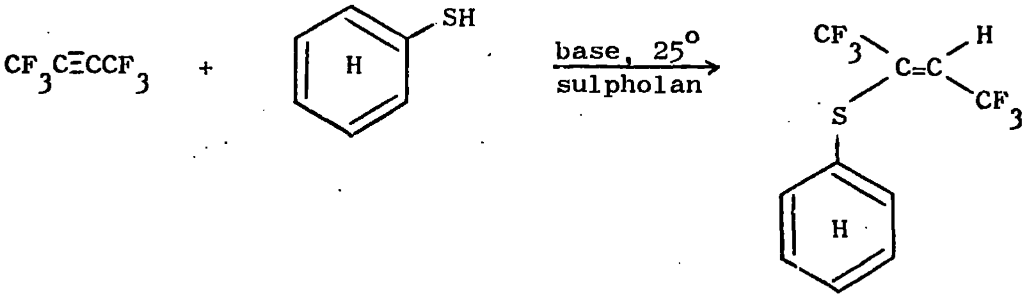
(137)

The fact that this compound was isolated from the base catalysed reaction at 100° whereas no perceptible reaction was observed at 100° in the absence of a catalyst may be due to the presence of a large proportion of the *trans* isomer (136) being present which acts as a carrier for the *cis* analogue (137). Similar high temperature *syn* additions of alcohols have been reported.[24]

IV.B.2 Base-catalysed Addition of Thiophenol

(a) Reaction conditions and products

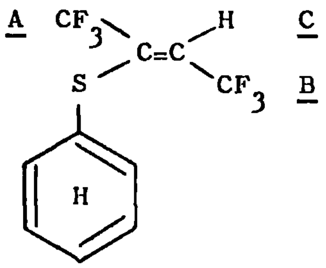
When hexafluorobut-2-yne was introduced from a flexible reservoir into a rapidly stirred solution of thiophenol in sulpholan containing a catalytic amount of sodium methoxide in the apparatus shown in Figure 1, *trans*-2H-3-thiophenoxy-hexafluorobut-2-ene (138) was produced.



(138); 93%

(b) Structure of product

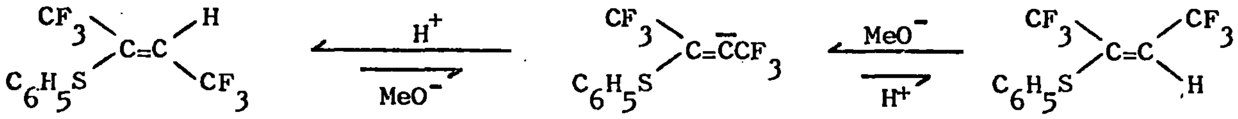
The product of the reaction was isolated from the solvent by vacuum transference at 80°. Analytical scale v.p.c. showed the presence of a single component (S.G.R., 250°) which was found to have satisfactory elemental analysis; similarly the mass spectrum of the material was found to show a parent peak. The configuration of the olefinic side chain was determined by ^{19}F n.m.r. spectroscopy. The presence of a 1·5 Hz. CF_3-CF_3 coupling, characteristic of trans trifluoromethyl groups in a but-2-ene system, indicated that the compound had a trans configuration. Confirmation of the stereochemistry of the compound was obtained from the i.r. spectrum where a weak absorption at 6·1μ characteristic of a trans substituted olefin was observed.[125]



J_{AB} (Hz.)	J_{BC} (Hz.)	J_{AC} (Hz.)
1·5	7·0	-

(c) Discussion

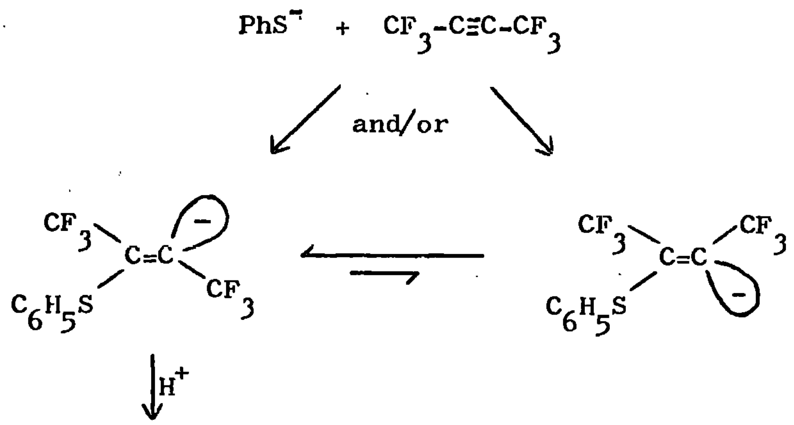
It was found that no change in the isomeric composition occurred when the trans olefin (138) was stirred in sulpholan with a trace of sodium methoxide for 17 hrs. Thus if the carbanion (139) is formed under these conditions it must be assumed that the trans isomer (138) is considerably more thermodynamically stable than the cis analogue.



(138) (139)

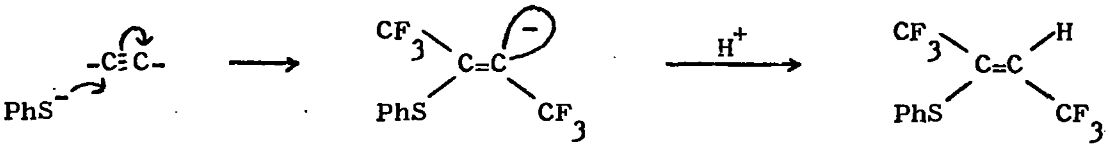
(Attempts to promote hydrogen-deuterium exchange could prove conclusively if the carbanion (<u>139</u>) is produced in the presence of methoxide ion).

Similarly, thermodynamic control of the reaction may be operative through a 'primary' equilibrium of the carbanion formed by attack of the nucleophile on the acetylene, i.e.



<u>trans</u> olefin (<u>138</u>) only

However, the results may be interpreted as being due to kinetic control in which an <u>anti</u> addition of the nucleophile may occur to produce an anion with a <u>trans</u> configuration. The carbanion so formed could be expected to have considerable configurational stability as theoretical calculations have shown that vinyl anions have high barriers to inversion and indeed it has been suggested that rotation about the double bond might be a competitive process in isomerisations of these species.[130] Thus the mechanism may be visualised as



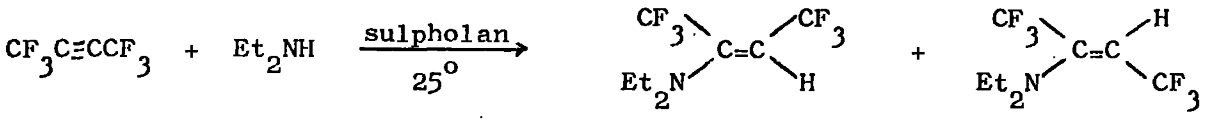
(<u>138</u>)

IV.B.3 <u>Addition of Diethylamine</u>

(a) <u>Reaction conditions and products</u>

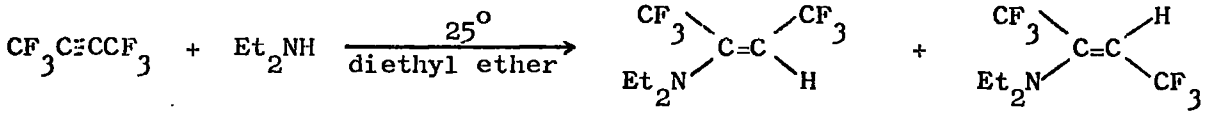
When hexafluorobut-2-yne was introduced into a rapidly stirred solution of diethylamine in sulpholan contained in the apparatus shown in

Figure 1 at 10:90, a cis:trans mixture of 2H-3-N,B-diethylamino-hexafluorobut-2-enes (140) and (141) was produced.



(140); 8% (141); 67%

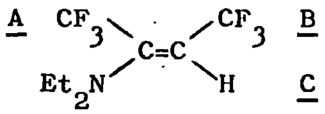
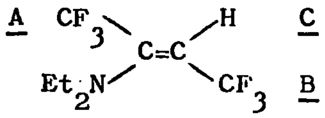
A similar reaction carried out with the acetylene and amine but using diethyl ether as the solvent produced a 76:24, cis:trans mixture.



(140); 61% (141); 19%

(b) Structure of products

The products from the reaction carried out in sulpholan were isolated by vacuum transference; the material had satisfactory elemental analysis and showed a parent peak at $^m/e$ 235 in the mass spectrum. ^{19}F n.m.r. spectroscopy clearly showed the presence of both cis and trans isomers, the observed coupling constants were used to assign the individual resonances in the two isomers.

	J_{AB} (Hz.)	J_{BC} (Hz.)	J_{AC} (Hz.)
	12·5	8·5	-
	1·5	8·0	-

(c) Discussion

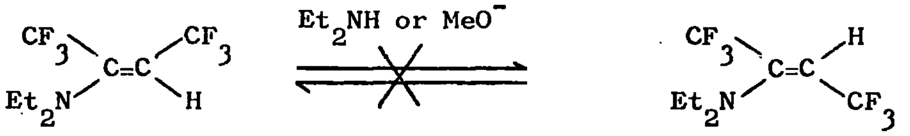
Dependence of the stereochemical results on the solvent used in the reaction has been observed in other additions of amines to acetylenes. Similar dependence on mixing processes, nature of the amine and acetylene has also been noted.[52]

It has been shown that under the conditions of the reactions carried out here, equilibration of the products does not occur. For example,

Products from reaction in ether 76% cis, 24% trans $\xrightarrow[\text{Et}_2\text{NH}]{\text{sulpholan}}$ No change in isomer ratio

Products from reaction in sulpholan 10% cis, 90% trans $\xrightarrow[\text{Et}_2\text{NH}]{\text{ether}}$ No change in isomer ratio

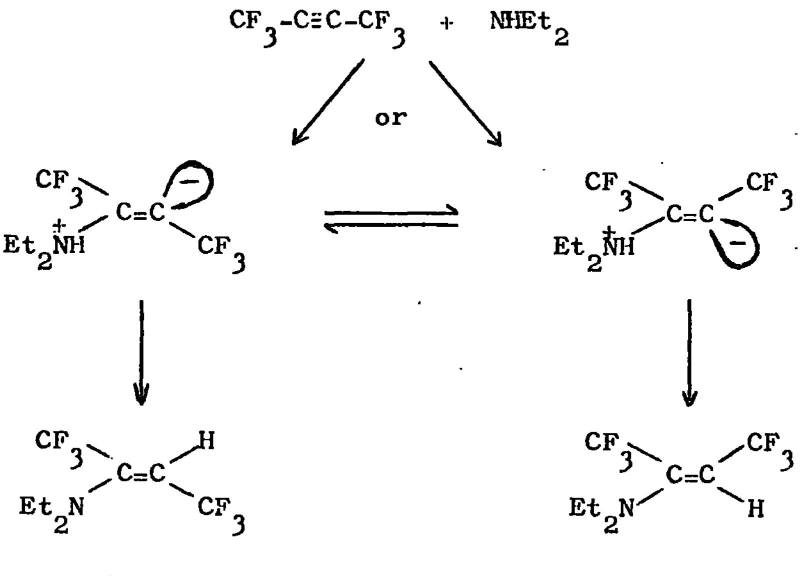
Similarly no change in the isomer ratios was observed under the influence of the more basic sodium methoxide in the two solvents. This rules out the possibility that the observed isomer compositions produced in the two solvents are formed by an equilibrium which is set up between the cis and trans olefins (140) and (141) under the basic conditions, the position of which is critically dependent on the solvent.



(140)

(141)

However, the possibility that a 'primary' equilibration of the carbanion which occurs before the initial protonation to produce the cis and trans isomers cannot be ruled out.


(<u>141</u>) (<u>140</u>)

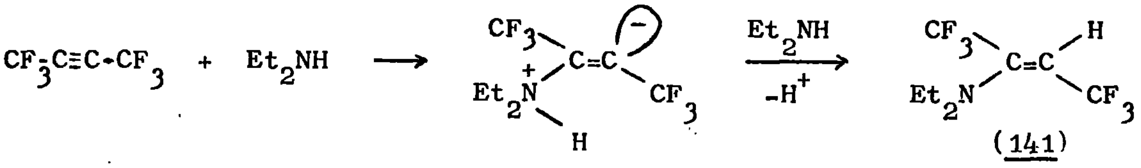
Attempts to promote hydrogen-isotope exchange on these compounds would give more insight into the mechanism of formation of these <u>cis:trans</u> mixtures.

As an alternative to this possible thermodynamic control of the reaction, the products may be formed under the influence of kinetic control, in which the competition between <u>syn</u> addition to produce a <u>cis</u> derivative (<u>140</u>) and <u>anti</u> to produce a <u>trans</u> olefin (<u>141</u>) is critically dependent on the solvent. If kinetic control is responsible for the results then a rationalisation can be found when the dielectric constants of the two solvent media, sulpholan and diethyl ether, are considered (at 20^{o}).

Sulpholan	=	44	Debye
Diethyl ether	=	4·3	Debye

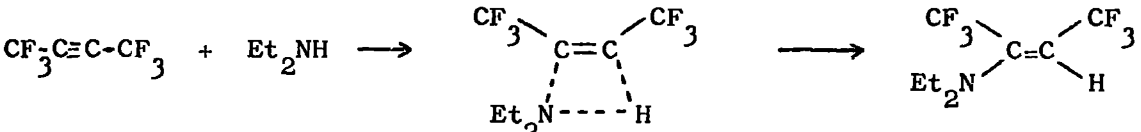
Although the dielectric constant of a medium is not the only criteria which must be applied when trying to explain the solvating properties of solvents, qualitative correlations between dielectric constant and 'solvating power' are observed. An explanation for the variation in isomer ratio between reactions carried out in ether and sulpholan can be made when the abilities of the two solvents to stabilise a carbanion are considered. From the dielectric constant values, sulpholan, a dipolar aprotic solvent is expected to stabilise a carbanion to a greater extent than diethyl ether. In sulpholan then a ready *anti* addition can presumably take place to yield a carbanion which is highly stabilised by the solvent. Intermolecular proton transfer may then take place to produce predominantly the *trans* olefin (141). In ether however, a discrete carbanion is much less likely to be formed and it can be envisaged that a more synchronous process involving a *syn* addition and an intramolecular proton transfer is the more favourable process. The predominant processes may be represented as,

(i) in sulpholan



(141)

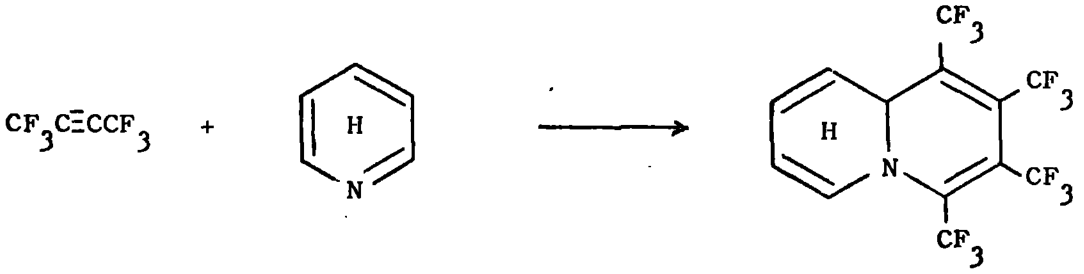
(i) in ether



(140)

IV.B.4 Reaction with Heterocyclic Compounds

Diels and Alder[60] showed that aromatic amines i.e. pyridine, reacted smoothly with dimethylacetylene dicarboxylate to produce 1:2 adducts. Thus it could have been expected that hexafluorobut-2-yne would react to give analogous products, i.e. (142). However, even though several solvent systems



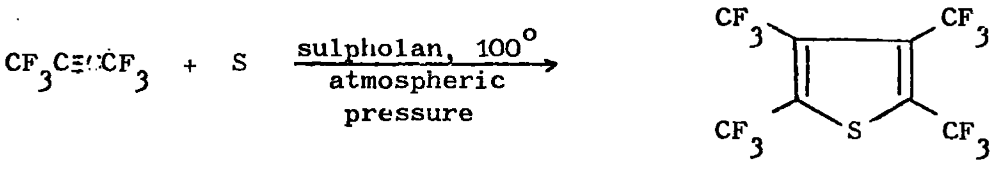
(142)

and heterocycles of different basicity combined with different temperatures have been used only high molecular weight tarry materials have been isolated. Thus if the initial product (142) is formed it must be assumed that further nucleophilic attack at the olefinic carbon atoms attached to the trifluoromethyl groups occurs which leads eventually to high molecular weight material.

IV.B.5 Reaction of Hexafluorobut-2-yne with Sulphur

(a) Reaction conditions and products

When hexafluorobut-2-yne was slowly introduced into a rapidly stirred suspension of sulphur in sulpholan contained in the apparatus shown in Figure 1, tetrakis-trifluoromethylthiophene (143) was produced in good yield.



(143); 68%

The initial reaction was carried out at 110° in the presence of fluoride ion, however a later reaction at the same temperature in the absence of an inorganic fluoride produced the thiophene derivative in similar yield.

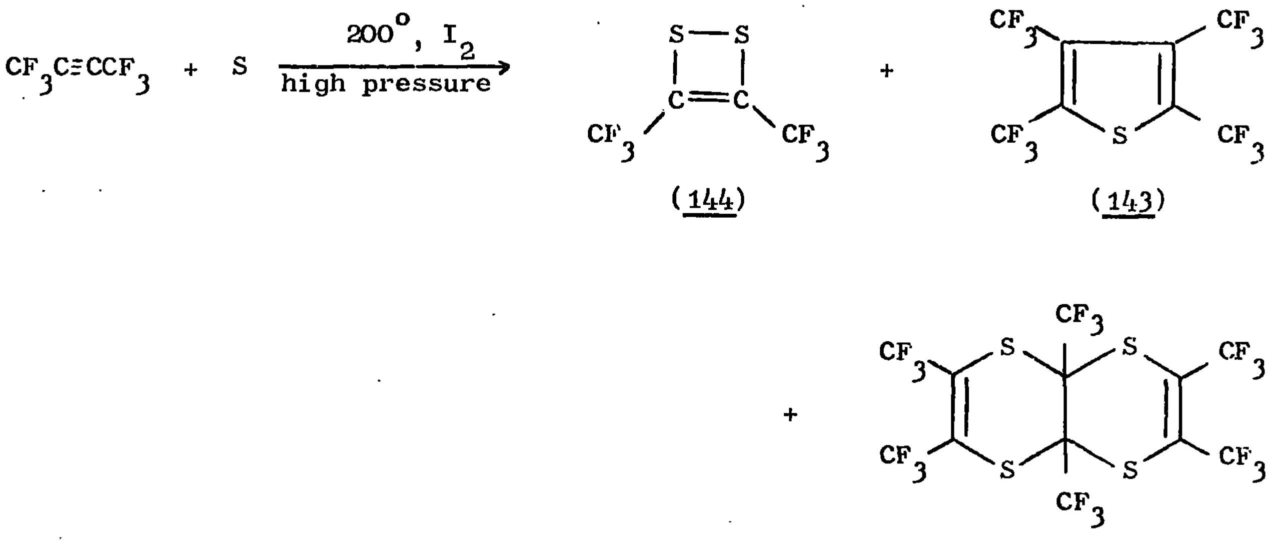
(b) Structure of product

The product had satisfactory elemental analysis and showed a parent peak in the mass spectrum. ^{19}F n.m.r. spectroscopy showed two resonances, the lower field one at $57{\cdot}4$ p.p.m. was attributed to the 3,4-trifluoromethyl groups whilst the one at higher field, $59{\cdot}1$ p.p.m. was attributed to the 1,5-trifluoromethyl groups. Absorptions at $6{\cdot}4$ and $6{\cdot}7\mu$ characteristic of aromatic unsaturation were observed in the i.r. spectrum.

(c) Discussion

As shown previously this is not a fluoride ion-initiated reaction and although the original reactions were carried out at 110°, it has been shown that even at 80° the process proceeds at a reasonable rate in similar yield.

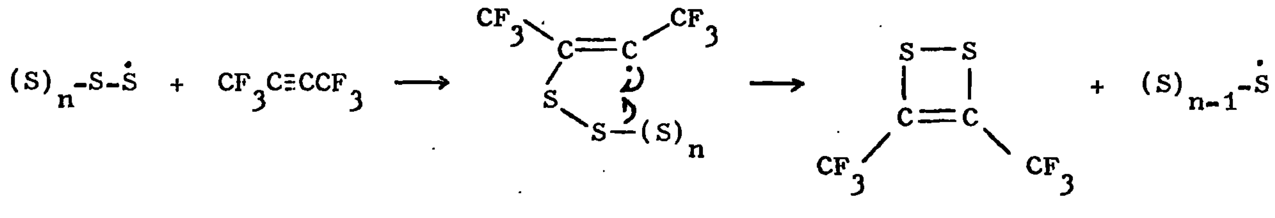
The reaction of hexafluorobut-2-yne with sulphur has been reported previously by Krespan and co-workers.[132] However, high temperatures and pressure were used and the reaction was shown to be initiated by iodine. Several products were isolated from the reaction and it was shown that by varying the conditions preferential formation of individual compounds could be promoted. Thus hexafluorobut-2-yne, sulphur and iodine when heated to 200° under pressure produced 3,4-bis(trifluoromethyl)-1,2-dithietene (144, 26%), tetrakis(trifluoromethyl)thiophene (143, 11%) and the bicyclic derivative (145).



(144) (143)

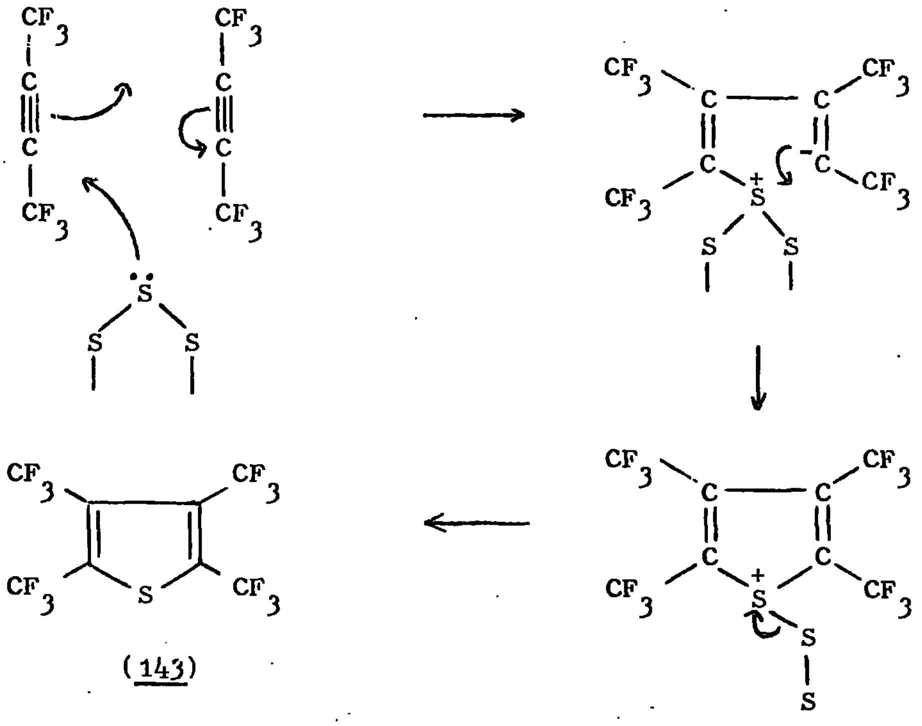
(145)

Further experiments showed that the dithietene (144) was the primary product from which the other compounds were formed. The reaction was proposed to proceed by a process in which the radical end of a sulphur chain adds to the triple bond to form a vinyl radical which then attacks the chain to give the dithietene (144).



(144)

Thus it is seen that reaction at high temperatures and pressures yield several products, whereas, at low temperature and atmospheric pressure only a single product, the thiophene derivative (143) is formed. The fact that reaction proceeds at a reasonable rate at 80° in the presence of a solvent with no other by-products being formed probably rules out a radical reaction. (The S-S bond strength is approximately 65 k.cals/mole and is of similar strength to an sp^3 carbon-bromine bond ≈ 65 k.cals/mole). The reaction therefore may proceed by an ionic mechanism which effectively involves a *syn* addition. For example,



IV.B.6 General Conclusions

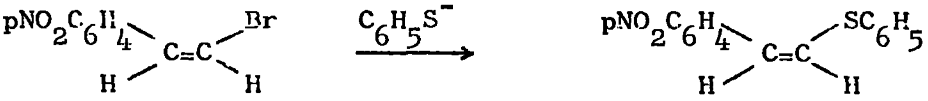
It has been shown that base catalysed addition of methanol to hexafluorobut-2-yne probably proceeds by a rapid *anti* route whereas at high temperatures a relatively slow uncatalysed reaction which follows a *syn* course may be operative to produce a *cis* olefin by an intramolecular proton transfer. The stereochemistry of addition of diethylamine has been shown to be critically dependent on the solvent, the higher the dielectric constant the greater the proportion of the trans olefin being formed. It is proposed that an intramolecular proton transfer by a syn route may be responsible for the high proportion of the cis olefin formed in solvents of low dielectric constant. Hexafluorobut-2-yne has been shown to react with elemental sulphur under mild conditions to produce tetrakis(trifluoromethyl)thiophene and it is proposed that an effective syn ionic pathway may be operative.

CHAPTER V

Nucleophilic Reactions of Polyfluorobut-2-enes

Introduction

The general rule that vinylic substitutions are more difficult to carry out than substitutions in saturated systems is true only when comparing simple systems. Various reports appear in the literature in which nucleophilic vinylic substitution of activated olefins is fairly facile. Thus the bromoethylene derivative (146) reacts readily with thiophenol under basic conditions[133] to produce the mono-substituted derivative (147).



(146) (147)

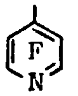
Similarly chloro-trifluoroethylene (148) reacts with sodium ethoxide[134] to produce the unsaturated ether (149).

$$C_2H_5ONa \; + \; CF_2{=}CClF \longrightarrow C_2H_5OCF{=}CClF$$

(149)

It is found that the general tendency of these reactions is for retention of configuration to occur, however, the effects of substituents, solvent, etc. have received little study and the factors which govern the stereochemical pathway of this type of reaction are still not well understood.

As we had available individual geometrical isomers of a series of model compounds it was decided to undertake a study of nucleophilic vinylic substitution. Under aprotic conditions it was found that fluoride ion was displaced from 2-substituted polyfluorobut-2-enes with varying degrees of stereospecificity.

(X = H, Cl, Br, )

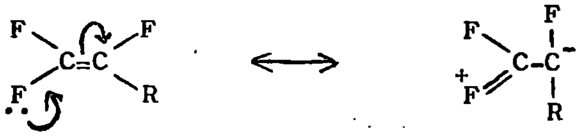
Under protic conditions, however, addition was found to compete with substitution in several of the compounds.

V.A Reactions with Methanolic Sodium Methoxide Solution

V.A.1 Introduction

Base catalysed additions of alcohols to fluoro-olefins have been known for many years, the original report appearing in 1946 when the results of reactions of tetrafluoroethylene with numerous alcohols appeared.[135] The high susceptibility of a terminal difluoromethylene group towards nucleophilic attack was recognised at this time. This can be rationalised when the electronegativity of fluorine is considered, replacement of a hydrogen by a fluorine atom results in the removal of electron density from the π system and renders the olefinic carbons highly electrophilic.

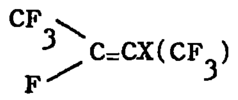
The preferential attack at a difluoromethylene group in a fluoro-olefin can be rationalised when the ability of vinylic fluorine to exert a mesomeric effect by its non-bonding p electrons is considered (i.e. return of electron density to the π system). Mesomeric electron release by vinylic fluorine is much more efficient than by the other halogens since fluorine and carbon are more similar in size thus facilitating p-π interaction, for example.



(R = Cl, Br, I, CF_3, H)

Therefore, it is proposed that because of this mesomeric effect (either in the ground state or transition state) nucleophilic attack takes place preferentially at the difluoromethylene group.

It has been found that in the substitution reactions of the but-2-enes studied here, i.e.



$$(CF_3)FC{=}CX(CF_3)$$

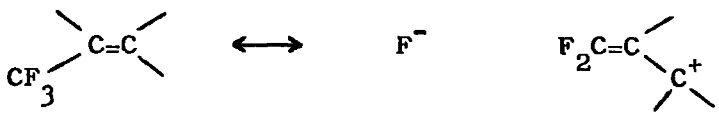
(X = H, Cl, Br)

where in principle substitution can take place at either the 2- or 3-positions, only vinylic fluorine is replaced by nucleophiles. This result is probably a consequence of both ground and transition state effects, i.e. the high electronegativity of fluorine (which renders the attached carbon highly electrophilic) and the preferential ability of the other atoms (H, Cl and Br) to stabilise the intermediate carbanion.

Very little information relating to the relative reactivities of fluoro-olefins under identical conditions is available. However, it has been shown that substitution of tetrafluoroethylene with trifluoromethyl groups increases the reactivity towards nucleophiles, i.e.

$$CF_2{=}CF_2 < CF_2{=}CFCF_3 < CF_2{=}C(CF_3)_2$$

This has been attributed to the fact that the trifluoromethyl groups cause only electron withdrawal (relative to F) from the π system by either an inductive or negative hyperconjugative effect, i.e.



A possible energy profile for this type of reaction can be represented schematically as in Figure 1.

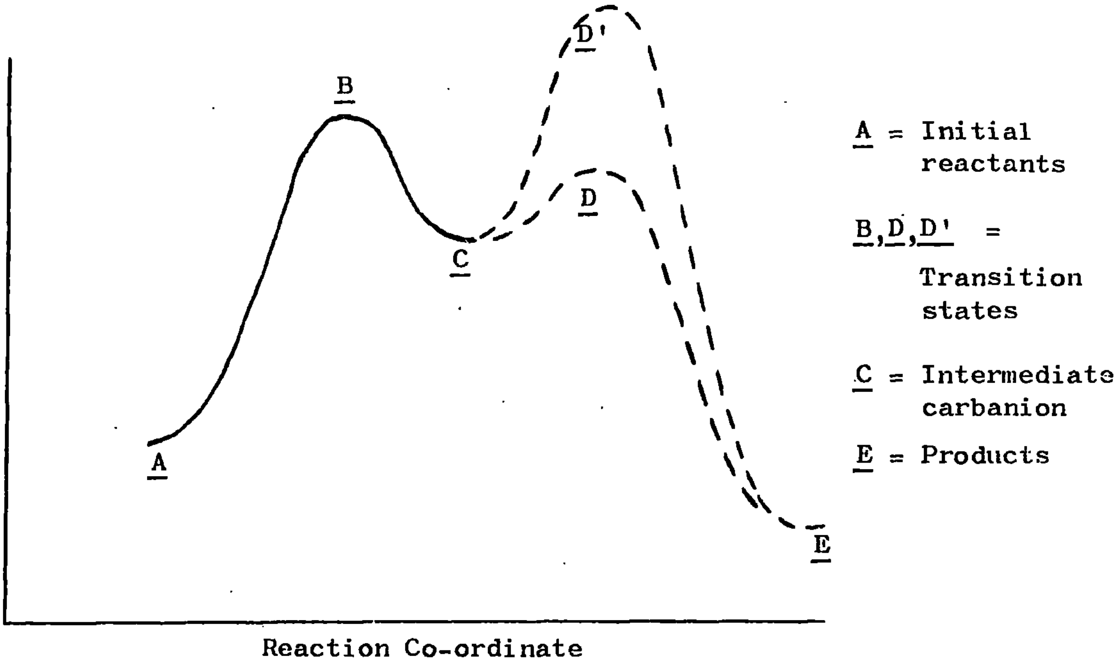
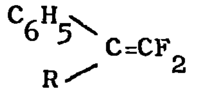


Figure 1

Obviously the rate of reaction will depend on the energy of the ground and transition states which will be critically dependent on the effect of substituents. These effects on the ground state have not been reported, however, the effects on the transition states can be approximated to those in the intermediate carbanion which have been discussed previously (I.A). The element effect has been applied to the results of recent kinetic studies carried out on a series of polyfluorobut-1-enes (150) with ethoxide ion and

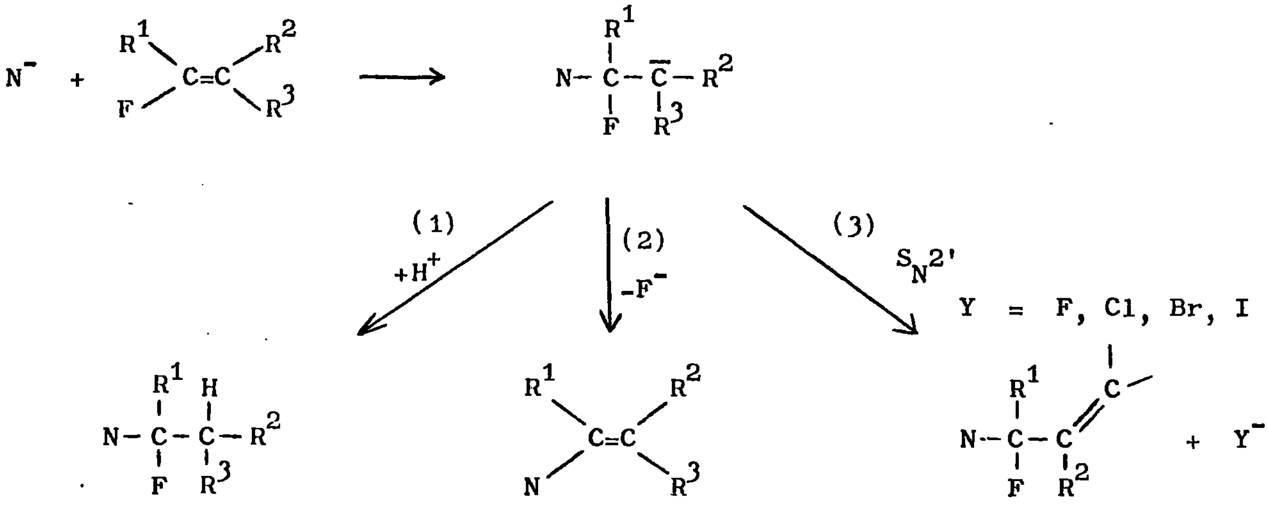


$(C_6H_5)(R)C{=}CF_2$ (R = CF_3, CF_2Cl, CF_2CF_3)

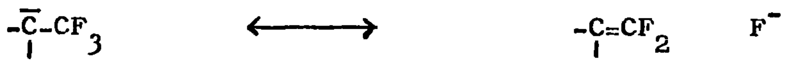
(150)

it has been proposed that in these systems attack by the nucleophile at the difluoromethylene group (i.e. formation of C) is the rate determining step.[136] However, the author points out that much more complex energy profiles may be operative in other systems.

Reaction of fluoro-olefins with nucleophiles under protic conditions can in principle lead to several different products derived from different mechanistic pathways. The three basic reactions can be summarized as,



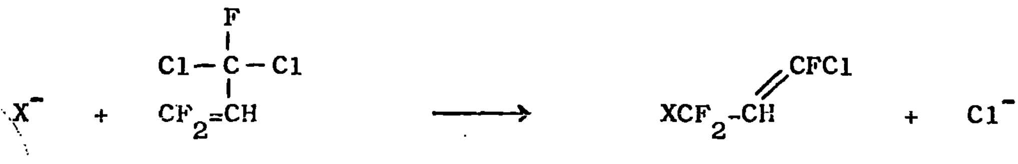
It is found that the lower molecular weight olefins i.e. tetrafluoroethylene prefer to undergo addition reactions (route 1). However, the proportion of unsaturated products is found to increase as the molecular weight of the olefin increases (route 2). For example perfluoroisobutene and perfluorocyclobutene react with alcohols to produce mainly unsaturated vinyl ethers. This has been explained in the perfluoroisobutene case as being due to high stability of the carbanion caused by the adjacent trifluoromethyl groups which



$$-\bar{C}-CF_3 \longleftrightarrow -C{=}CF_2 \quad F^-$$

will decrease the susceptibility of the ion towards electrophilic attack by a proton, and increase the tendency to eliminate fluoride ion.

Several reactions appear in the literature in which allylic halogen is eliminated in preference to vinylic substitution. As would be expected from bond energy considerations the heavier halogens are more readily displaced than is fluorine. Thus the propene derivative (151) undergoes an S_N2' reaction with halide ion to produce (152) by elimination of chloride, i.e.

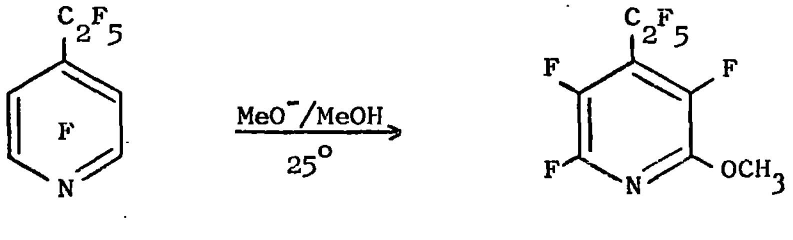


(151) (152)

Therefore in polyfluorobut-2-ene compounds there is the possibility of any of the three mechanisms being operative under protic conditions and therefore these systems are model compounds for the study of the factors which are responsible for determining the preferred mechanism.

V.A.2 Reaction of Perfluoro-trans-4-(2-butenyl)pyridine

Perfluoroalkylpyridines have been shown to react readily with methoxide to form a 2-methoxy derivative, thus perfluoro-(4-ethylpyridine) reacts with methoxide to produce 4-pentafluoroethyl-2-methoxy-3,5,6-trifluoropyridine[137] (153).

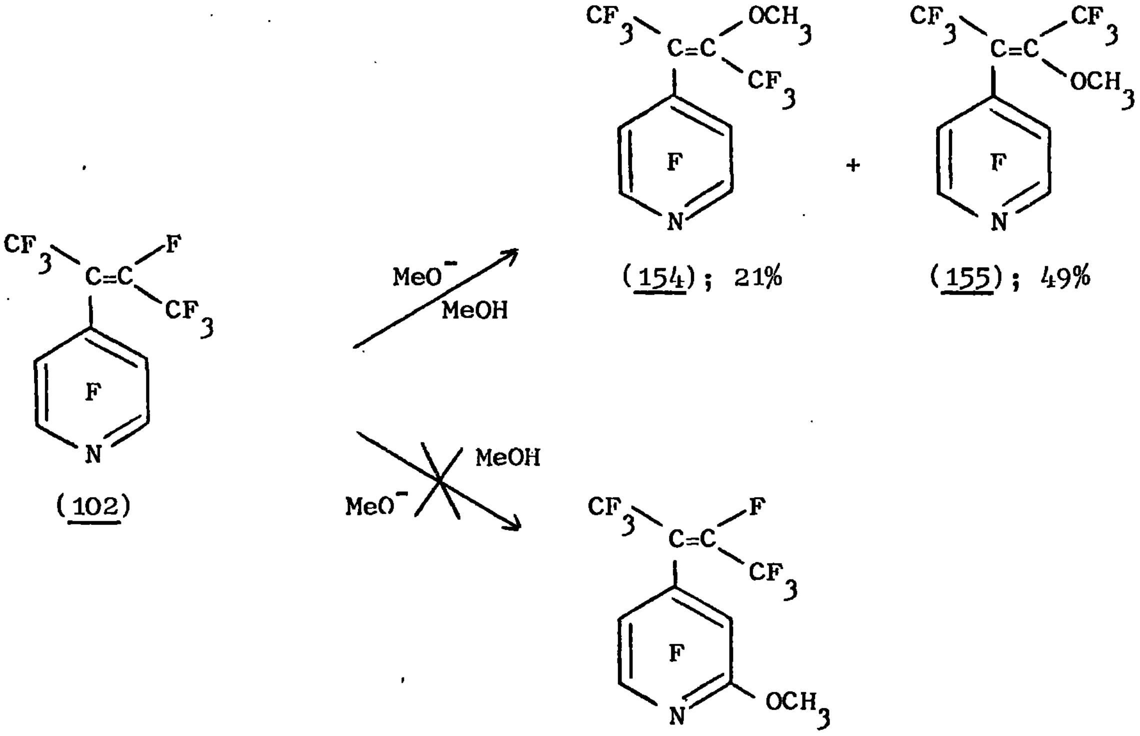


(153); 80%

Therefore within the 4-(2-butenyl)pyridine molecule nucleophilic attack can proceed at two positions. Nucleophilic aromatic substitution at the ring carbon atoms will lead to the 2-methoxy derivative; alternatively nucleophilic substitution of the vinylic fluorine may occur to produce an unsaturated ether.

When sodium methoxide solution (molar ratio olefin:MeO^- = 1:1) was added to perfluoro-trans-4-(2-butenyl)pyridine (102) in methanol at 0°, two products, which were found to have similar retention times on v.p.c., were formed. Mass spectroscopy and elemental analysis of the liquid isolated showed that the material contained only mono-methoxy derivatives. Inspection of the chemical shifts and coupling constants in the ^{19}F n.m.r. spectrum of the material showed that replacement of vinylic fluorine had occurred in preference to substitution within the aromatic ring (i.e. at the 2- and 6-positions).

Comparison of the trifluoromethyl group coupling constants with those observed in cis- and trans-2-phenyl-heptafluorobut-2-enes[118,119] was used to assign the individual resonances in the *cis* and *trans* butenyl pyridines (154) and (155) (Table 1). Integration of these resonances showed that a 70:30 mixture of the *cis* and *trans* olefins had been produced; comparison of this ratio with that obtained from the v.p.c. spectrum (di-n-decylphthalate, 100°) showed that the *trans* isomer had the shorter retention time. The mechanism of formation of these compounds will be discussed later in this chapter.



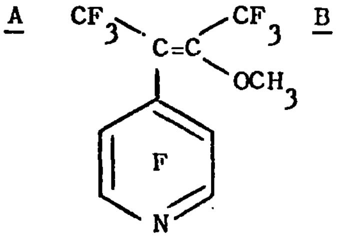
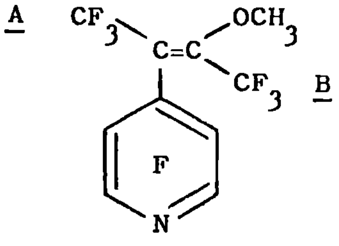
(102)

(154); 21%

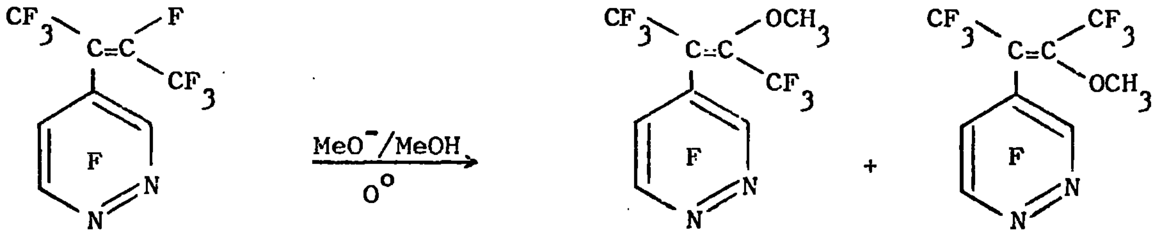
(155); 49%

TABLE 1

Coupling Constants (Hz.) in Perfluoro-*cis*- and -*trans*-2-(2',3',5',6'-tetrafluoropyridyl)-3-methoxy-but-2-enes

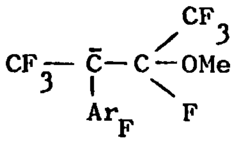
	J_{AB}
	12
	1·5

A similar reaction of perfluoro-4-(2-butenyl)pyridazine has been reported[112] in which substitution of vinylic fluorine is more favourable than nucleophilic aromatic substitution. When sodium methoxide solution was added to the pyridazine derivative (156) in methanol at 0° a *cis-trans* mixture of the mono-methoxy compounds (157) and (158) was obtained.



(156) (157); 34% (158); 66%

This again shows the high reactivity of vinylic fluorine towards nucleophilic attack as perfluoro-monosubstituted pyridazine derivatives have been shown to be susceptible to nucleophilic attack at the 5-ring position. However, no evidence for nucleophilic aromatic substitution was obtained and with both the butenyl-pyridine (102) and -pyridazine (156) compounds no addition products are observed in the reactions. This can be rationalised when the stability of the respective carbanions is considered. The anions (159) generated by attack of methoxide on the perfluorobutenyl group are tertiary, and are presumably relatively stable due to the influence of the trifluoromethyl and perfluoro-heterocyclic groups, i.e.



$$CF_3-\bar{C}(Ar_F)-C(CF_3)(F)-OMe$$

(159).

It is reasonable to suppose that this carbanion is less likely to be protonated by abstraction of a proton from the solvent than is a less stable primary or secondary anion. Alternatively, if protonation occurs the proton can readily be lost under the basic conditions followed by elimination of fluoride ion to produce the olefin.

V.A.3 Reaction of Perfluorobut-2-ene

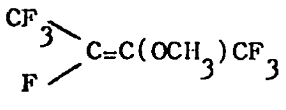
Although this reaction has been carried out previously and has been reported to produce a di-addition product,[138] full characterisation of the compound was not carried out.

In an exploratory reaction, octafluorobut-2-ene and methanolic sodium methoxide solution were allowed to react together at 50° for 3 hrs. Analysis of material, isolated from the solvent, by v.p.c. (both di-n-decylphthalate and S.G.R. columns) at various temperatures showed that several products had been formed. Attempts to separate these compounds by v.p.c. proved to be unsuccessful due to the extreme similarity of the retention times of the products. Similarly separation by fractional distillation proved unsuccessful.

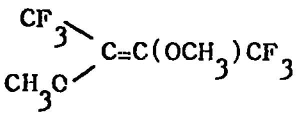
A second reaction was carried out in which the conditions of the reaction were made less severe (i.e. pre-cooled methanolic sodium methoxide was added to the olefin at -10° and reaction was allowed to continue for ½ hr.). V.p.c. analysis of the material isolated from the solvent again indicated a complex reaction mixture, the components of which were inseparable.

Due to the fact that the products from these reactions could not be isolated in a pure state, no further work was carried out with this olefin and methanolic sodium methoxide solution.

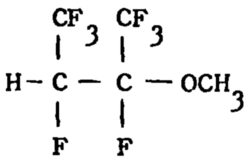
The complex mixtures isolated from these reactions presumably contain products resulting from mono-substitution (160) and di-substitution (161) which may be present as *cis* and *trans* isomers. Similarly, addition of methanol will produce saturated ethers which can exist in diastereoisomeric forms (162).



(160)



(161)



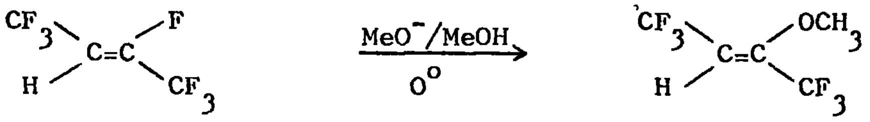
$$H-\underset{F}{\overset{CF_3}{C}}-\underset{F}{\overset{CF_3}{C}}-OCH_3$$

(162)

V.A.4 Reaction of Trans-2H-heptafluorobut-2-ene

(a) Reaction conditions and products

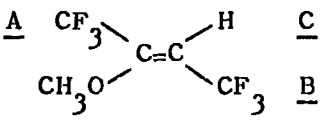
When trans-2H-heptafluorobut-2-ene was reacted with methanolic sodium methoxide solution (molar ratio olefin:MeO^- = 1:1) a highly volatile liquid was produced which was identified as trans-2H-3-methoxy-hexafluorobut-2-ene (136).



(163) (136); 53%

(b) Structure of the product

Analysis by v.p.c. (acetonyl acetone, 0^o) of the material isolated from the reaction showed that only a single product had been formed. The mass spectrum of the compound showed a parent peak but due to the high volatility of the compound elemental analysis proved difficult, however, correct results were obtained. The trans configuration of the trifluoromethyl groups was determined by comparison of the ^{19}F n.m.r. spectrum with those of cis- and trans-2-phenyl-heptafluorobut-2-ene.[118,119] A CF_3-CF_3 coupling of 1·5 Hz. characteristic of trans trifluoromethyl groups confirmed the geometrical structure of the compound.



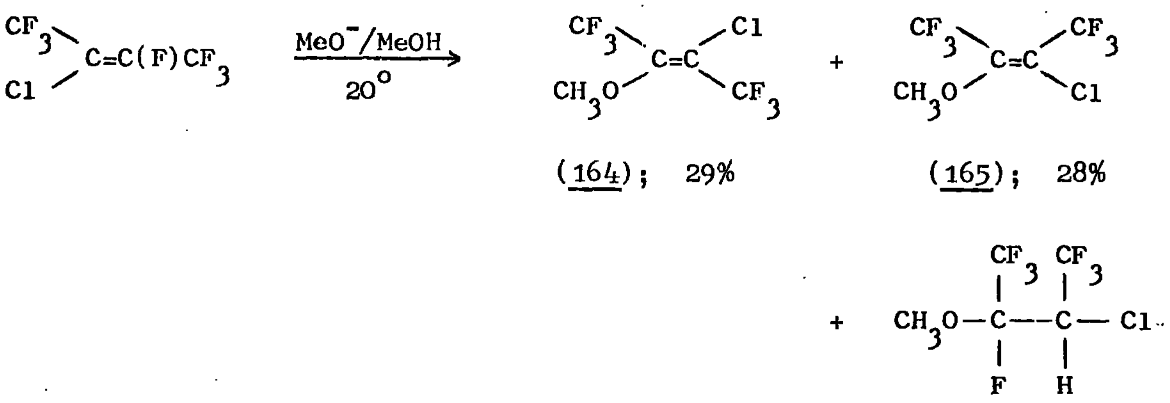
J_{AB} (Hz.)	J_{BC} (Hz.)
1·5	8

Further confirmation of the trans structure of the compound came from the i.r. spectrum where a relatively weak olefinic absorbtion at 5·9μ characteristic of a trans substituted olefin was observed.[125]

V.A.5 Reaction of 2-Chloro-heptafluorobut-2-ene

(a) Reaction conditions and products

When a mixture of cis- and trans-2-chloro-heptafluorobut-2-ene (cis:trans ratio = 59:41) was reacted with methanolic sodium methoxide (molar ratio olefin:MeO^- = 1:1) at 20° several products were found to be formed, i.e.



(164); 29% (165); 28%

(166) and (167); 17%

(two diastereomers)

(b) Structure of the products

Separation of the components of the mixture was carried out using preparative scale v.p.c. (di-n-decylphthalate, 60°) the products being identified as (in order of emergence from the column):

(i) trans-2-chloro-3-methoxy-hexafluorobut-2-ene (164)

The ^{19}F n.m.r. spectrum of the material clearly indicated a trans structure for the compound, a CF_3-CF_3 coupling of 1·5 Hz. being observed. Further confirmation of the trans structure came from the i.r. spectrum where a very weak olefinic C=C stretching absorption at 6·1μ was observed.[125]

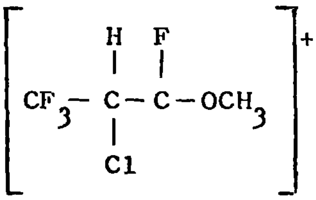
(ii) cis-2-chloro-3-methoxy-hexafluorobut-2-ene (165)

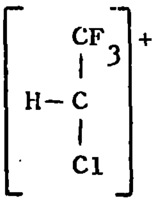
Elemental analysis of this compound was found to be satisfactory, similarly its mass spectrum showed an appropriate parent peak. A CF_3-CF_3 coupling of 12·5 Hz. was observed in the ^{19}F n.m.r. spectrum which clearly indicated a <u>cis</u> configuration of the trifluoromethyl groups. Again the i.r. spectrum of the material provided further confirmation of the structure; a relatively strong olefinic stretching vibration at 6·1μ, characteristic of a <u>cis</u> olefin, being observed.[125]

(iii) 1st diastereomer of 2H-2-chloro-3-methoxy-heptafluorobutane (<u>166</u>).

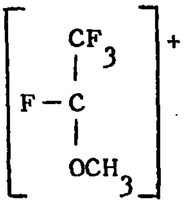
(iv) 2nd diastereomer of 2H-2-chloro-3-methoxy-heptafluorobutane (167).

The mass spectra of these compounds did not show parent peaks which is characteristic of saturated fluorocarbons. However, minor peaks corresponding to loss of fluorine and a methoxy group from the parent appear in the spectrum. Major peaks present correspond to loss of a trifluoromethyl group and fragments formed by rupture of the central carbon-carbon bond, for example:


$\left[CF_3-\underset{Cl}{\overset{H}{C}}-\overset{F}{C}-OCH_3\right]^+$,

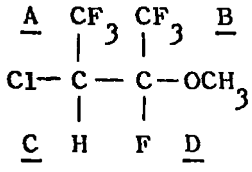

$\left[H-\underset{Cl}{\overset{CF_3}{C}}\right]^+$

and


$\left[F-\underset{OCH_3}{\overset{CF_3}{C}}\right]^+$

Further evidence for the saturated structures comes from the i.r. spectra of the compounds where no C=C stretching vibrations in the region 5·8-6·4μ are observed.

The ^{19}F n.m.r. spectrum of the first diastereomer (<u>166</u>) consists of three resonances at 69·9, 78·5 and 133·4 p.p.m. (from $CFCl_3$) of relative intensity 3:3:1 assigned to the two trifluoromethyl groups and the tertiary fluorine. Similarly, the proton spectrum consists of a singlet at 2·8 p.p.m. and an overlapping doublet of quartets at 3·7 p.p.m. assigned to the methoxy group and the single hydrogen respectively. Observed coupling constants are in agreement with those observed in similar compounds.[139]


$\underset{\underline{C}}{Cl}-\overset{\underline{A}\;CF_3}{\underset{H}{C}}-\overset{CF_3\;\underline{B}}{\underset{F\;\underline{D}}{C}}-OCH_3$

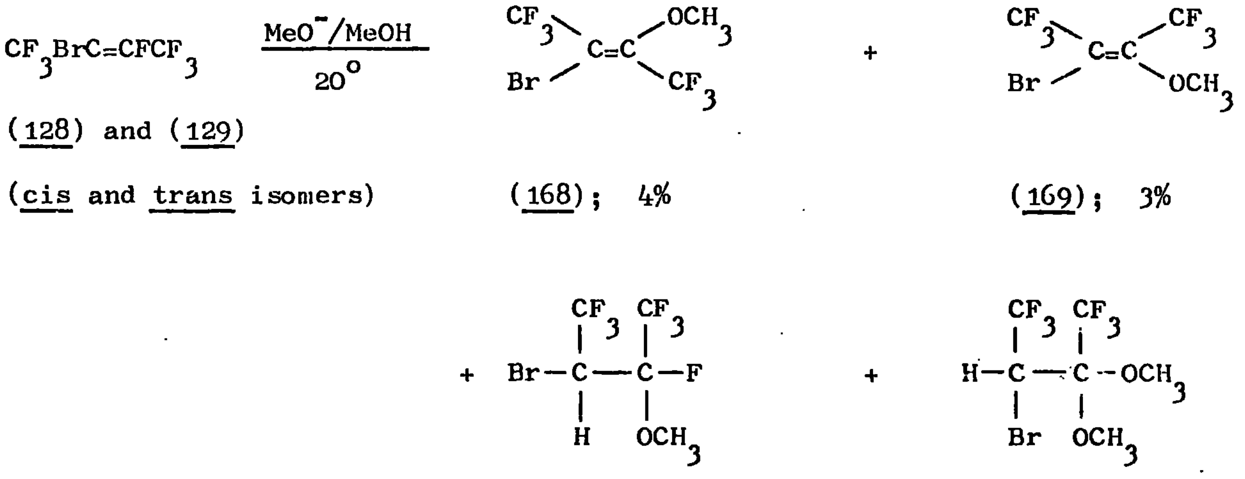
$\underline{J_{AB}}$ (Hz.)	$\underline{J_{AC}}$ (Hz.)	$\underline{J_{AD}}$ (Hz.)	$\underline{J_{DC}}$ (Hz.)
6	6	9	8·5

Due to the low concentration of the second diastereomer (167) in the reaction mixture only a small amount of pure material was isolated and the n.m.r. spectrum was not well resolved. However resonances at 70·4, 77·3 and 130·0 p.p.m. (from $CFCl_3$) in the ^{19}F spectrum assigned to the trifluoromethyl groups and the tertiary fluorine were apparent, a CF_3-F coupling of 15 Hz. was observed. Similarly the proton spectrum showed two poorly resolved resonances at 2·8 and 3·7 p.p.m. (from T.M.S.) assigned to the methoxy group and single hydrogen respectively.

V.A.6 Reaction of 2-Bromo-heptafluorobut-2-ene

(a) Reaction conditions and products

When a mixture of *cis*- and *trans*-2-bromo-heptafluorobut-2-ene (128) and (129) (*cis*:*trans* ratio = 35:65) was reacted with methanolic sodium methoxide (molar ratio olefin:MeO^- = 1:1) at 20° several products (168), (169), (170), (171) and (172) were formed.



(128) and (129)

(*cis* and *trans* isomers)

(168); 4%

(169); 3%

(170) and (171); 12%

(two diastereomers)

(172); 53%

(b) Structure of the products

Only partial separation of the complex reaction mixture was affected by preparative scale v.p.c. (di-n-decylphthalate). The compounds were identified as (in order of emergence from column):

(i) trans-2-bromo-3-methoxy-hexafluorobut-2-ene (168)

As is characteristic of unsaturated fluorocarbons a strong parent peak (with appropriate isotope pattern) was observed in the mass spectrum. ^{19}F n.m.r. spectroscopy was used to determine the configuration of the trifluoromethyl groups about the double bond. A characteristic CF_3-CF_3 coupling of 1·5 Hz. indicated a trans structure. Further evidence of the trans structure came from the i.r. spectrum where a very weak olefinic C=C stretching absorption at 6·1μ characteristic of a symmetrically substituted trans olefin was observed.[125]

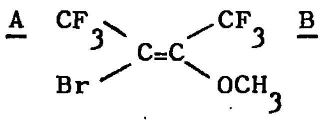
(ii) The second component of the mixture separated by v.p.c. was shown by n.m.r. spectroscopy to be a mixture of two compounds which were identified as,

(a) cis-2-bromo-3-methoxy-hexafluorobut-2-ene (169);

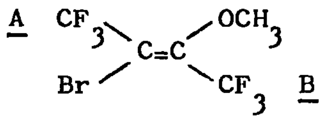
(b) 1st diastereomer of 2H-2-bromo-3-methoxy-heptafluorobutane (170).

Obviously, elemental analysis of the mixture could not be used to characterise the two components present. However, the mass spectrum of the mixture was found to consist of two distinct fragmentation patterns which were superimposed. These individual patterns were found to be identical with those of samples of the trans olefin (168) and the second diastereoisomeric addition product (171) which were isolated in a pure state by v.p.c. from the product mixture. Detailed investigation of the ^{19}F and ^{1}H n.m.r. spectra clearly showed the presence of two components. Two quartets in the ^{19}F spectrum, relative intensity 1 were assigned to the trifluoromethyl group resonances in the cis olefin (169). Other resonances at 67·4 and 76·4 p.p.m. (from external $CFCl_3$), relative intensity 3, were attributed to the trifluoromethyl group resonances in the addition product (170), a high field resonance at 128·4 p.p.m. relative intensity 1, was assigned to the tertiary fluorine in this compound.

J_{AB} (Hz.)



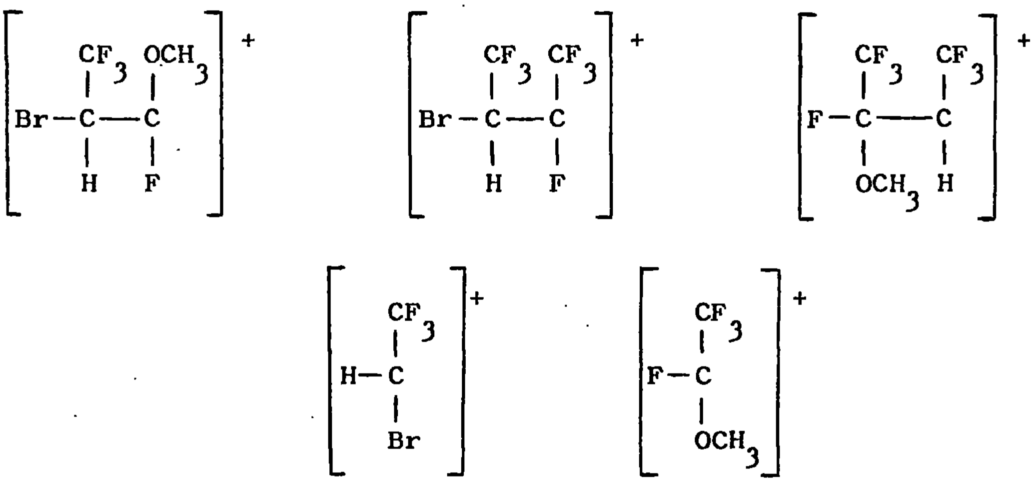
13



1·5

(iii) 2nd diastereomer of 2H-2-bromo-3-methoxy-heptafluorobutane (171).

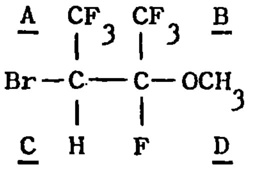
Again the mass spectrum of this product failed to show a parent peak, characteristic of a saturated fluorocarbon. However, peaks corresponding to loss of $-CF_3$, $-OCH_3$ and -Br from the parent along with those derived from rupture of the central carbon-carbon bond were found to be prominent, for example:



The absence of a C=C stretching vibration in the i.r. spectrum gave further indication of the saturated nature of the compound.

The ^{19}F n.m.r. spectrum showed resonances at 67·4, 77·4 and 124·8 p.p.m. (from $CFCl_3$) attributed to the two trifluoromethyl groups and the tertiary fluorine respectively. Similarly, in the proton spectrum two resonances at 3·6 and 4·4 p.p.m. (from T.M.S.) were assigned to the methoxy group and the single hydrogen.

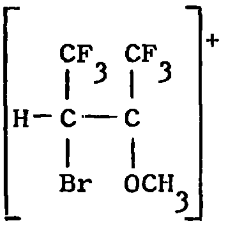
Coupling Constants (Hz.) in 2H-2-bromo-3-methoxy-heptafluorobutanes

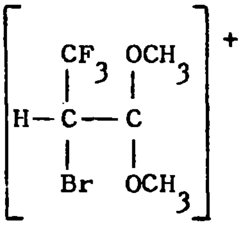

$\mathrm{Br{-}CH(CF_3){-}CF(CF_3){-}OCH_3}$

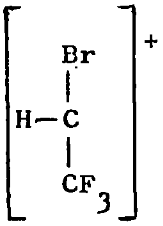
	J_{AB}	J_{AC}	J_{AD}	J_{CD}
1st diastereomer	-	7	14	-
2nd diastereomer	8	≈ 8	8	≈ 8

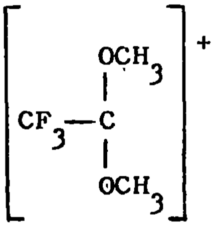
(iv) 2H-2-bromo-3,3-dimethoxy-heptafluorobutane (172)

The absence of a C=C stretching vibration in the i.r. spectrum and a parent peak in the mass spectrum was indicative of a saturated structure. Major peaks corresponding to loss of -OMe, and $-CF_3$ along with those caused by ions derived from rupture of the central C-C bond however were observed, for example:

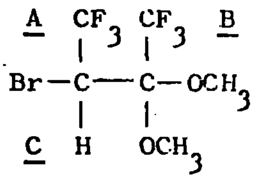

$[\mathrm{H{-}C(CF_3)(Br){-}C(CF_3)(OCH_3)}]^+$


$[\mathrm{H{-}C(CF_3)(Br){-}C(OCH_3)(OCH_3)}]^+$


$[\mathrm{H{-}C(Br)(CF_3)}]^+$


$[\mathrm{CF_3{-}C(OCH_3)(OCH_3)}]^+$

(A bromine isotope pattern was observed in several of these ions). ^{19}F n.m.r. spectroscopy showed only two resonances at 65·2 and 73·5 p.p.m. (from $CFCl_3$), relative intensity 1 which were assigned to the trifluoromethyl groups. The proton n.m.r. spectrum similarly showed two resonances at 3·5 and 4·4 p.p.m. (from T.M.S.), relative intensity 6:1 which were assigned to the protons of the methoxy groups and the hydrogen at the 2-position. Coupling constants were in agreement with those found in similar compounds.[139]


$\mathrm{Br{-}CH(CF_3){-}C(CF_3)(OCH_3){-}OCH_3}$

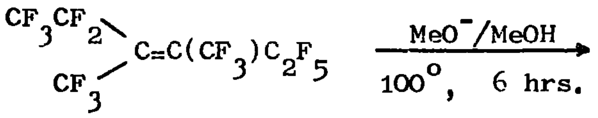
J_{AB} (Hz.)	J_{AC} (Hz.)
7	7

V.A.7 Reaction of Perfluoro-2,3-diethyl-but-2-ene

As discussed previously (V.A.1) a characteristic reaction of perhalo-olefins with nucleophiles is an allylic S_N2' process. Thus, replacement of allylic chlorine occurs in the reaction of 3-chloropentafluoropropene with sodium methoxide,[140] for example:

$$CH_3O^- \quad + \quad CF_2{=}CFCF_2{-}Cl \longrightarrow CH_3OCF_2CF{=}CF_2 \quad + \quad Cl^-$$

With this mode of reaction in mind an attempted substitution of perfluoro-2,3-diethylbut-2-ene (173), a compound not containing the highly reactive vinylic fluorine, with methoxide was carried out. It was found, however, that even at 100° no substitution was found to occur.



$$(CF_3CF_2)(CF_3)C{=}C(CF_3)C_2F_5 \xrightarrow[100^\circ,\ 6\ hrs.]{MeO^-/MeOH} \text{No reaction}$$

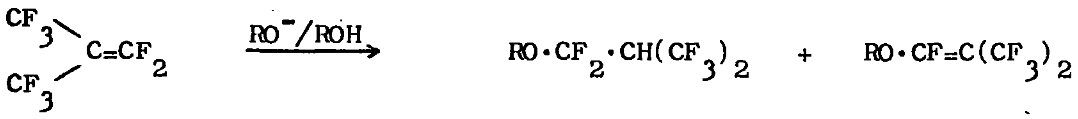
V.A.8 Discussion

It has been shown in numerous investigations that as one traverses the fluoro-olefin series the proportion of saturated products obtained from reactions in alcoholic alkoxide solutions decreases as the molecular weight increases.[96] Tetrafluoroethylene has been shown to add various alcohols to produce saturated ethers,

$$C_2H_5OH \quad + \quad CF_2{=}CF_2 \xrightarrow{Na} C_2H_5OCF_2{\cdot}CHF_2$$

similarly, hexafluoropropene produces analogous compounds. Conversely, isobutene produces substantial proportions of unsaturated ethers. As mentioned previously the change in product composition has been attributed to an increase in the stability of the carbanion due to progressive substitution by perfluoroalkyl groups. However, it is to be expected that steric effects may have some influence on the product composition, i.e. steric interactions in the intermediate carbanion or addition product will favour production of the vinyl ether in which the distance between the various substituents is increased.

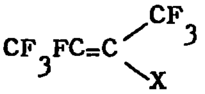
Evidence for the influence of steric factors can be seen in the reactions of perfluoroisobutene (<u>174</u>) with various alkoxides in alcoholic solution,[96] i.e.



As R changes yields of unsaturated product increase in the order,

$$C_2H_5 < nC_3H_7 < iC_3H_7 < nC_4H_9$$

Therefore, in the polyfluorobut-2-enes studied here, i.e.

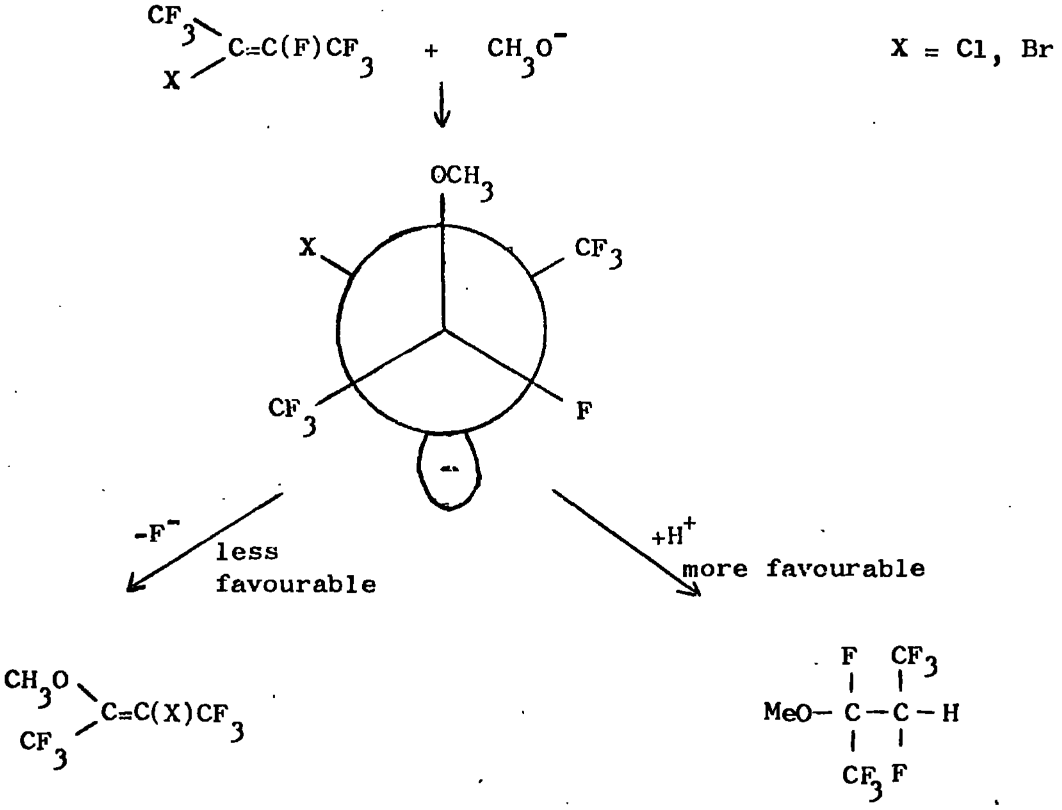


X = H, Cl, Br, 

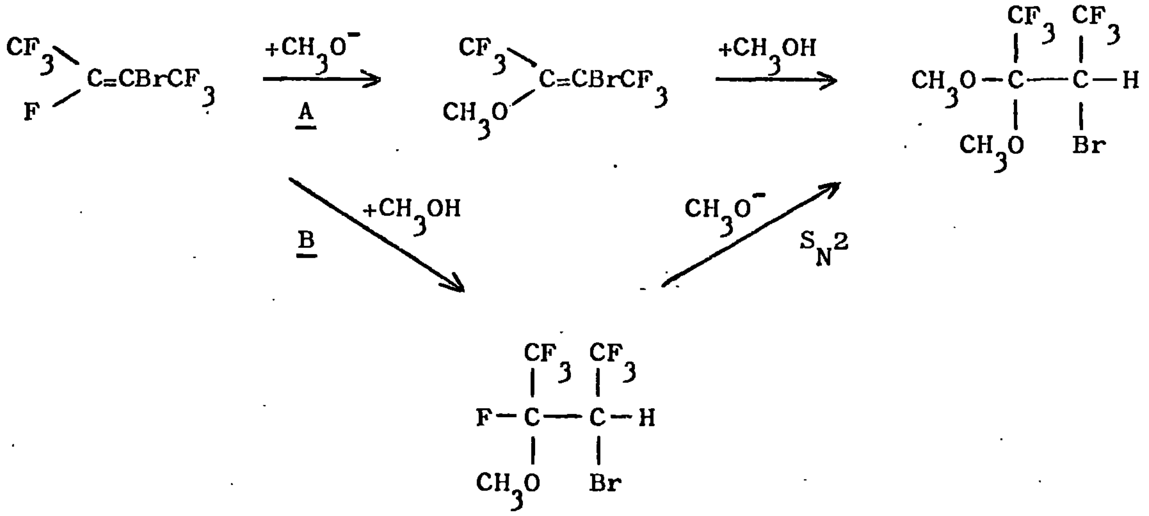
by analogy it was anticipated that there would be a steady decrease in the proportion of addition products along the series from X = H to X = tetrafluoropyridyl, but the results described show that this is definitely not the case.

X	Proportion of olefinic products	Proportion of addition products
H	100	0
Cl	77	23
Br	10	90
	100	0

As would be expected from both the stability of the intermediate carbanion and steric considerations the butenyl pyridine (<u>102</u>) does not undergo methanol addition whereas the 2-bromo (128, 129) and 2-chloro (132, 133) analogues do. In the case of the 2-hydro olefin (163) where substantial addition could be expected, none is in fact observed, which suggests that the factors which govern the competition between addition and substitution in these systems are more complex than previous discussions of the subject imply. It is worth noting, however, that the bromo- and chloro-olefins (which lead to the saturated products) are those with the most sterically demanding substituents as has been shown by equilibration studies (IV.A.8.c). It is possible then that in the intermediate carbanions produced from the reaction of methoxidp with these olefins steric effects may increase the barriers to rotation sufficiently so as to inhibit the elimination step relative to the addition of a proton from the solvent.



Comparison of the reactions of the 2-chloro (132, 133) and 2-bromo (128, 129) olefins shows that although both saturated and unsaturated compounds are produced the major product derived from the latter is a dimethoxy compound (172). This in principle can be produced by either vinylic substitution followed by addition (scheme A) or addition followed by an S_N2 displacement of fluoride ion (scheme B).



However, as the 2-chlorobut-2-enes (132, 133) do not produce a dimethoxy analogue it seems reasonable to suppose that the reaction proceeds by route A and that the difference between the two olefins is caused by the increased ability of bromine to stabilise the intermediate carbanion.

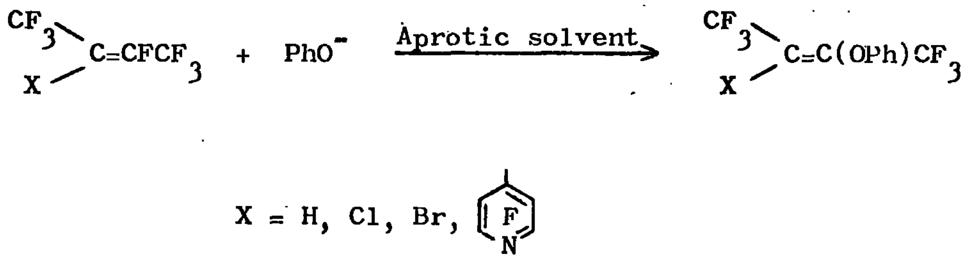
Previous discussion indicated that a further possibility that might have been expected from these reactions was an allylic S_N2' process, however, in the compounds studied here in which a vinylic fluorine was present no evidence was obtained for this process having occurred. Similarly, with the but-2-ene derivative (173) in which no vinylic fluorine is present and which could have been expected to undergo this type of reaction, no reaction was found to occur with methanolic sodium methoxide.

V.B. Reactions with Sodium Phenoxide

V.B.1 Introduction

As has been shown previously, reactions of polyfluorobut-2-enes with methoxide under protic conditions are complicated by the production of addition compounds. As a result information on the stereochemical course of nucleophilic vinylic substitution cannot be obtained for some of these compounds under these conditions. To avoid this difficulty it was decided to carry out similar reactions with sodium phenoxide using an aprotic solvent.

Initial reactions were carried out on a relatively large scale with sodium phenoxide in N,N-dimethylformamide (D.M.F.) or dioxane to enable characterisation of the products to be carried out. Subsequent reactions of pure geometrical isomers were then carried out on a small scale, the product ratio being determined by ^{19}F n.m.r. spectroscopy. In all of the compounds studied only derivatives produced from vinylic substitution by phenoxide were observed, for example:



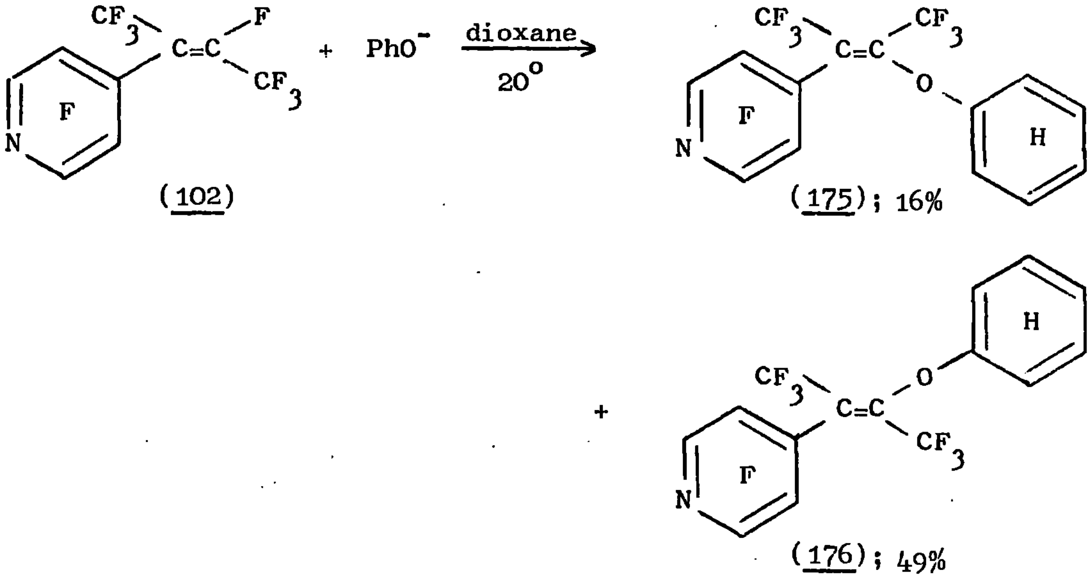
which makes this type of reaction system ideal for the study of nucleophilic substitution in these compounds. As discussed previously (III.C), many reports appear in the literature in which nucleophilic vinylic substitution of activated olefins occurs and it has been found that retention of the configuration of the parent olefin is the usual result. Carbanions have been proposed as intermediates in these reactions and with this in mind it was decided to study the effect of solvent and substituents on the stereospecificity on this type of reaction. Three solvents were chosen which had different dielectric constants, they were dioxane, dimethylformamide (D.M.F.) and N-methylacetamide (N.M.A.).

Solvent	Dielectric constant (Debye)
Dioxane	9·93 (25°)
D.M.F.	37 (25°)
N.M.A.	165 (40°)

V.B.2 Reaction of Perfluoro-trans-4-(2-butenyl)pyridine in dioxane

(a) Reaction conditions and products

When perfluoro-trans-4-(2-butenyl)pyridine (102) was reacted with sodium phenoxide in dioxane at 20° v.p.c. analysis of the reaction mixture (S.G.R., 200°) showed the presence of two components with very similar retention times. The two compounds were identified as cis- and trans-2-phenoxy-3-(4-tetrafluoropyridyl)hexafluorobut-2-ene (175) and (176).

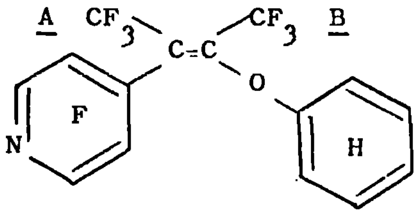


As in the analogous reaction with methoxide (V.A.2) no nucleophilic aromatic substitution of the pyridine nucleus was found to occur.

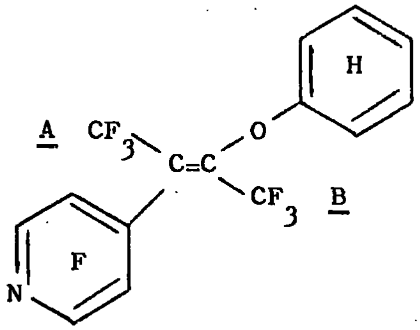
(b) Structure of the products

Separation of the cis:trans mixture by preparative scale v.p.c. was found to be impossible due to the similarity of retention times of the two compounds. The two isomers were analysed as a mixture which had satisfactory elemental analysis and showed a parent peak in the mass spectrum. ^{19}F n.m.r. spectroscopy clearly showed the presence of two components, study of the chemical shifts and relative intensities of the observed resonances indicated that the two compounds were 4-substituted tetrafluoropyridines. Four resonances at 58·9, 62·3, 64·9 and 66·0 p.p.m. (from $CFCl_3$) were assigned to the trifluoromethyl groups of the olefinic side chains. Comparison of the CF_3-CF_3 coupling constants with those found in *cis*- and *trans*-2-phenylheptafluorobut-2-ene[118,119] indicated that olefins with both *cis* and *trans* configurations of the trifluoromethyl groups were present, similarly, these constants were used to assign the individual resonances. Integration of the peak areas showed that a 25:75, *cis*:*trans* ratio of the isomers had been produced. Further evidence for a *cis*:*trans* mixture came from the i.r. spectrum where two olefinic C=C stretching vibrations were observed at 6·0 and 6·05µ.

J_{AB} (Hz.)



12·5



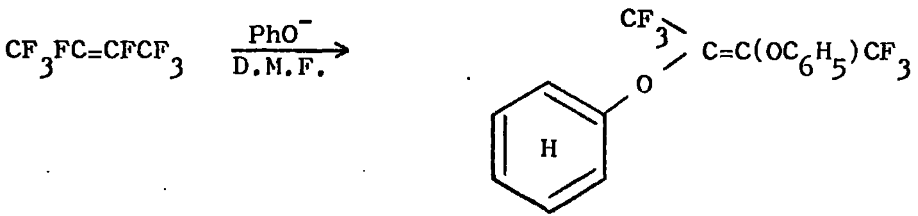
1·5

V.B.3 Reaction of Octafluorobut-2-ene

(a) Reaction conditions and products

An attempted reaction of octafluorobut-2-ene with sodium phenoxide in dioxane was carried out at 20°, however, it was found that even with a prolonged reaction time no conversion of the olefin had taken place. (The olefin appeared to be highly insoluble in the reaction medium). Similar results were obtained with sodium phenoxide in D.M.F. solution.

However using a solution of phenoxide in D.M.F. at 50° a small quantity of a white crystalline solid was isolated from the reaction mixture which was identified as 2,3-diphenoxyhexafluorobut-2-ene (177).



(177); 40%

(b) Structure of the product

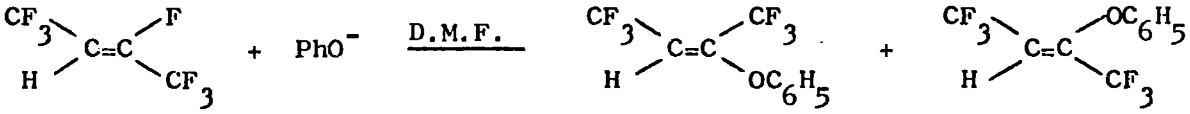
The material isolated was found to have satisfactory elemental analysis; similarly the mass spectrum showed a parent peak.

Although it was found impossible to assign the configuration of the material unambiguously it was thought to consist mainly of the trans isomer. No olefinic C=C stretching vibration was observed in the i.r. spectrum of the material as would be expected from a symmetrically substituted trans olefin.[125] Similarly, as only a single resonance at 57·0 p.p.m. (from $CFCl_3$), assigned to a trifluoromethyl group, was observed in the ^{19}F n.m.r. spectrum of an ethereal solution, it was thought likely that the compound was present mainly as a single isomer. (Some cis isomer was thought to be present as the material was found to melt over a range of approximately 3°.

V.B.4 Reaction of trans-2H-heptafluorobut-2-ene

(a) Reaction conditions and products

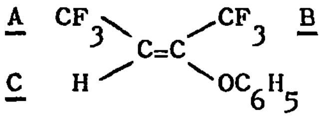
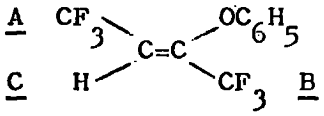
When trans-2H-heptafluorobut-2-ene (163) was reacted with sodium phenoxide in D.M.F. two products were formed which were separated by preparative scale v.p.c. and subsequently shown to be cis- and trans-2H-3-phenoxy-hexafluorobut-2-ene (178) and (179).



(163) (178); 17·5% (179); 55·5%

(b) Structure of the products

Both the cis and trans olefins had satisfactory elemental analysis, similarly the mass spectra of the two compounds showed appropriate parent peaks. ^{19}F n.m.r. spectroscopy was used to determine the configuration of the two olefins; a CF_3-CF_3 coupling of 1•5 Hz. being observed in the trans isomer (179) with a corresponding coupling of 11•0 Hz. being present in the cis analogue (178).

	J_{AB} (Hz.)	J_{AC} (Hz.)
	11•0	9•0
	1•5	8•0

Further confirmation of these assignments came from the i.r. spectra of the two compounds where the trans isomer was found to show a weak olefinic stretching vibration at 5•85µ, as would be expected, whereas the corresponding absorption in the cis analogue was found to be of relatively strong intensity at 5•9µ.[125]

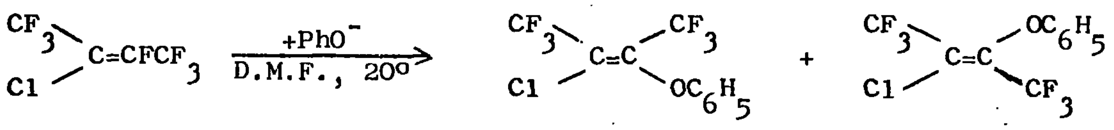
It was found that using a polar column for v.p.c. analysis and separation, (di-n-decylphthalate) the trans isomer had the shorter retention time, a result which was found to be generally applicable to all of the isomeric mixtures of but-2-enes studied in the course of this work.

V.B.5 Reactions of a Cis-Trans Mixture of 2-Chloro-heptafluorobut-2-ene

(a) Reaction conditions and products

When a cis:trans mixture of 2-chloro-heptafluorobut-2-enes (132) and (133) (cis:trans ratio = 59:41) was reacted with sodium phenoxide in D.M.F. (ratio of olefin:PhO$^-$ = 1:1) cis- and trans-2-chloro-3-phenoxy-hexafluorobut-2-ene

(180) and (181) were produced in good yield.



(132) and (133) (180); 43% (181); 28%

cis and *trans* isomers

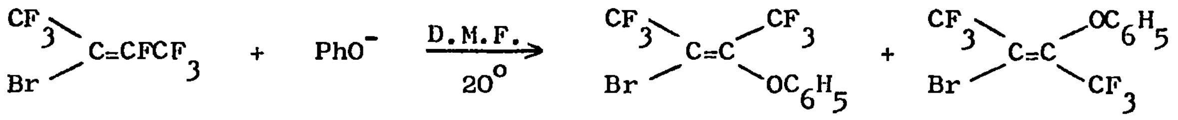
(b) Structure of the products

The components of the product mixture were separated by v.p.c. and were characterised separately. Both compounds had satisfactory elemental analysis and showed a parent peak in their mass spectra (with corresponding ^{37}Cl isotope peak). ^{19}F n.m.r. spectroscopy readily enabled the configuration of the two olefins to be determined. In the *trans* isomer (181) two quartets of relative intensity 1 with a coupling constant of 1·5 Hz. were observed. For the *cis* isomer (180), however, the spectrum was found to consist of an AB system in which the difference in the chemical shifts of the two trifluoromethyl groups was relatively small. This caused overlapping and perturbations in the line intensities. However, inspection of the spectrum clearly showed the presence of a 12 Hz. CF_3-CF_3 coupling, characteristic of a *cis* configuration. Further confirmation of the structures was again obtained from the i.r. spectra of the two isomers where the *trans* olefin (181) was found to have a very weak olefinic stretching vibration at 6·0μ, the *cis* analogue (180), however, showed a corresponding absorption at 6·05 of medium intensity.[125]

V.B.6 Reaction of a Cis-Trans Mixture of 2-Bromo-heptafluorobut-2-ene

(a) Reaction conditions and products

When a *cis:trans* mixture of 2-bromo-heptafluorobut-2-ene (*cis:trans* ratio = 35:65) was reacted with sodium phenoxide in D.M.F. (molar ratio olefin:PhO$^-$ = 1:1) a mixture of the isomeric 2-bromo-3-phenoxy-hexafluorobut-2-enes (182) and (183) was produced.

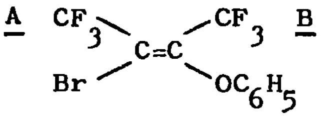
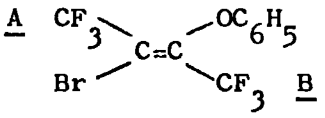


(128) and (129) (182); 28% (183); 52%

cis and trans isomers

(b) Structure of the products

Analytical scale v.p.c. (di-n-decylphthalate) of the material showed the presence of two components with very similar retention times; separation of the mixture by this method proved impossible, consequently complete characterisation was carried out on the mixture of isomers. Elemental analysis proved satisfactory and the mass spectrum of the mixture was found to show a parent peak (with corresponding ^{81}Br isotope peak). ^{19}F n.m.r. spectroscopy clearly showed the presence of two components; resonances at 60·1 62·3, 62·7 and 64·7 p.p.m. (from $CFCl_3$) being observed which were assigned to the various trifluoromethyl groups of the two olefins. Characteristic CF_3-CF_3 couplings of 1·5 Hz. in the trans isomer (183) and 13 Hz. in the cis isomer (182) were apparent in the spectrum.

	J_{AB} (Hz.)
	13
	1·5

Further evidence for a cis:trans mixture came from the i.r. spectrum of the material where two olefinic stretching absorptions were observed at 6·1μ and 6·2μ.

V.C Reactions of Pure Geometrical Isomers with Sodium Phenoxide in Various Aprotic Solvents

V.C.1 Discussion of Technique

A standard procedure was adopted for carrying out these reactions and determining the product composition. In all the reactions 1·0 molar sodium phenoxide solution was used. In brief, with the volatile olefins the sodium phenoxide solution (molar ratio olefin:PhO^- = 1:1) was introduced into a small Carius tube and the olefin was then condensed in, using vacuum line techniques. The tube was sealed and vigorously shaken in a constant temperature bath. For the less volatile olefin, i.e. the butenyl pyridine (102) the substrate was slowly added to the sodium phenoxide in a small flask which was cooled in a constant temperature bath. Determination of the proportion of the geometrical isomers present in the reaction mixture was carried out by integration of the trifluoromethyl group resonances in the ^{19}F n.m.r. spectrum. In this way accurate, reproducible results were obtained.

V.C.2 Reactions of Trans-2H-heptafluorobut-2-ene

Solvent (ϵ)	Temp. °C	% cis (178)	% trans (179)
Dioxane (9·93)	18	~ 3	97
	80	~ 3	97
D.M.F. (37)	18	24	76
N.M.A. (165)	18	18	82
	80	17	83

V.C.3 Reactions of Cis-2-chloro-heptafluorobut-2-ene

Solvent	Temp. °C	% cis (180)	% trans (181)
Dioxane	18	95	5
	80	94	6
D.M.F.	18	72	28
N.M.A.	18	81	19
	80	80	20

V.C.4 Reactions of Trans-2-chloro-heptafluorobut-2-ene

Solvent	Temp. °C	% cis (180)	% trans (181)
Dioxane	18	8	92
	80	12	88
D.M.F.	18	29	71
N.M.A.	18	28	72
	80	25	75

V.C.5 Reactions of Cis-2-bromo-heptafluorobut-2-ene

Solvent	Temp. °C	% cis (182)	% trans (183)
Dioxane	18	93	7
	80	92	8
D.M.F.	18	73	27
N.M.A.	18	90	10
	80	89	11

V.C.6 Reactions of Trans-2-bromo-heptafluorobut-2-ene

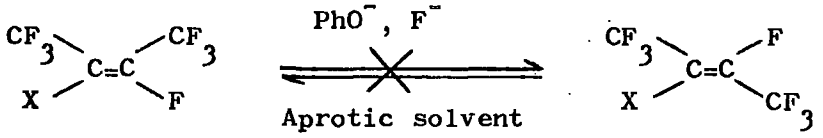
Solvent	Temp. °C	% cis (182)	% trans (183)
Dioxane	18	12	88
	80	13	87
D.M.F.	18	35	65
N.M.A.	18	32	68
	80	35	65

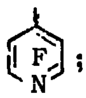
V.C.7 Reactions of Perfluoro-trans-4-(2-butenyl)pyridine

Solvent	Temp. °C	% cis (175)	% trans (176)
Dioxane	18	25	75
	80	24	76
D.M.F.	18	77	23
N.M.A.	18	77	23
	80	78	22

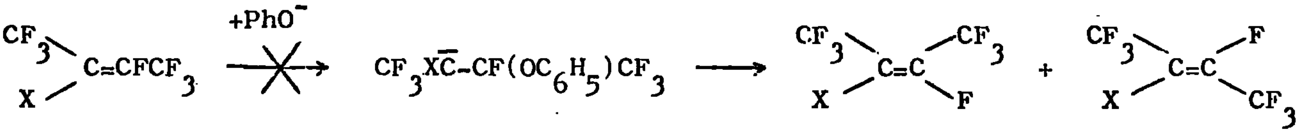
V.C.8 Attempted Equilibration Reactions

Although it is apparent from the results obtained from the reactions of pure geometrical isomers that these nucleophilic substitution processes are not thermodynamically controlled, attempts were made to equilibrate the cis and trans products under the conditions of the reactions. Thus when pure geometrical isomers of the mono-phenoxy products (or cis-trans mixtures of known composition) were stirred with phenoxide and fluoride ion in the various solvents, no equilibration was found to occur in any of the systems studied, i.e.



X = H, Cl, Br,  ; solvents, dioxane, D.M.F., N.M.A.

Similarly, to eliminate the possibility that a rapid pre-equilibrium was operative in these processes pure geometrical isomers of the parent olefins were reacted with a 75% deficiency of sodium phenoxide in the three solvents, dioxane, D.M.F. and N.M.A. The unreacted olefin was isolated from the reaction medium and the isomeric composition of the material determined using ^{19}F n.m.r. spectroscopy. With none of the olefins studied was there any indication that this type of process was operative, for example:



pure geometrical
isomer

X = H, Cl, Br,  ; solvents, dioxane, D.M.F., N.M.A.

V.C.9 Competition Reactions of Polyfluorobut-2-enes

(a) Introduction

As discussed previously (III.B) two mechanistic extremes are possible for nucleophilic vinylic substitution in the type of compounds studied here. A synchronous process analogous to S_N2 reactions in saturated systems is possible; alternatively a stepwise addition-elimination mechanism involving a discrete carbanion may be operative. It was thought that providing accurate quantitative analysis of the components present in competition reaction mixtures was possible, some order of the relative reactivities of the 2-butenes could be obtained. From the order and the magnitude of the differences in reactivity it was thought that information on the mechanism of the reaction could be obtained. Accordingly a series of competition reactions was carried out to determine the relative reactivities of the various but-2-enes. Practical problems prohibited the direct competition of the individual cis and trans isomers of an olefin; these had to be obtained from crossover experiments. The trans-2H-heptafluorobut-2-ene (163) was found to be very much less reactive than the other olefins and the experimental procedure could not be used to give an accurate estimate of its relative reactivity.

Initial reactions were carried out using a 75% deficienty of sodium phenoxide in dioxane; consistent results being obtained. Unfortunately, however, similar reactions using phenoxide in D.M.F. or N.M.A. proved unsuccessful due to differences in solubility of the competing olefins in the reaction medium.

(b) Results

Competition experiments carried out in dioxane at 18°.

(i) Cis-$CF_3ClC{=}CFCF_3$ vs. cis-$CF_3BrC{=}CFCF_3$

$$K\ \frac{\text{cis-}CF_3BrC{=}CFCF_3}{\text{cis-}CF_3ClC{=}CFCF_3} = 1{\cdot}3$$

(ii) *Cis*-$CF_3ClC{=}CFCF_3$ vs. *trans*-$CF_3BrC{=}CFCF_3$

$$K\,\frac{\textit{trans-}CF_3BrC{=}CFCF_3}{\textit{cis-}CF_3ClC{=}CFCF_3} = 1{\cdot}5$$

(iii) *Trans*-$CF_3ClC{=}CFCF_3$ vs. *cis*-$CF_3BrC{=}CFCF_3$

$$K\,\frac{\textit{cis-}CF_3BrC{=}CFCF_3}{\textit{trans-}CF_3ClC{=}CFCF_3} = 1{\cdot}4$$

(iv) *Trans*-$CF_3ClC{=}CFCF_3$ vs. *trans*-$CF_3BrC{=}CFCF_3$

$$K\,\frac{\textit{trans-}CF_3BrC{=}CFCF_3}{\textit{trans-}CF_3ClC{=}CFCF_3} = 1{\cdot}4$$

(v) Perfluoro-*trans*-4-(2-butenyl)pyridine vs. *cis*-$CF_3ClC{=}CFCF_3$

$$K\,\frac{\text{perfluoro-}\textit{trans}\text{-4-(2-butenyl)pyridine}}{\textit{cis-}CF_3ClC{=}CFCF_3} = 11{\cdot}5$$

(vi) Perfluoro-*trans*-4-(2-butenyl)pyridine vs. *trans*-$CF_3ClC{=}CFCF_3$

$$K\,\frac{\text{perfluoro-}\textit{trans}\text{-4-(2-butenyl)pyridine}}{\textit{trans-}CF_3ClC{=}CFCF_3} = 11{\cdot}7$$

(vii) Perfluoro-*trans*-4-(2-butenyl)pyridine vs. *cis*-$CF_3BrC{=}CFCF_3$

$$K\,\frac{\text{perfluoro-}\textit{trans}\text{-4-(2-butenyl)pyridine}}{\textit{cis-}CF_3BrC{=}CFCF_3} = 7{\cdot}5$$

(viii) Perfluoro-*trans*-4-(2-butenyl)pyridine vs. *trans*-$CF_3BrC{=}CFCF_3$

$$K\,\frac{\text{perfluoro-}\textit{trans}\text{-4-(2-butenyl)pyridine}}{\textit{trans-}CF_3BrC{=}CFCF_3} = 7{\cdot}6$$

From these results it can be deduced that the relative reactivities of the individual *cis* and *trans* isomers are of the order:

(ix) $$K\ \frac{\textit{cis}\text{-}CF_3ClC{=}CFCF_3}{\textit{trans}\text{-}CF_3ClC{=}CFCF_3} \approx 1{\cdot}1$$

(x) $$K\ \frac{\textit{cis}\text{-}CF_3BrC{=}CFCF_3}{\textit{trans}\text{-}CF_3BrC{=}CFCF_3} \approx 1{\cdot}0$$

V.C.10 Discussion

From the results obtained in these reactions with phenoxide in the various solvents several conclusions can be drawn.

(a) There is a general tendency towards retention of the configuration of the original olefin.

(b) The least reactive olefins lead to the highest stereospecificity.

(c) Stereospecificity decreases with increasing dielectric constant of the solvent.

(d) The pyridine derivative (102) leads to the lowest stereospecificity and in solvents of high dielectric constant the preferential route leads to inversion of the configuration of the parent olefin.

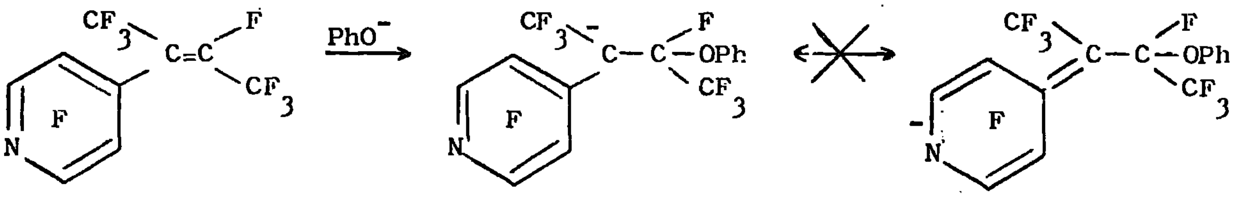
(e) Steric effects cannot be very important because similar degrees of stereospecificity are obtained from *cis* and *trans* isomers and, clearly, the reactions are not equilibrium controlled.

Previous reports of this type of reaction, in which retention of configuration has been observed, have proposed both planar[103] and tetrahedral[101] carbanions as the intermediates from which the product olefins are formed. However, it is thought that in the compounds studied here, a tetrahedral species is responsible for the observed results. Evidence for this may come from the relative reactivity studies where it was found that the pyridine derivative (102) was not as reactive, compared to the chloro (132), (133) and bromo (128), (129) analogues as could have been expected.

$$K\ \frac{\text{perfluoro-4-(2-butenyl)pyridine}}{\textit{cis}\text{- and }\textit{trans}\text{-}CF_3ClC{=}CFCF_3} \approx 11{\cdot}7$$

$$K\ \frac{\text{perfluoro-4-(2-butenyl)pyridine}}{\textit{cis}\text{- and }\textit{trans}\text{-}CF_3BrC{=}CFCF_3} \approx 7{\cdot}5$$

If the carbanions in these reactions are planar, then in the pyridine (102) case a stabilising mesomeric interaction could be expected in the intermediate anion (184), rendering this compound considerably more reactive than the other compounds in the series. However as can be seen from the results this is not the case.



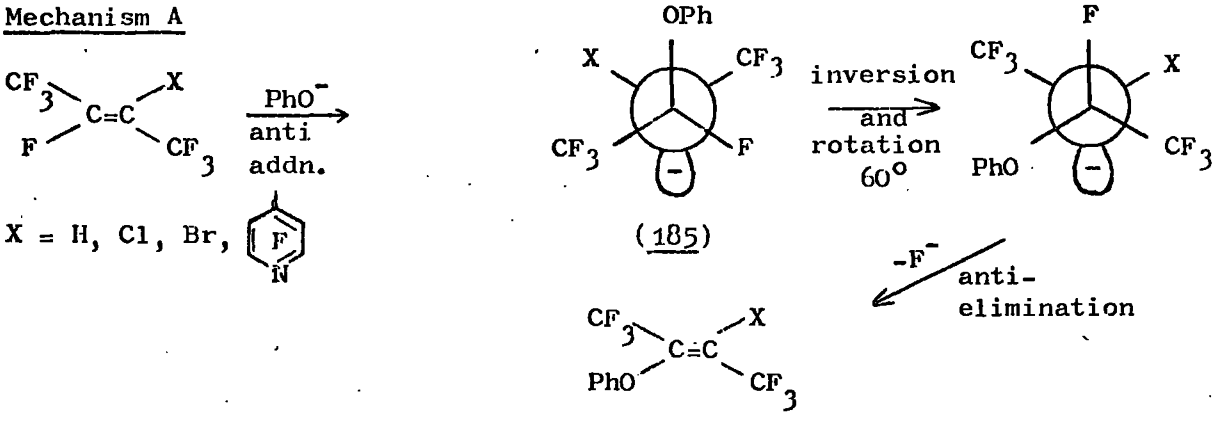
(102) (184)

Similarly, as discussed previously (I.B.1) in simple carbanions not stabilised by resonance a pyramidal structure with sp^3 hybridisation is favoured over a planar configuration (in which the non-bonding electrons are localised within a p orbital) on electronic grounds.

Thus assuming a tetrahedral carbanion is the intermediate from which the products are formed, two basic reaction schemes which will lead to retention of the original configuration of the starting olefin can be envisaged (i.e. cis → cis; trans → trans).

In the first (mechanism A) formation of the carbanion (185) takes place by an anti addition of the nucleophile to the olefinic system. This carbanion then rapidly inverts and rotates through 60° to produce the diastereoisomeric anion (186) which can then eliminate fluoride ion in an anti manner, for example:

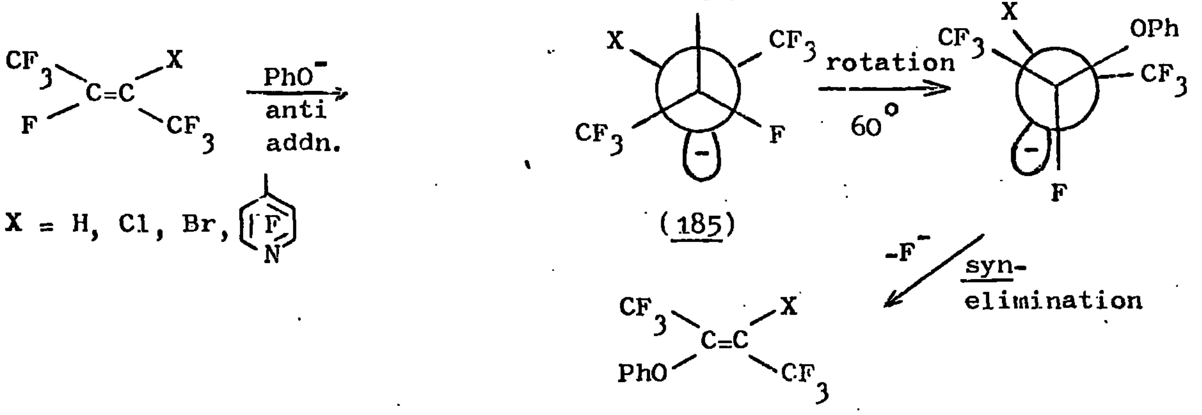
Mechanism A



(185)

The alternative mechanism (B), again is proposed to involve an *anti* addition of the nucleophile to form a tetrahedral carbanion (185), simple rotation through 60° followed by a *syn* elimination will give a product with the same configuration as the starting olefin, for example:

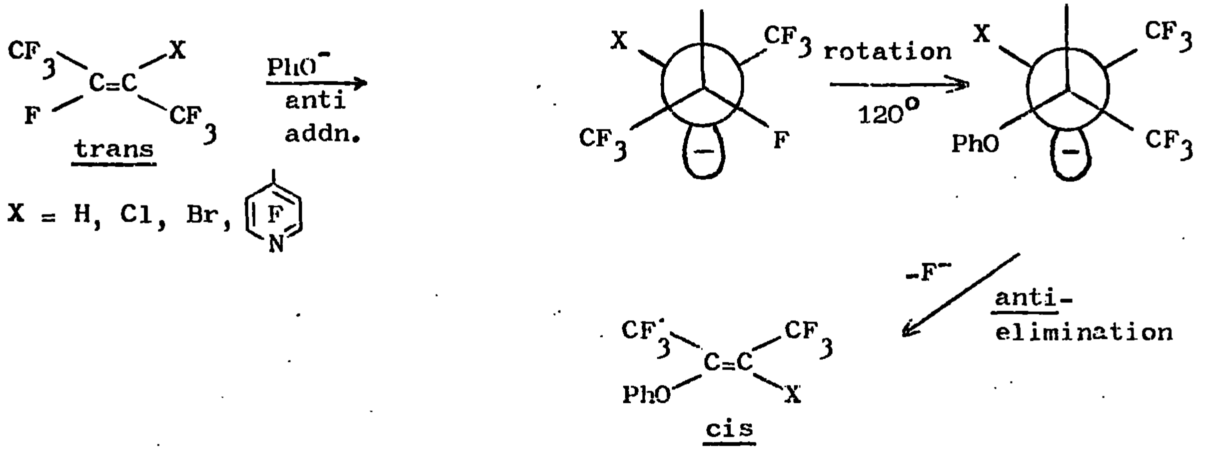
Mechanism B



(Alternatively a *syn* addition followed by rotation through 60° and an *anti* elimination would give a product with retention, however, this does not alter the nature of the arguments).

The mechanism involving the two *anti* steps (route A), although favoured on steric grounds,[107] appears rather unlikely when the time required for the inversion and rotation processes is considered. If sufficient time is available for these processes, it is expected that sufficient time should be available for simple rotation through 120° followed by *anti* elimination to yield the olefin with overall inversion of the original configuration, for example with a *trans* olefin.

Mechansim C



Thus route A seems unlikely.

The second route (B) appears to be more likely, i.e. formation of a tetrahedral carbanion, which has considerable configurational stability, which eliminates fluoride ion in a syn manner. With this mechanism in mind a possible rationalisation of the results and solvent effects in these reactions can be obtained i.e. loss of stereospecificity with increasing dielectric constant.

The highest stereospecificity is observed with the trans-2H-butene (163), the compound which is expected to produce the carbanion of lowest stability (I.A.2). Therefore in dioxane little time is expected to be available for the elimination step which may then be forced to proceed by a syn mechanism. In solvents of higher dielectric constant i.e. D.M.F. and N.M.A., the stability and hence the lifetime of the intermediate is increased thus allowing more time for inversion and/or rotation to occur (routes A and C) which will produce an anion from which an anti elimination step will lead to an olefin with overall inversion of the original configuration.

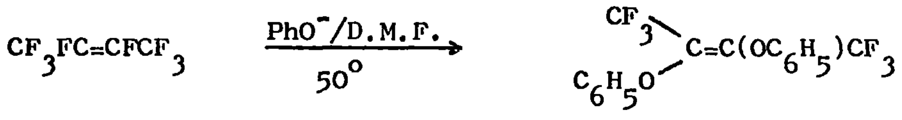
With the 2-chloro (132 and 133) and 2-bromo-but-2-enes (128 and 129) which are expected to produce carbanions of greater stability and a longer lifetime the reaction could be expected to proceed with lower stereospecificity than for the 2H-butene (163).

In the pyridine system (102), which is expected to produce an anion of high relative stability the reaction in dioxane is seen to have low stereospecificity as may have been expected. Indeed in D.M.F. and N.M.A. the reaction is seen to proceed with preferential inversion of configuration. Thus the results of these experiments have been rationalised on the relative lifetimes of the intermediate carbanions produced by an initial anti attack by phenoxide.

As discussed previously both tetrahedral and planar carbanions have been proposed as being responsible for the stereochemical results of these reactions, however, in one case[101] the high stereospecificity has been rationalised as involving anti addition followed by a syn elimination.

Although not directly related, E2 reactions in acyclic systems have been shown in many cases to proceed by an anti route which has been rationalised on steric grounds. This has led in the past to the general rule that facile eliminations only proceed when the leaving groups are in a trans diaxial conformation. However, recent work, especially by Sicher,[107] has shown that this is not always the case and that substantial contributions from a syn elimination pathway are operative in many of these reactions. Similarly a syn elimination has recently been reported in an E1c.b. elimination from two sulphonyl fluoroethanes.[108] The authors have proposed the formation of an ion pair which collapses to the products via an overall syn course (III.D).

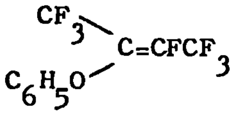
In the reaction of perfluorobut-2-ene the diphenoxy derivative (177) was produced; no indication of the presence of this compound was observed in



$$CF_3FC{=}CFCF_3 \xrightarrow[50^{o}]{PhO^{-}/D.M.F.} (CF_3)(C_6H_5O)C{=}C(OC_6H_5)CF_3$$

(177)

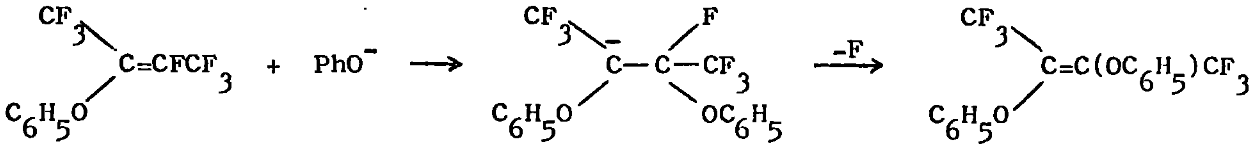
the reactions of the 2-chloro and 2-bromo analogues with phenoxide. This is probably an indication of the effect of fluorine on both the ground and transition states, i.e. it renders the attached carbon highly electrophilic in the mono-phenoxy derivative (186) which is presumably an intermediate product. Similary, as it is in a β position relative to the negative charge



$$(CF_3)(C_6H_5O)C{=}CFCF_3$$

(186)

in the anion (187) derived from (186) and phenoxide in the subsequent reaction it stabilises the transition state, i.e



(186) (187) (177)

V.C.11 General Conclusions

It has been shown that the stereochemical results of these reactions of the polyfluorobut-2-enes with phenoxide studied here are critically dependent on the solvent and substituents.

A general trend, 'the higher the dielectric constant of the medium, the lower the tendency towards retention of the original configuration of the starting olefin' has been observed. The highest stereospecificity is observed with the 2H-but-2-ene with the lowest being observed with perfluoro-trans-4-(2-butenyl)pyridine.

These trends are thought to be due to the formation of a tetrahedral carbanion, by an anti addition of the nucleophile, the lifetime of which is critically dependent on the solvent.

Retention of configuration is thought to be a consequence of a syn elimination of fluoride ion after rotation of the carbanion through 60°. An anti elimination after rotation and/or inversion is thought to be responsible for the formation of products with inverted stereochemistry.

CHAPTER VI

Organometallic Chemistry

VI.A Introduction

Numerous reports have appeared in the literature in which perfluoro- and polyfluoro-organometallic derivatives have been prepared;[141] many of these compounds tend to be more stable than their hydrocarbon analogues, however, exceptions to this are known i.e. extension of the organoboron chemistry developed by H.C. Brown to organofluorine compounds has proved unsuccessful.

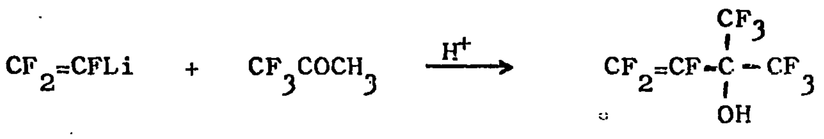
Many of these fluorocarbon organometallic compounds are easily synthesised and several methods are available for their preparation including metal-halogen (i.e. Cl, Br or I) or hydrogen exchange. As we had available heptafluorobut-2-enes containing hydrogen or halogen it was thought that attempts to prepare the corresponding organometallic derivatives followed by their subsequent reactions could provide a useful route for the introduction of a perfluoro-2-butenyl group into numerous organic molecules.

VI.B Organo-lithium Derivatives

1. Perfluoro-2-butenyl-lithium

Several reports appear in the literature in which fluorine containing vinyl organo-lithium derivatives have been prepared by metal-halogen or metal-hydrogen exchange using butyl or methyl-lithium.[142-4] Their subsequent *in situ* reactions with reactive substrates i.e. carbonyl compounds, triethylchlorosilane etc. have provided a valuable route to unsaturated polyfluoro compounds. For example, trifluorovinyl-lithium reacts readily with trifluoroacetone in tetrahydrofuran or diethyl ether to produce the vinyl alcohol (188).

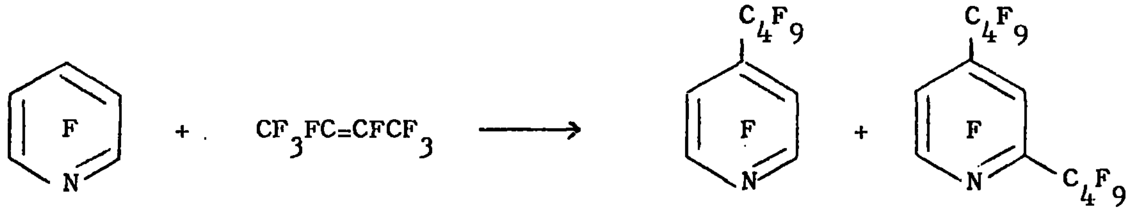
$$CF_2{=}CFBr \quad + \quad BuLi \quad \xrightarrow[T.H.F.]{-78^{o}} \quad CF_2{=}CFLi \quad + \quad BuBr$$



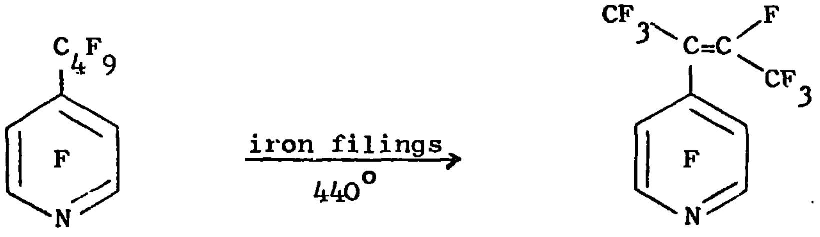
$$CF_2{=}CFLi \quad + \quad CF_3COCH_3 \quad \xrightarrow{H^+} \quad CF_2{=}CF{-}\underset{\displaystyle OH}{\overset{\displaystyle CF_3}{C}}{-}CF_3$$

(188); 73%

Consequently it was thought that by using similar techniques the butenyl-lithium derivatives (190) could be prepared and used to synthesise numerous heptafluoro-2-butenyl derivatives which to date are not readily available. For example, perfluoro-4-(2-butenyl)-pyridine (102) is normally prepared by a two stage route using perfluorobut-2-ene, caesium fluoride and pentafluoropyridine to produce the 4-sec-butyl derivative (189) which is subsequently defluorinated to the 2-butenyl compound.[112]



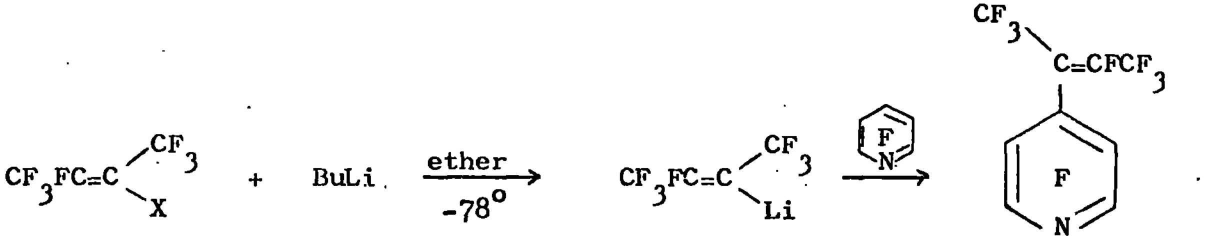
(189)



(189)

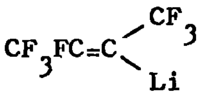
(102)

It was thought that this derivative could have been prepared by a simple one step process using the butenyl-lithium derivative, i.e.



(190)

A large number of experiments in which attempts to trap the heptafluorobutenyl-lithium derivative (190), prepared by metal halogen exchange on the

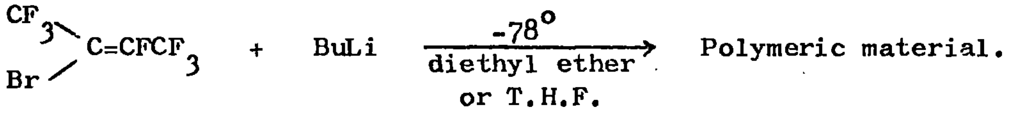


$CF_3FC=C(CF_3)Li$

(190)

2-bromo derivatives (128 and 129) using butyl-lithium were carried out. The metal-halogen exchange reaction was thought to proceed fairly readily as tests for butyl lithium, half an hour after it's addition produced negative results.[145]

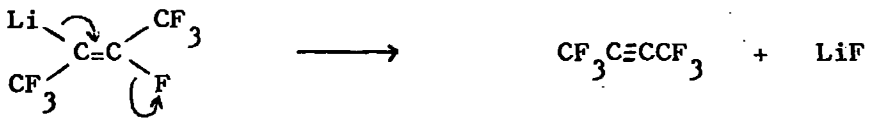
Numerous trapping agents, including HCl gas, chlorotrimethylsilane [$(CH_3)_3SiCl$], mercuric chloride, diethyl carbonate and carbon dioxide were used. However, even though the conditions of the reaction i.e. addition times of BuLi solution, time allowed for exchange etc. were varied, only high molecular weight polymeric material was isolated from these reactions.



Similar results were obtained from analogous reactions of trans-2H-heptafluorobut-2-ene. Investigation of this polymeric material showed it to have a similar structure to homopolymer derived from fluoride ion initiated reactions of hexafluorobut-2-yne, i.e.

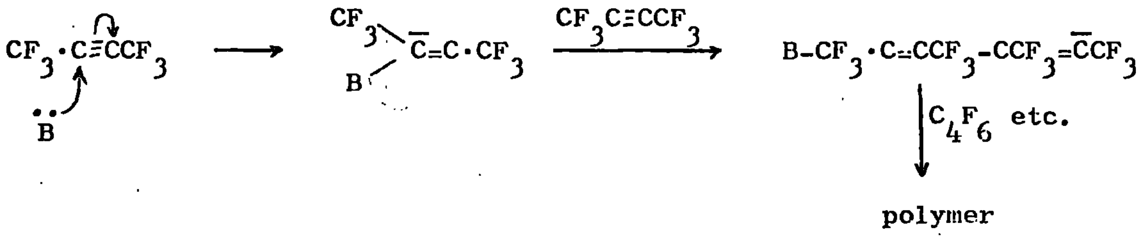
$$\left[(CF_3)C{=}C(CF_3)\right]_n$$

With these observations in mind the results of these reactions can best be rationalised by assuming that initial generation of the lithium derivative (190) occurs fairly readily but that the compound is relatively unstable and under the conditions of the reaction readily eliminates lithium fluoride to produce hexafluorobut-2-yne, i.e.



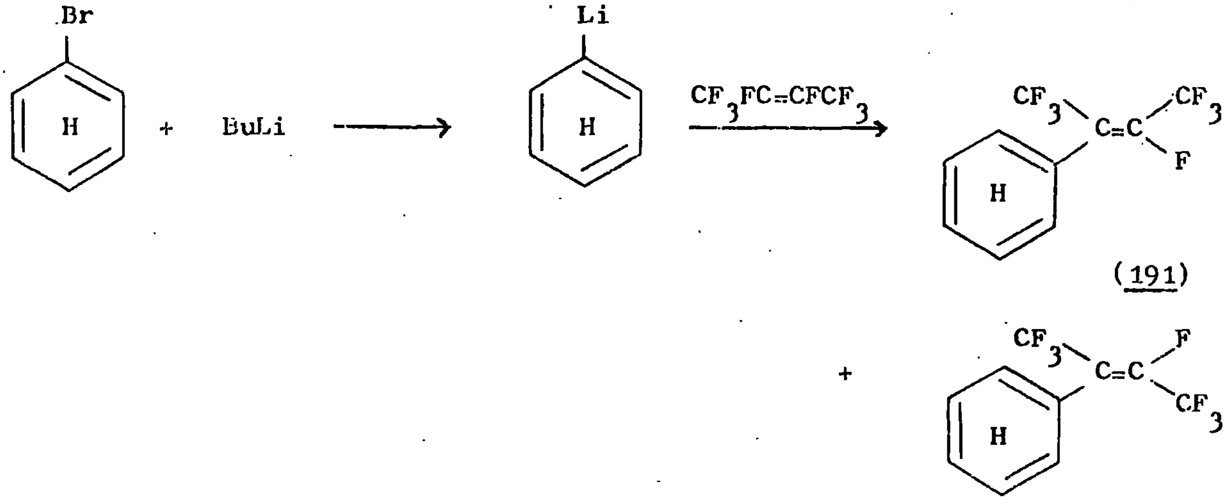
(190)

which in turn polymerises under the basic conditions, i.e.



2. Attempted preparation of perfluoro-4-(2-butenyl)-pyridine

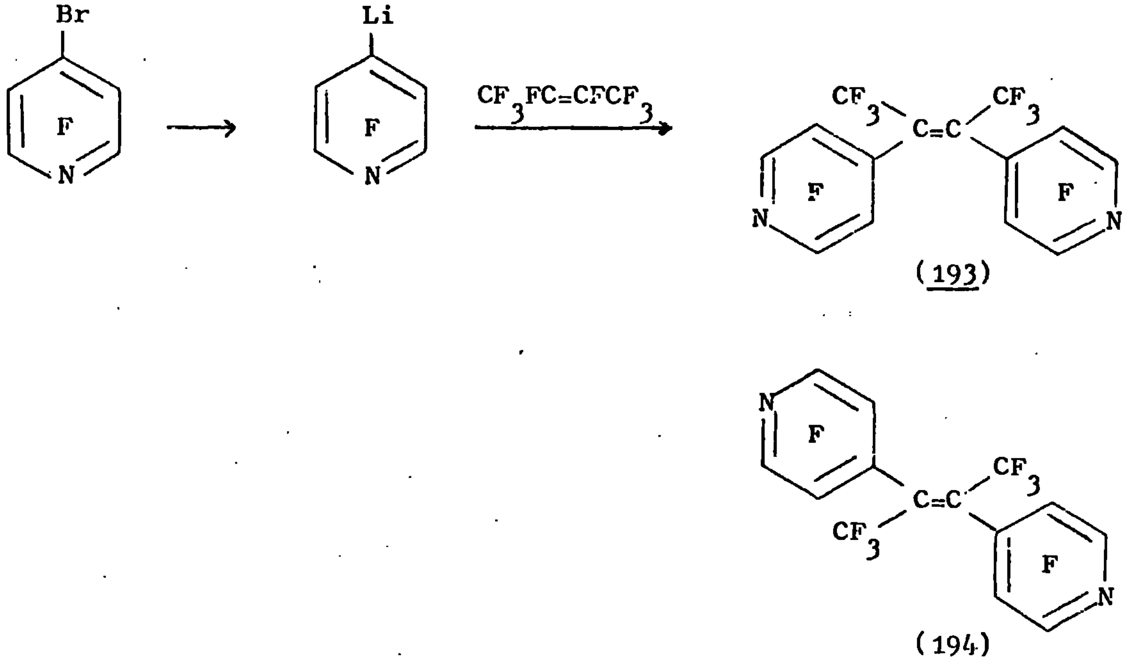
Andreades[118] showed that reaction of phenyl-lithium with perfluorobut-2-ene at low temperature produced a cis-trans mixture of 2-phenyl-heptafluorobut-2-enes (191) and (192) in good yield, i.e.



(191)

(192)

Attempts to extend this reaction to the preparation of perfluoro-4-(2-butenyl)-pyridine, however, have not been successful. Thus it was found that when perfluorobut-2-ene was allowed to react with tetrafluoropyridyl-lithium a mixture of cis- and trans-perfluoro-2,3-di-(4-pyridyl)but-2-ene (193) and (194) was produced.



(193)

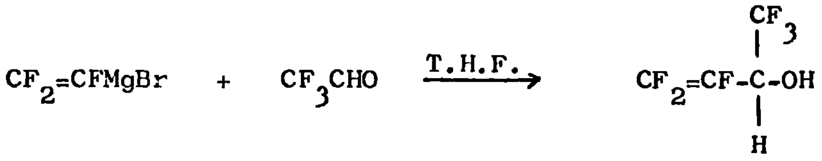
(194)

Variation of the reaction conditions i.e. addition of tetrafluoropyridyllithium to an excess of octafluorobut-2-ene similarly produced only the disubstituted derivatives (193) and (194) which must be an indication of the differences in reactivity between perfluorobut-2-ene and perfluoro-4-(2-butenyl)-pyridine.

Separation of the two isomers was not attempted and characterisation was carried out on the cis-trans mixture. ^{19}F n.m.r. spectroscopy clearly showed that the compounds contained the perfluoro-4-pyridyl nucleus, resonances at 87·3 p.p.m., attributed to the 2,6 fluorines, and 134·6 (from $CFCl_3$) being assigned to the 3,5 fluorines. Broad uncoupled resonances at 62·7 and 59·6 p.p.m., assigned to the trifluoromethyl groups in the two isomers, further confirmed the structure of the compounds. Due to the absence of trifluoromethyl group couplings it was found impossible to assign these resonances.

VI.C Organo-magnesium Derivatives

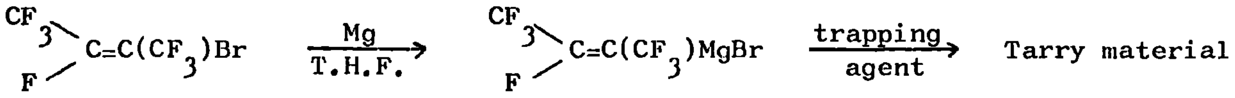
Analogous to vinyl-lithium derivatives unsaturated fluorinated organomagnesium compounds have provided useful intermediates in the preparation of unsaturated polyfluoro compounds.[144] For example, trifluorovinylmagnesium bromide reacts readily with trifluoroacetaldehyde to produce the expected secondary alcohol (195).



$$CF_2{=}CFMgBr + CF_3CHO \xrightarrow{T.H.F.} CF_2{=}CF\text{-}\underset{H}{\overset{CF_3}{C}}\text{-}OH$$

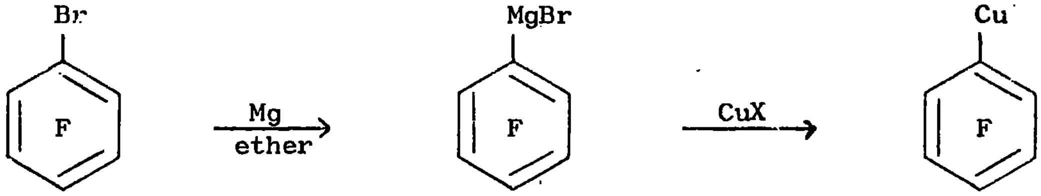
(195)

Extension of this type of reaction to 2-bromoheptafluorobut-2-ene however has met with no success. Formation of the Grignard appears to take place readily in T.H.F. but not in diethyl ether, however, attempted trapping with mercuric chloride, perfluoropyridazine, and carbon dioxide produced only tarry material derived from the butene.

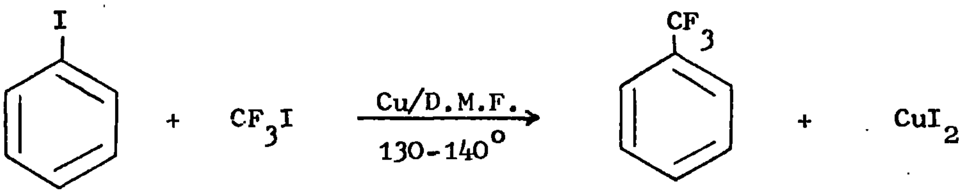


VI.D Organo-copper Derivatives

Numerous reports appear in the literature in which organo-copper derivatives of fluorocarbons have been prepared.[146-149] In certain cases these organometallic derivatives have been isolated as their dioxane complexes and have been found to be more stable than the perhydro analogues.[146] For example pentafluorophenyl copper has been isolated in 70% yield from the Grignard reagent with a cuprous halide in ether, i.e.

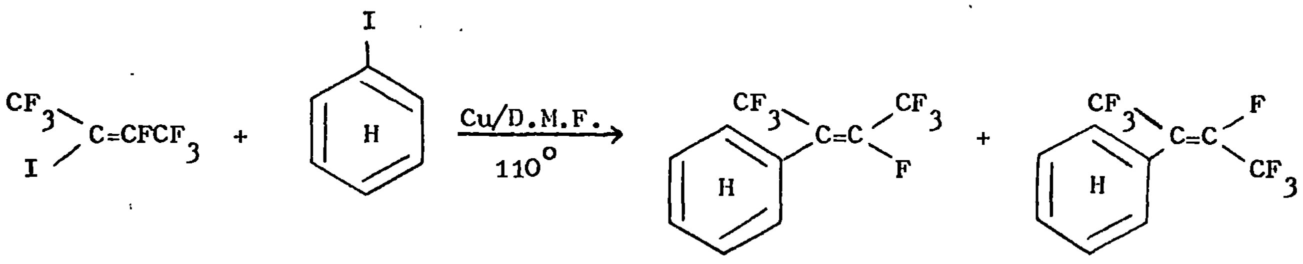


Also it has been shown that it is possible to introduce a perfluoroalkyl group into an aromatic ring by heating the perfluoroalkyl halide, the aromatic halide and metallic copper in an aprotic solvent.[148] For example trifluoromethyliodide reacts with iodobenzene at 130° ⟶ 140° in D.M.F. to produce benzotrifluoride (196) in good yield.



(196); 74%

Extension of this type of reaction to 2-iodo-heptafluorobut-2-ene (126) and (127) with iodobenzene in D.M.F. at 110° produced a *cis-trans* mixture of 2-phenyl-heptafluorobut-2-enes (197) and (198) in good yield.

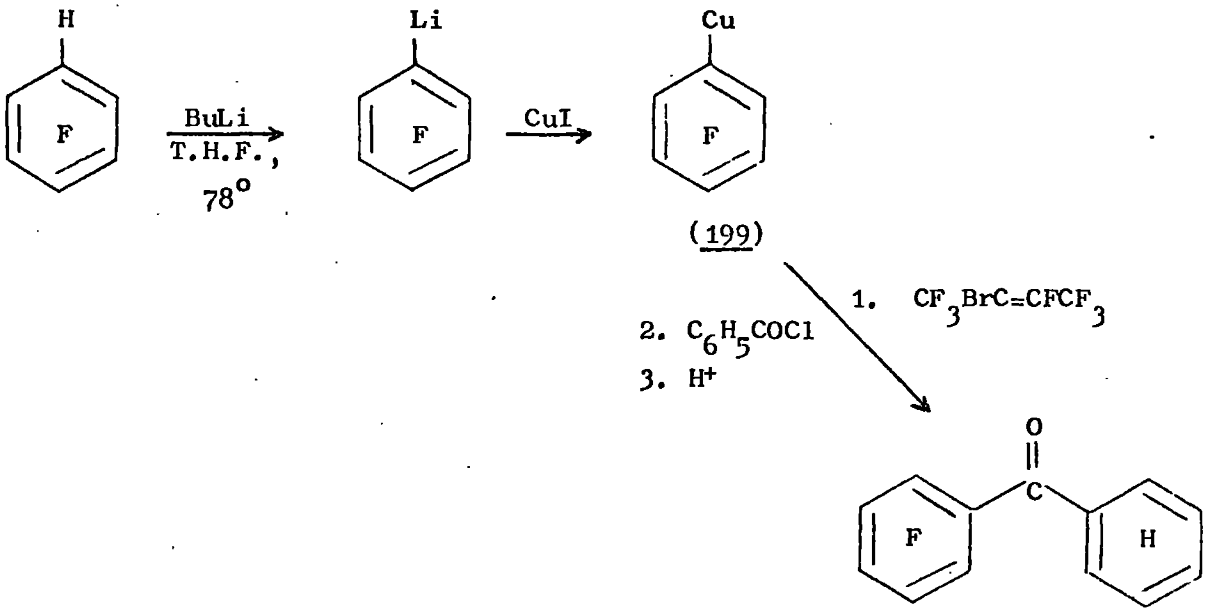


(197); 38·5% (198); 31·5%

Attempts to extend this reaction to the more readily available 2-bromoheptafluorobut-2-ene (128) and (129) were made, however, although numerous reactions were carried out with various temperatures and reaction times it appears that at the temperature required for formation of the copper derivative from this compound, decomposition of the organometallic derivative occurs and substantial quantites of 2H-heptafluorobut-2-ene are produced, presumably by extraction of a hydrogen atom from the solvent.

It was thought that this method could be readily extended to prepare other derivatives of heptafluorobut-2-ene.

Several reactions in which attempts were made to prepare the 2-butenylcopper derivative (199) by exchange, using pentafluorophenyl copper and 2-bromo-heptafluorobut-2-ene proved unsuccessful. Thus when benzoyl chloride was added to solutions of pentafluorophenyl-copper[150] and the bromobutene (128) and (129) only pentafluorobenzophenone was isolated, indicating


(199)

that formation of the butenyl copper derivatives had not occurred.

EXPERIMENTAL

CHAPTER VII

Reactions of Hexafluorobut-2-yne with Nucleophiles

VII.A Fluoride Ion-inititated Reactions

VII.A.1 Trapping with Perfluoroheterocyclic Compounds

VII.A.1.a Reactions with tetrafluoropyrimidine

(i) at 20°

Reaction was carried out at almost atmospheric pressure in a simple apparatus which has been described previously. Caesium fluoride (3·0g., 20·0 m.mole), sulpholan (25 ml.) and tetrafluoropyrimidine (1·5 gm., 10 m.mole) were contained in a flask equipped with a magnetic stirrer and a two way adaptor, the outlets from which were connected to a football bladder and a vacuum line. (All the apparatus had previously been baked at 110° and purged with dry nitrogen). The flask was cooled in liquid air and evacuated, and the pressure inside the system then adjusted to approximately 10 cms. Hg. with dry nitrogen. Hexafluorobut-2-yne was admitted from the bladder until the pressure within the system was atmospheric. A vacuum slowly developed within the system when the mixture was stirred vigorously. Small quantities of the acetylene were further introduced when a vacuum developed within the apparatus. Addition was regarded as being completed when no further uptake of acetylene occurred. The total weight of hexafluorobut-2-yne (1·6 gm., 10 m.mole) consumed in the reaction was deduced by re-weighing the bladder. Distillation of the reaction mixture under vacuum, up to ca. 70° produced, after removal of unreacted hexafluorobut-2-yne by atmospheric distillation, a clear liquid (1·8 gm., 63% based on 70% conversion of hexafluorobut-2-yne). Analysis of the liquid by v.p.c. showed that it contained three major components one of which was identified as starting material by chromatographic methods using the mixed injection technique. The products of the reaction were separated from the starting material using preparative scale v.p.c. (di-n-decylphthalate, 90°). The products were characterised as a mixture and were identified as perfluoro-cis- and -trans-4-(2-butenyl)pyrimidine, b.p. 110° (Siwoloboff). [Found: C, 30·5; F, 60·2; N, 9·1%; M^+, 314. $C_8F_{10}N_2$ requires C, 30·6; F, 60·5; N, 8·9; M, 314]. The individual geometrical isomers could readily be identified by their ^{19}F n.m.r. spectra. Integration of the trifluoromethyl group resonances indicated a 10:90, cis:trans ratio of the geometrical isomers. Infrared spectrum No. 9.

(ii) at 100°

In a similar experiment, a mixture of caesium fluoride (2·5 gm., 16·4 m.mole), tetrafluoropyrimidine (1·5 gm., 10 m.mole) and sulpholan (25 ml.) was vigorously stirred at 100°. Hexafluorobut-2-yne (1·7 gm., 10·5 m.mole) was slowly introduced into the system. Volatile materials (2·3 gm.) were distilled from the apparatus under vacuum at ca. 70°. V.p.c. showed the presence of two major components with a small amount of material (< 10%) of higher retention time. Preparative scale v.p.c. (di-n-decylphthalate; 90°) was used to separate the major components which were shown to be (in order of emergence from column):

(a) perfluoro-trans-4,6-di-(2-butenyl)pyrimidine, 31%, b.p. ≈ 120° (Siwoloboff). [Found: C, 30·2; F, 63·7; N, 5·5; M^+, 476. $C_{12}F_{16}N_2$ requires C, 30·3; F, 63·9; N, 5·8; M, 476]. Infrared spectrum No. 10.

(b) perfluoro-trans-4-(2-butenyl)pyrimidine, 26%, which was identified by comparison of its i.r. spectrum with that of an authentic sample prepared from a similar reaction carried out at 20°.

Although not isolated a small amount of perfluoro-cis-4-(2-butenyl)-pyrimidine was identified as a component of the mixture by analytical scale v.p.c. (di-n-decylphthalate, 90°).

VII.A.1.b Reaction with cyanuric fluoride

Cyanuric fluoride (1·5 gm., 11·1 m.mole), caesium fluoride (2·0 gm., 13·0 m.mole) and sulpholan (25 ml.) were vigorously stirred together in the standard atmospheric pressure system which was maintained at 20°. Hexafluorobut-2-yne (1·8 gm., 11·1 m.mole) was slowly introduced into the apparatus from the flexible reservoir. When addition of the acetylene was complete attempts were made to isolate products of the reaction by vacuum distillation at 60°. However, only a small amount (ca. 0·1 gm.) of starting material was recovered. The solution was then poured into water (100 ml.) and substantial quantities of intractable tars were isolated along with some solid polymeric material.

VII.A.2 Reaction with Mercuric Chloride

Freshly sublimed mercuric chloride (2·3 gm., 8·5 m.mole), caesium fluoride (1·5 gm., 10·0 m.mole) and sulpholan (25 ml.) were vigorously agitated in the atmospheric pressure system previously described (VII.A.1) which was maintained at 110° by extermal heating. Hexafluorobut-2-yne (1·0 gm., 6·2 m.mole) was slowly introduced from the flexible reservoir; reaction was seen to take place slowly by observing the formation of a slight vacuum within the system. After approximately 4 hrs., a white crystalline solid began to accumulate in the neck of the flask. Upon completion of addition of the acetylene, a white solid (1·5 gm.), which was found to be contaminated with sulpholan, was sublimed from the flask (25°, 0·05 mm. Hg.). Recrystallisation from carbon tetrachloride yielded a white crystalline solid (1·1 gm., 64%, based on hexafluorobut-2-yne) which was identified as <u>perfluoro-trans-bis(2-butenyl)mercury</u>, m.p. 70°. [Found: C, 16·9; F, 47·4; Hg, 35·6%; M^+, 560 (with correct isotope pattern for Hg.). $C_8F_{14}Hg$ requires C, 17·1; F, 47·3; Hg, 35·6%; M, 560 with Hg isotope peaks]. Infrared spectrum No. 11.

VII.A.3 Trapping with Halogens

VII.A.3.a Reaction with iodine

Iodine (2·8 gm., 11·0 m.mole), caesium fluoride (1·6 gm., 10·0 m.mole) and sulpholan (25 ml.) were vigorously stirred in the atmospheric pressure apparatus previously described. Hexafluorobut-2-yne (1·6 gm., 10·0 m.mole) was slowly introduced from the flexible reservoir, reaction was seen to take place fairly readily by observing the formation of a slight vacuum within the system. Volatile materials (2·4 gm., 79% based on hexafluorobut-2-yne) were transferred from the apparatus under vacuum; analytical scale v.p.c. (di-n-decylphthalate, 70°) showed the presence of two components with very similar retention times. The material was identified as a mixture of cis- and trans-2-iodo-heptafluorobute-2-ene, b.p. 70° (Siwoloboff). [Found: C, 15·7; F, 43·2; I, 41·0%; M^+, 308. C_4F_7I requires C, 15·6; F, 43·2; I, 41·2%; M, 308]. Cis:trans ratio = 68·32. Infrared spectrum No. 12.

VII.A.3.b Reaction with bromine

Bromine (1·0 gm., 6·25 m.mole), caesium fluoride (2·0 gm., 13·1 m.mole) and sulpholan (25 ml.) were vigorously stirred together in the atmospheric pressure apparatus described previously. Hexafluorobut-2-yne (0·8 gm., 5·0 m.mole) was slowly introduced from the flexible reservoir; reaction took place fairly rapidly. Volatile materials (0·95 gm., 73%, based on hexafluorobut-2-yne) were transferred from the apparatus under vacuum, analytical scale v.p.c. (di-n-decylphthalate, 50°) showed the presence of two components with almost identical retention times. The material was identified as a mixture of cis- and trans-2-bromo-heptafluorobut-2-ene by comparison of its i.r. and ^{19}F n.m.r. spectra with those of an authentic sample.[126] Cis: trans ratio = 56:44.

VII.A.3.c Control experiments

In order to ascertain that the reactions with halogen and fluoride ion did not proceed by formation of a 1,2-dihalo-but-2-ene followed by nucleophilic displacement of halide ion by fluoride, reactions were carried out with hexafluorobut-2-yne in the absence of caesium fluoride.

The halogen (approx. 1·0 gm.) and sulpholan (25 ml.) were vigorously agitated in the presence of hexafluorobut-2-yne at room temperature. With both bromine and iodine no reaction was found to take place i.e. no vacuum developed within the system and no volatile materials were isolated from the apparatus.

VII.A.4 Equilibration Reactions of Polyfluorobut-2-enes Promoted by Fluoride Ion

VII.A.4.a With perfluoro-*trans*-4-(2-butenyl)pyridine

Perfluoro-*trans*-4-(2-butenyl)pyridine (prepared by defluorination of perfluoro-4-sec-butylpyridine (VIII.G.4)^{112}) (1·0 gm., 3·0 m.mole), caesium fluoride (0·5 gm., 3·3 m.mole) and sulpholan (25 ml.) were vigorously stirred together in a small flask fitted with a reflux condenser which was sealed with a drying tube. The flask was heated to 100° for 6 hrs. and the volatile materials were then removed under vacuum (0·8 gm., 80%). Analytical scale v.p.c. (di-n-decylphthalate) showed the presence of two components which had almost identical retention times. The material was identified as a mixture of *cis*- and *trans*-perfluoro-4-(2-butenyl)pyridine. [Found: C, 32·5; N, 4·5; F, 63·0%; M^+, 331. Calc. for $C_9F_{11}N$: C, 32·6; N, 4·3; F, 63·1%; M, 331]. *Cis*:*trans* ratio = 17:83.

VII.A.4.b With a mixture of perfluoro-*cis*- and -*trans*-4-(2-butenyl)pyridine

Due to the extreme similarity of the v.p.c. retention times and the low proportion of the *cis* isomer in the equilibrium mixture, it was found impossible to isolate substantial quantites of this isomer in a pure state from the equilibrium mixture. Accordingly enrichment of the proportion of the *cis* isomer present in the mixture was affected by preparative scale v.p.c. (di-n-decylphthalate, 80°). A small quantity of this *cis* enriched mixture (1·0 gm., 3·0 m.mole, *cis*:*trans* ratio = 45:55), caesium fluoride (0·3 gm., 1·2 m.mole) and sulpholan (15 ml.) were treated under the same conditions as those previously described for the *trans* isomer (VII.A.4.a). Volatile materials were removed under vacuum (0·9 gm.). Analytical scale v.p.c. (G.D.B., di-n-decylphthalate, 90°) showed that the cis:trans ratio had changed to its equilibrium composition of 17:83. This was confirmed by integration of the trifluoromethyl group resonances of the two compounds in the ^{19}F n.m.r. spectrum.

VII.A.4.c With perfluoro-trans-4-(2-butenyl)pyrimidine

Perfluoro-trans-4-(2-butenyl)pyrimidine (0·8 gm., 2·5 m.mole), caesium fluoride (0·3 gm., 1·2 m.mole) and sulpholan (5 ml.) were stirred together at room temperature for 8 hrs. in a small sealed flask. Volatile materials (0·7 gm.) were removed from the solvent under vacuum at 40°. Analytical scale v.p.c. (di-n-decylphthalate, 90°) showed the presence of two components which were identifed by v.p.c. and ^{19}F n.m.r. spectroscopy as (in order of emergence from column) perfluoro-trans- and -cis-4-(2-butenyl)pyrimidine. V.p.c. using a Gas Density Balance detector and ^{19}F n.m.r. spectroscopy were used to determine the isomeric composition which was found to be 10% cis, 90% trans.

VII.A.4.d With a mixture of perfluoro-cis- and -trans-4-(2-butenyl)pyrimidine

For similar reasons as those described previously (VII.A.4.b) a 35:65, cis:trans mixture of the 4-(2-butenyl)pyrimidines was obtained from the equilibrium composition using preparative scale v.p.c. (di-n-decylphthalate, 90°). A small quantity of this mixture (0·8 gm., 2·5 m.mole), caesium fluoride (0·3 gm., 1·2 m.mole) and sulpholan (5 ml.) were stirred together at room temperature in a small stoppered flask. Volatile materials (0·8 gm.) were removed from the apparatus under vacuum at room temperature. Analytical scale v.p.c. (di-n-decylphthalate, 90°) and ^{19}F n.m.r. spectroscopy were used to show that the material was a 10% cis, 90% trans mixture of perfluoro-4-(2-butenyl)pyrimidines.

VII.A.4.e With cis-2-bromo-heptafluorobut-2-ene

Cis-2-bromo-heptafluorobut-2-ene (0·3 gm., 1·2 m.mole), caesium fluoride

(0·3 gm., 2·0 m.mole) and sulpholan (15 ml.) were vigorously stirred together at room temperature in a small stoppered flask for 6 hrs. Volatile material (0·3 gm., 100%) was transferred from the flask under vacuum and identified as a 56:44 mixture of cis- and trans-2-bromo-heptafluorobut-2-ene by comparison of its i.r. and ^{19}F n.m.r. spectra with those of authentic samples of the pure geometrical isomers.[126]

VII.A.4.f With trans-2-bromo-heptafluorobut-2-ene

Trans-2-bromo-heptafluorobut-2-ene (0·4 gm., 1·5 m.mole), caesium fluoride (0·3 gm., 2·0 m.mole) and sulpholan (15 ml.) were vigorously stirred together at room temperature in a small stoppered flask for 6 hrs. Volatile material (0·35 gm., 88%) was transferred from the flask and identified as a 56:44 mixture of cis- and trans-2-bromo-heptafluorobut-2-ene by comparison of its i.r. and ^{19}F n.m.r. spectra with those of authentic samples of the pure geometrical isomers.[126]

VII.A.4.g With cis-2-chloro heptafluorobut-2-ene

Cis-2-chloro-heptafluorobut-2-ene (0·3 gm., 1·4 m.mole), caesium fluoride (0·3 gm., 2·0 m.mole) and sulpholan (15 ml.) were treated as previously described (VII.A.4.e). Volatile material (0·3 gm., 100%) was isolated and identified as a 44:56 mixture of cis- and trans-2-chloro-heptafluorobut-2-ene by comparison of its i.r. and ^{19}F n.m.r. spectra with those of authentic samples of the pure geometrical isomers.[126]

VII.A.4.h With trans-2-chloro-heptafluorobut-2-ene

Trans-2-chloro-heptafluorobut-2-ene (0·3 gm., 1·4 m.mole) when treated under identical conditions to those previously described for the cis analogue was found, by integration of the trifluoromethyl group resonances in the ^{19}F n.m.r. spectrum of the isolated material, to produce a 44:56 mixture of cis- and trans-2-chloro-heptafluorobut-2-ene (0·3 gm., 100%).

VII.A.4.i With a cis-trans mixture of 2-iodo-heptafluorobut-2-ene

Again, due to the similarity of the v.p.c. retention times it was found impossible to separate the individual isomers by this method. Accordingly an isomeric mixture, different to that produced in the preparation from hexafluorobut-2-yne, CsF and iodine (VII.A.3.a), was prepared by reaction of perfluoro-bis-trans-2-butenyl mercury (VII.C.1.a) with iodine. Thus when a 21:79, cis:trans mixture of 2-iodo-heptafluorobut-2-ene (1·0 gm., 3·25 m.mole), caesium fluoride (0·5 gm., 3·3 m.mole) and sulpholan (10 ml.) were vigorously stirred in a small sealed flask at room temperature for 8 hrs., ^{19}F n.m.r. spectroscopy of the isolated material (0·9 gm., 90%) showed that a 68:32 cis:trans mixture of 2-iodo-heptafluorobut-2-ene had been produced.

VII.A.5 Miscellaneous Reactions

VII.A.5.a Reaction of cis- and trans-2,3-dibromo-hexafluorobut-2-ene with caesium fluoride

A cis:trans mixture of 2,3-dibromo-hexafluorobut-2-ene (1·6 gm., 5·0 m.mole), caesium fluoride (0·5 gm., 3·3 m.mole) and sulpholan (20 ml.) were vigorously stirred together in a small stoppered flask at room temperature. Volatile material (1·0 gm.) was transferred from the flask under vacuum and was identified as a mixture of cis- and trans-2-bromo-heptafluorobut-2-ene (77%) by comparison of its i.r. and ^{19}F n.m.r. spectra with those of authentic samples prepared by dehydrobromination of 2H-2,3-dibromo-heptafluorobutane.[126] Cis:trans ratio = 56:44.

VII.A.5.b Reaction of cis- and trans-2,3-dichloro-hexafluorobut-2-ene with caesium fluoride

A cis:trans mixture of 2,3-dichloro-hexafluorobut-2-ene (1·5 gm., 6·5 m.mole), caesium fluoride (0·5 gm., 3·3 m.mole) and sulpholan (20 ml.) were vigorously stirred together in a small stoppered flask at room temperature for 6 hrs. Volatile material (1·1 gm.) was transferred from the flask under vacuum and was identified as a mixture of cis- and trans-2-chloro-heptafluorobut-

-2-ene (79%) by comparison of its i.r. and ^{19}F n.m.r. spectra with those of authentic samples prepared by dehydrochlorination of 2H-2,3-dichloroheptafluorobutane.[126] Cis:trans ratio = 44:56.

VII.B Other Nucleophilic Reactions of Hexafluorobut-2-yne

VII.B.1 Base Catalysed Addition of Methanol

VII.B.1.a In methanol at 20°

The reaction was carried out in the usual atmospheric pressure apparatus described previously. Methanol (25 ml.) and sodium methoxide in methanol (0·5 ml., 1·0M) were placed in the apparatus and vigorously agitated. Hexafluorobut-2-yne (1·0 gm., 6·17 m.mole) was slowly introduced from the flexible reservoir. Reaction was seen to take place very rapidly. Analytical scale v.p.c. of the reaction mixture (di-n-decylphthalate, 25°) showed the presence of a single product which was isolated by distillation (0·7 gm., 58%) using a micro-distillation apparatus at atmospheric pressure. The compound was identified as trans-2H-3-methoxy-hexafluorobut-2-ene by comparison of its i.r. and ^{19}F n.m.r. spectra with those of an authentic sample of the compound prepared by the reaction of methanolic sodium methoxide with trans-2H-heptafluorobut-2-ene. Infrared spectrum No. 23.

VII.B.1.b In sulpholan at 20°

Methanol (0·2 gm., 6·25 m.mole with a catalytic quantity of sodium methoxide) was reacted with hexafluorobut-2-yne (1·0 gm., 6·25 m.mole) in sulpholan (25 ml.) at atmospheric pressure in the apparatus described previously. The product of the reaction was isolated by vacuum transference to yield a clear liquid (1·0 gm., 83%) which was identified as trans-2H-3-methoxy-hexafluorobut-2-ene by comparison of its i.r. and n.m.r. spectra with those of an authentic sample.

VII.B.1.c In sulpholan at 100°

Methanol (0·2 gm., 6·25 m.mole with a catalytic quantity of sodium methoxide) was reacted with hexafluorobut-2-yne (1·0 gm., 6·25 m.mole) in sulpholan (25 ml.) at 100°. The reaction was carried out at atmospheric pressure in the apparatus described previously. The products of the reaction were isolated by vacuum transference to yield a clear liquid (0·9 gm., 75%) which was identified as a mixture of *cis*- and *trans*-2H-3-methoxy-hexafluorobut-2-ene. The geometrical isomers were inseparable by v.p.c. and were characterised as a mixture. [Found: C, 40·0; H, 1·8; F, 58·9%; M^+, 194. $C_5H_4F_6O$ requires C, 30·9; H, 2·1; F, 58·8%; M, 194]. *Cis*:*trans* ratio = 11:89.

VII.B.1.d Equilibration reactions

(i) With methoxide in methanol at 20°

Cis:*trans*-2H-3-methoxy-hexafluorobut-2-ene (0·5 gm., 2·58 m.mole, *cis*:*trans* ratio = 11:89) and sodium methoxide in methanol (0·5 ml., 1·0*M*) were sealed together in an n.m.r. tube which was vigorously shaken for 36 hrs. at 20°. Determination of the isomer ratio by ^{19}F n.m.r. spectroscopy after this time showed that no equilibration had occurred.

(ii) With methoxide in sulpholan at 100°

Trans-2H-3-methoxy-hexafluorobut-2-ene (0·5 gm., 2·58 m.mole) and sodium methoxide in methanol (0·5 ml., 1·0*M*) were sealed together in a small Carius tube with sulpholan (4 ml.) which was heated to 100° for 6 hrs. The tube was opened and the volatile materials transferred to an n.m.r. tube, determination of the isomer content by ^{19}F n.m.r. spectroscopy showed that no equilibration had taken place.

VII.B.2 Base Catalysed Addition of Thiophenol at 20°

Thiophenol (0·6 gm., 5·5 m.mole with a trace of sodium methoxide) was reacted with hexafluorobut-2-yne (0·9 gm., 5·5 m.mole) in sulpholan (25 ml.) at atmospheric pressure in the apparatus described previously. Vacuum transference of the volatile material from the apparatus at 50° yielded a clear liquid (1·4 gm., 93%) which was identified as *trans*-2H-3-thiophenoxy-hexafluorobut-2-ene, b.p. 128° (Siwoloboff). [Found: C, 44·3; H, 2·0; F, 41·7; S, 11·6%; M^+, 272. $C_{10}H_6F_6S$ requires C, 44·1; H, 2·2; F, 41·9; S, 11·8%; M, 272]. Infrared spectrum No. 13.

VII.B.3 Addition of Diethylamine at 20°

VII.B.3.a In sulpholan

Diethylamine (0·8 gm., 11·0 m.mole) was reacted with hexafluorobut-2-yne (1·8 gm., 11·1 m.mole) in sulpholan (25 ml.) at atmospheric pressure in the apparatus described previously. The products of the reaction were transferred from the apparatus under vacuum to yield a clear liquid (1·95 gm., 75%, based on hexafluorobut-2-yne) which was identified as a mixture of cis- and trans-2H-3-N,N-diethylamino-hexafluorobut-2-ene, b.p. 87° (Siwoloboff). [Found: C, 40·7; H, 4·6; N, 6·1; F, 48·3%; M^+, 235. $C_8H_{11}NF_6$ requires C, 40·8; H, 4·7; N, 5·9; F, 48·5%; M, 235]. Cis:trans ratio = 10:90. Infrared spectrum No. 14.

VII.B.3.b In diethyl ether

Diethylamine (0·8 gm., 11·0 m.mole) was reacted with hexafluorobut-2-yne (1·8 gm., 11·1 m.mole) in dry diethyl ether (25 ml.) at atmospheric pressure in the apparatus described previously. The ether was removed by distillation at atmospheric pressure to yield a clear liquid (2·1 gm., 80%) which was identified as a mixture of cis- and trans-2H-3-N,N-diethylamino-hexafluorobut-2-ene by comparison of its i.r. and n.m.r. spectra with those of an authentic sample. Integration of the trifluoromethyl group resonances in the ^{19}F n.m.r. spectrum indicated a 76:24, cis:trans mixture.

VII.B.3.c Equilibration reactions

(i) Under the reaction conditions

1. Cis:trans-2H-3-N,N-diethylamino-hexafluorobut-2-ene (0·5 gm., 2·1 m.mole, cis:trans ratio = 10:90) and diethylamine (0·15 gm., 2·4 m.mole) were weighed into a small flask containing diethyl ether (5 ml.). The solution

was stirred at room temperature for 10 hrs., the ether was then distilled off and the isomer ratio of the olefins determined by integration of the trifluoromethyl group resonances in the ^{19}F n.m.r. spectrum. No equilibration was found to have occurred.

2. Cis:trans-2H-3-N,N-diethylamino-hexafluorobut-2-ene (0·5 gm., 2·1 m.mole, cis:trans ratio = 76:24) and diethylamine (0·15 gm., 2·4 m.mole) were rapidly stirred together in sulpholan (5 ml.) at 25° for 10 hrs. The volatile materials were transferred from the solution under vacuum, determination of the isomer ratio by ^{19}F n.m.r. spectroscopy showed that no equilibration had occurred.

(ii) Under the influence of sodium methoxide

1. Cis:trans-2H-3-N,N-diethylamino-hexafluorobut-2-ene (0·5 gm., 2·1 m.mole, cis:trans ratio = 10:90), sodium methoxide in methanol (0·1 ml., 2·6M) and diethyl ether (5 ml.) were vigorously stirred in a small flask at 20° for 7 hrs. The ether was removed by distillation and the isomer ratio of the but-2-enes determined by ^{19}F n.m.r. spectroscopy. No equilibration was found to have occurred.

2. Cis:trans-2H-3-N,N-diethylamino-hexafluorobut-2-ene (0·5 gm., 2·1 m.mole, cis:trans ratio = 76:24), sodium methoxide in methanol (0·1 ml., 2·6M) and sulpholan (5 ml.) were vigorously stirred in a small flask at 25° for 7 hrs. The volatile materials were transferred from the solvent under vacuum; determination of the isomer ratio of the but-2-enes by ^{19}F n.m.r. spectroscopy showed that no equilibration had taken place.

VII.B.4 Reactions with Heterocyclic Compounds

VII.B.4.a With isoquinoline in sulpholan at 20°

Isoquinoline (1·5 gm., 11·6 m.mole) and sulpholan (25 ml.) were rapidly stirred together in the normal atmospheric pressure apparatus at room temperature. Hexafluorobut-2-yne (1·6 gm., 10·0 m.mole) was slowly introduced into the system from the flexible reservoir. The solution became dark brown and was poured into water (100 ml.); extraction with ether followed by evaporation of the solvent yielded 2·8 gm. of a very viscous dark brown liquid.

Due to the retention times of any compounds present in the mixture being very long, analysis of the material by v.p.c. (S.G.R., 250°) proved impossible. The mass spectrum of the material showed that compounds in the mixture had large molecular weights (> 1000). Several resonances were observed in the ^{19}F and ^{1}H n.m.r. spectra, however, these resonances were very weak and could not be resolved.

VII.B.4.b With pyridine in sulpholan at 20°

Pyridine (1·0 gm., 13·5 m.mole) and sulpholan (25 ml.) were rapidly stirred together in the normal atmospheric pressure apparatus. Hexafluorobut-2-yne (1·7 gm., 10·5 m.mole) was slowly introduced, the solution immediately became a light brown colour which gradually deepened in colour as more acetylene was added. The solution was poured into water (50 ml.); extraction with ether followed by evaporation of the solvent produced a dark brown viscous liquid.

Again separation of the components of the mixture proved impossible by v.p.c. (S.G.R., 250°), mass spectroscopy of the material showed that high molecular weight (> 1000) species were present. Weak, poorly resolved resonances were again observed in the ^{19}F and ^{1}H n.m.r. spectra.

Several other reactions of hexafluorobut-2-yne and pyridine were carried out in which solvent, temperature etc. were varied, however, in all these reactions only high molecular weight tarry material was isolated.

VII.B.5 Reaction with Sulphur

VII.B.5.a In the presence of fluoride ion at 110°

Sulphur (2 gm.), caesium fluoride (2·0 gm., 13·0 m.mole) and sulpholan (25 ml.) were vigorously agitated in the atmospheric pressure apparatus described previously which was maintained at 110° by external heating. Hexafluorobut-2-yne (2·0 gm., 12·3 m.mole) was slowly introduced into the apparatus; reaction was seen to occur by observing the development of a slight vacuum within the system. Volatile materials were transferred from the apparatus under vacuum to yield a clear liquid (1·1 gm., 50%, based on hexafluorobut-2-yne) which was shown by v.p.c. (S.G.R., 150°) to contain a single component which was identified as tetra-kis-trifluoromethylthiophene, b.p. 133° (Siwoloboff). [Found: C, 26·9; F, 63·8; S, 9·1%; $M^{+\cdot}$, 356. Calculated for $C_8F_{12}S$: C, 27·0; F, 64·0; S, 9·0%; M, 356]. Infrared spectrum No. 15.

Homo-polymer of the acetylene ($\approx$ 0·8 gm.) was isolated from the reaction mixture.

VII.B.5.b In the absence of fluoride ion at 100°

An identical procedure to the above was carried out with the omission of caesium fluoride. Reaction proceeded smoothly, volatile material was transferred from the apparatus under vacuum to yield a clear liquid (1·5 gm., 68%). Analytical scale v.p.c. showed the presence of a single component which was identified as tetra-kis-trifluoromethylthiophene by comparison of its i.r. and ^{19}F n.m.r. spectra with those of an authentic sample.

VII.B.5.c In the absence of fluoride ion at 80°

Sulphur (2 gm.) and hexafluorobut-2-yne (0·9 gm., 5·6 m.mole) were reacted together at 80° in sulpholan in the usual atmospheric pressure apparatus. Reaction proceeded very slowly; volatile materials were removed from the apparatus under vacuum (0·7 gm., 71%, based on hexafluorobut-2-yne).

Analytical scale v.p.c. showed the presence of a single component which was identified as tetra-kis-trifluoromethylthiophene by comparison of its i.r. and n.m.r. spectra with those of an authentic sample.

VII.C.1 Cleavage Reactions of Perfluoro-bis-*trans*-2-butenyl mercury

VII.C.1.a With iodine

Perfluoro-bis-*trans*-2-butenyl mercury (1·0 gm., 1·78 m.mole) and iodine (2·1 gm., 8·27 m.mole) were sealed together in a small evacuated Carius tube which was heated in a constant temperature oil bath to 180° for 6 hrs. The tube was removed and opened; volatile materials were transferred from the tube under vacuum to yield a clear liquid (1·0 gm., 91%). Analytical scale v.p.c. (di-n-decylphthalate, 70°) showed the presence of two components with very similar retention times. Separation of the two compounds proved impossible, characterisation of the mixture showed that the material was composed of *cis*- and *trans*-2-iodo-heptafluorobut-2-ene, b.p. 70° (Siwoloboff). [Found: C, 15·7; F, 43·5; I, 41·0%; M^+, 308. Calculated for C_4F_7I: C, 15·6; F, 43·2; I, 41·2%; M, 308]. The geometrical isomers could be readily identifed by their ^{19}F n.m.r. spectra. Integration of the trifluoromethyl group resonances showed that the material was a 21:79, *cis*:*trans* mixture of the two isomers.

VII.C.1.b With bromine

Perfluoro-bis-*trans*-2-butenyl mercury (1·2 gm., 2·14 m.mole) and bromine (1·45 gm., 9·06 m.mole) were sealed together in a small glass Carius tube which was immersed in a constant temperature bath at 150° for 6 hrs. The tube was opened and volatile material removed from the tube under vacuum to yield a clear liquid (1·10 gm., 91%). The material was identified as a *cis* and *trans* mixture of 2-bromo-heptafluorobut-2-ene by comparison of its i.r. and ^{19}F n.m.r. spectra with those of authentic samples prepared by dehydrobromination of 2H-2,3-dibromo-heptafluorobutane.[126] Integration of the trifluoromethyl group resonances showed a 50% cis:50% trans isomer composition.

VII.C.1.c In the presence of sulpholan

Perfluoro-bis-trans-2-butenyl mercury (approx. 1·0 gm., 1·78 m.mole) contaminated with a small amount of sulpholan (0·3 gm.) was sealed in a small glass Carius tube which was immersed in a constant temperature bath at 150° for 6 hrs. The tube was opened to yield a small amount of highly volatile material (0·2 gm.) which was identified as 2H-heptafluorobut-2-ene by comparison of its mass and i.r. spectra with those of an authentic sample. Insufficient material was obtained to carry out a ^{19}F n.m.r. spectrum by which the isomer ratio could be determined. Similarly the i.r. spectrum of the material proved to be of little value for determining the isomer ratio. Only a single olefinic absorption was observed at 5·7μ, the presence of the cis isomer could however not be ruled out.

VII.C.2 Attempted Equilibration Reactions

VII.C.2.a With 2-iodo-heptafluorobut-2-ene

A 68:32, cis:trans mixture of 2-iodo-heptafluorobut-2-ene (1·1 gm., 3·5 m.mole), mercuric iodide (1·5 gm., 3·3 m.mole) and a small amount of iodine (approx. 0·2 gm.) were sealed together in a small glass Carius tube which was heated to 180° for 6 hrs. in a constant temperature oil bath. Volatile material was removed from the tube under vacuum (1·1 gm.) and was shown to be a 68:32, cis:trans mixture of 2-iodo-heptafluorobut-2-ene by ^{19}F n.m.r. spectroscopy, i.e. equilibration had not occurred.

VII.C.2.b With 2-bromo-heptafluorobut-2-ene

A 40:60, cis:trans mixture of 2-bromo-heptafluorobut-2-ene (1·0 gm., 3·8 m.mole), mercuric bromide (1·0 gm., 2·8 m.mole) and a small amount of bromine (approx. 0·2 gm.) were sealed together in a small Carius tube which was heated to 150° for 6 hrs. The volatile material was transferred from the tube under vacuum (1·1 gm.) and was slightly contaminated with bromine. The material was shown to be a 40:60, cis:trans mixture of 2-bromo-heptafluorobut-2-ene by ^{19}F n.m.r. spectroscopy, i.e. equilibration had not occurred.

CHAPTER VIII

Nucleophilic Reactions Of Polyfluorobut-2-enes

VIII.A Purification of Solvents

(1) Methanol

Magnesium (40 gm.) was placed in a round bottomed flask (5 l.) fitted with reflux condenser, dropping funnel and nitrogen inlet.

Methanol (100 ml.) was run into the flask from the dropping funnel and the reaction initiated with a crystal of iodine. The remainder of the methanol (2½ l.) was added at a rate sufficient to maintain gentle reflux. After completion of the methanol addition the solution was refluxed for 6 hrs. under a slow stream of dry nitrogen. Dry methanol (approx. 1½ l.) was then distilled off and stored under dry nitrogen.

(2) Dioxane

Dioxane (2½ l.), concentrated hydrochloric acid and water (250 ml.) were heated under reflux conditions for 12 hrs. under a slow stream of nitrogen.

The solution was cooled and potassium hydroxide pellets (50 gm.) were added. The aqueous layer was run off and the dioxane was left over potassium hydroxide (10 gm.) for 24 hrs. The liquid was decanted off, excess sodium added and the solution refluxed for 12 hrs. under a slow stream of nitrogen.

Dry dioxane (1½ l., B.P. 101·5, 760 mm.) was then distilled off and stored under dry nitrogen at -15°.

(3) Dimethylformamide (D.M.F.)

The solvent was stirred with anhydrous barium oxide for 24 hrs. Dry D.M.F. was then distilled off under vacuum and stored over molecular sieve (Type 4A) under an atmosphere of dry nitrogen.

(4) N-Methylacetamide (N.M.A.)

Dried using molecular sieve (Type 4A) and stored under dry nitrogen.

VIII.B Preparation of Solutions

(1) Methoxide

Freshly cut sodium (approx. 15 gm.) was slowly added to dry methanol (250 ml.) contained in a flask flushed with dry nitrogen.

Titration of this solution with standard acid showed it to be 2·6M in methoxide.

(2) Sodium phenoxide in dioxane, D.M.F. and N.M.A.

A standard procedure was adopted to ensure that the molarity of phenoxide was the same in all three solvents.

Phenol (9·4 gm.) was dissolved in a small amount of the solvent (30 ml.) in a flask flushed with dry nitrogen. Freshly cut sodium (2·3 gm.) was slowly dissolved in the solution which was then transferred to a standard flask (50 ml.) which was made up to the mark with the relevant solvent.

These solutions were stored under dry nitrogen and in the case of dioxane the solution was kept at -15°.

VIII.C Reactions of Sodium Phenoxide with Polyfluorobut-2-enes Characterisation of Products

VIII.C.1 Reaction with Perfluoro-trans-4-(2-butenyl)pyridine

(a) In dioxane at 20°

Sodium phenoxide solution (5 ml., 1·0M, 5·0 m.mole) was slowly added over $\frac{1}{4}$ hr. from a small syringe to perfluoro-*trans*-4-(2-butenyl)pyridine (1·65 gm. 5·0 m.mole) contained in a small flask. Mixing was accomplished using a magnetic stirrer and the flask was immersed in a constant temperature bath at 20°. The products were isolated from the solvent by pouring the solution into water followed by extraction with ether (2 x 15 ml.). The ether layer was removed and washed with water (20 ml.); after drying ($MgSO_4$) the solvent was removed to leave a clear liquid (1·3 gm., 64·5%). Analytical scale v.p.c. (di-n-decylphthalate, 150°) showed the presence of two components which were characterised as a mixture and identified as cis- and trans-2-phenoxy-3-(4-tetrafluoropyridyl)-hexafluorobut-2-ene, b.p. 164° (Siwoloboff). [Found: C, 44·2; F, 47·1; H, 0·9; N, 3·4%; M^+, 405. $C_{15}H_5F_{10}NO$ requires C, 44·4; F, 46·9; H, 1·2; N, 3·5%; M, 405]. A 25:75 ratio of the cis and trans isomers was confirmed using both v.p.c. analysis (G.D.B., di-n-decylphthalate) and ^{19}F n.m.r. integration of the trifluoromethyl group resonances. Infrared spectrum No. 16.

VIII.C.2 Reaction with Perfluorobut-2-ene

(a) In dioxane at 20°

A preliminary reaction carried out with sodium phenoxide in dioxane proved to be unsuccesful after a reaction time of 13 hrs. at room temperature. The olefin was found to be highly insoluble in the reaction medium.

(b) In D.M.F. at 20°

Octafluorobut-2-ene (2·0 gm., 10 m.mole) and sodium phenoxide in D.M.F. (10 ml., 1·0M, 10 m.mole) were sealed together in an evacuated Carius tube and vigorously shaken for 24 hrs. at room temperature. Again the olefin appeared insoluble in the reaction medium, however, upon agitation, the olefin slowly dissolved in the solvent. The tube was opened and the solution poured into water (50 ml.), extracted with ether (2 x 15 ml.) and the organic layer separated and dried ($MgSO_4$).

Evaporation of the solvent yielded a white crystalline solid (1·4 gm., 40%) which after recrystallisation from dry hexane was identified as 2,3-diphenoxy-hexafluorobut-2-ene, m.p. 112-115° (possibly a cis-trans mixture). [Found: C, 55·2; H, 3·0; F, 32·7%; M^+, 348. $C_{16}H_{10}F_6O_2$ requires C, 55·2; H, 2·9; F, 32·8%; M, 348]. Infrared spectrum No. 17.

VIII.C.3 Reaction with Trans-2H-heptafluorobut-2-ene

(a) In D.M.F. at 20°

Trans-2H-heptafluorobut-2-ene (3·6 gm., 19·8 m.mole) and sodium phenoxide in D.M.F. (19·8 ml., 1·0M, 19·8 m.mole) were sealed together in an evacuated Carius tube which was agitated for 5 hrs. at room temperature. The tube was opened and the solution poured into water (100 ml.). The aqueous solution was extracted with ether (2 x 20 ml.), the ether layer separated, washed with water (20 ml.) and dried ($MgSO_4$). Evaporation of the solvent yielded a clear liquid (3·7 gm., 73%). Vapour phase chromatography showed the presence of two components which were separated by preparative scale v.p.c. (di-n-decylphthalate, 140°) and identified as (in order of emergence from the column):

(i) trans-2H-3-phenoxy-hexafluorobut-2-ene, b.p. 117° (Siwoloboff). [Found: C, 46·7; H, 2·1; F, 44·4%; M^+, 256. $C_{10}H_6F_6O$ requires C, 46·9; H, 2·3; F, 44·5%; M, 256]. Infrared spectrum No. 18.

(ii) cis-2H-3-phenoxy-hexafluorobut-2-ene, b.p. 124° (Siwoloboff). [Found: C, 46·8; H, 2·1; F, 44·4%; M^+, 256. $C_{10}H_6F_6O$ requires C, 46·9; H, 2·3; F, 44·4%; M, 256]. Infrared spectrum No. 19.

A 24:76 ratio of the cis and trans isomers was confirmed using both v.p.c. analysis (G.D.B., 140°) and ^{19}F n.m.r. integration of the trifluoromethyl group resonances.

VIII.C.4 Reaction with a Mixture of Cis- and Trans-2-chloro-heptafluorobut-2-en

(a) In D.M.F. at 20°

A cis:trans mixture of 2-chloro-heptafluorobut-2-ene (2·2 gm., 10·2 m.mole, cis:trans ratio ≈ 60:40) and sodium phenoxide in D.M.F. (10·2 ml., 1·0M, 10·2 m.mole) were sealed together in an evacuated Carius tube which was vigorously shaken for 3 hrs. at 20°. The tube was opened and the contents poured into water (70 ml.). Work-up involved an identical procedure as that used for isolation of products from trans-2H-heptafluorobut-2-ene (VIII.C.3). After extraction a pale yellow liquid was isolated (2·1 gm., 71%) which was shown by analytical scale v.p.c. to contain two components. Preparative scale v.p.c.

(di-n-decylphthalate, 150°) was used to separate the two compounds which were identified as (in order of emergence from column):

(i) trans-2-chloro-3-phenoxy-hexafluorobut-2-ene, b.p. 137° (Siwoloboff). [Found: C, 40·1; H, 1·8; F, 39·3; Cl, 12·4%; M^+, 290 (Parent), 292 (P+2 corresponding to ^{37}Cl). $C_{10}H_5F_6ClO$ requires C, 41·3; H, 1·7; F, 39·3; Cl, 12·2%; M, 290 with ^{37}Cl isotope peak at 292]. Infrared spectrum No. 20.

(ii) cis-2-chloro-3-phenoxy-hexafluorobut-2-ene, b.p. 137° (Siwoloboff). [Found: C, 40·1; H, 1·5; F, 39·4; Cl, 12·1%; M^+, 290 (Parent), 292 (P+2 corresponding to ^{37}Cl). $C_{10}H_5F_6ClO$ requires C, 41·3; H, 1·7; F, 39·3; Cl, 12·2%; M, 290 with ^{37}Cl isotope peak at 292]. Infrared spectrum No. 21.

Again v.p.c. and n.m.r. analysis was used to confirm a 60:40 ratio of the cis and trans isomers in the mixture.

VIII.C.5 Reaction with a Mixture of Cis- and Trans-2-bromo-heptafluorobut-2-ene

(a) In D.M.F. at 20°

A cis:trans mixture of 2-bromo-heptafluorobut-2-ene (2·6 gm., 10 m.mole) and sodium phenoxide in D.M.F. (10 ml., 1·0M, 10 m.mole) were sealed together in an evacuated Carius tube which was vigorously shaken for 3 hrs. at 20°. The tube was opened and the contents poured into water (70 ml.). Work-up involved an identical procedure as that used for the isolation of the analogous products from trans-2H-heptafluorobut-2-ene (VIII.C.3). After extraction a clear liquid was isolated (2·7 gm., 80%), analytical scale v.p.c. (S.G.R., 150°) showed the presence of two components with very similar retention times which proved inseparable by this method. Due to problems of separation the material was characterised as a mixture which was shown to consist of cis- and trans-2-bromo-3-phenoxy-hexafluorobut-2-ene. [Found: C, 35·9; H, 1·8; F, 34·1; Br, 23·9%; M^+, 335 (Parent), 337 (P+2 corresponding to ^{81}Br). $C_{10}H_5F_6BrO$ requires C, 35·8; H, 1·5; F, 34·0; Br, 23·9%; M, 335 with ^{81}Br isotope peak at 337].

Comparison of peak areas from v.p.c. analysis with the integrated peak areas in the n.m.r. spectrum of the mixture indicated that the trans isomer had the lower v.p.c. retention time. Integration of the trifluoromethyl group resonances in the ^{19}F n.m.r. spectrum confirmed a 28:72 ratio of the cis-trans products. Infrared spectrum No. 22.

VIII.D Reactions of Sodium Phenoxide with Pure Geometrical Isomers of Polyfluorobut-2-enes

A standard procedure was adopted to study the nucleophilic reactions of the polyfluorobut-2-enes. The olefin (ca. 0·3 - 0·5 gm.) was accurately weighed out and transferred to a small glass Carius tube (volume approx. 10 cc.) (vacuum line techniques were used for the more volatile compounds). The tube was cooled to -180°, the sodium phenoxide solution (1·0 molar) added (molar ratio olefin:phenoxide = 1:1) and the tube sealed. The reactions were carried out in constant temperature baths at 18° and 80° with a reaction time of ½ hr. The tube was then opened and a small amount of the solution transferred to an n.m.r. tube. Integration of the trifluoromethyl group resonances in the products was used to determine the isomer ratio. In none of the reactions carried out was there any indication of the presence of unreacted starting material after a reaction time of ½ hr.

VIII.D.1 Reactions with trans-2H-heptafluorobut-2-ene

(a) At 18°

(i) In dioxane

Trans-$CF_3HC{=}CFCF_3$, 0·35 gm., (1·9 m.mole);

Sodium phenoxide solution, 1·9 ml. (1·9 m.mole);

Isomer ratio of products, cis:trans = 3:97

(ii) In D.M.F.

Olefin, 0·43 gm. (2·35 m.mole);

Sodium phenoxide solution, 2·35 ml. (2·35 m.mole);

Isomer ratio of products cis:trans = 24:76.

(iii) In N.M.A.

Olefin, 0·45 gm. (2·47 m.mole);

Sodium phenoxide solution, 2·47 ml. (2·47 m.mole);

Isomer ratio of products cis:trans = 18:82.

(b) At 80°

(i) In dioxane

Trans-$CF_3HC=CFCF_3$, 0·30 gm., (1·65 m.mole);

Sodium phenoxide solution, 1·65 ml. (1·65 m.mole);

Isomer ratio of products, cis:trans = 3:97.

(ii) In N.M.A.

Olefin, 0·30 gm. (1·65 m.mole);

Sodium phenoxide solution, 1·65 ml. (1·65 m.mole);

Isomer ratio of products, cis:trans = 17:83.

VIII.D.2 Reactions with cis-2-chloro-heptafluorobut-2-ene

(a) At 18°

(i) In dioxane

Cis-$CF_3ClC=CFCF_3$, 0·35 gm., (1·6 m.mole);

Sodium phenoxide solution, 1·60 ml. (1·60 m.mole)

Isomer ratio of products, cis:trans = 95:5.

(ii) In D.M.F.

Cis-$CF_3ClC=CFCF_3$, 0·30 gm., (1·4 m.mole);

Sodium phenoxide solution, 1·4 ml. (1·4 m.mole);

Isomer ratio of products, cis:trans = 72:28.

(iii) In N.M.A.

Cis-$CF_3ClC=CFCF_3$, 0·30 gm., (1·4 m.mole);

Sodium phenoxide solution, 1·4 ml. (1·4 m.mole);

Isomer ratio of products, cis:trans = 81:19.

(b) At 80°

(i) In dioxane

Cis-$CF_3ClC=CFCF_3$, 0·35 gm., (1·6 m.mole);

Sodium phenoxide solution, 1·6 ml. (1·6 m.mole);

Isomer ratio of products, cis:trans = 94:6

(ii) In N.M.A.

Cis-$CF_3ClC=CFCF_3$, 0·30 gm., (1·4 m.mole);

Sodium phenoxide solution, 1·4 ml. (1·4 m.mole);

Isomer ratio of products cis:trans = 80:20.

VIII.D.3 Reactions with trans-2-chloro-heptafluorobut-2-ene

(a) At 18°

(i) In dioxane

Trans-$CF_3ClC=CFCF_3$, 0·4 gm., (1·9 m.mole);

Sodium phenoxide solution, 1·9 ml. (1·9 m.mole);

Isomer ratio of products cis:trans = 8:92.

(ii) In D.M.F.

Trans-$CF_3ClC=CFCF_3$, 0·35 gm., (1·6 m.mole);

Sodium phenoxide solution, 1·6 ml. (1·6 m.mole);

Isomer ratio of products cis:trans = 29:71.

(iii) In N.M.A.

Trans-$CF_3ClC=CFCF_3$, 0·35 gm., (1·6 m.mole);

Sodium phenoxide solution, 1·6 ml. (1·6 m.mole);

Isomer ratio of products cis:trans = 28:72.

(b) At 80°

(i) In dioxane

Trans-$CF_3ClC=CFCF_3$, 0·3 gm., (1·4 m.mole);

Sodium phenoxide solution, 1·4 ml. (1·4 m.mole);

Isomer ratio of products cis:trans = 12:28.

(ii) In N.M.A.

Trans-$CF_3ClC=CFCF_3$, 0·4 gm., (1·9 m.mole);

Sodium phenoxide solution, 1·9 ml. (1·9 m.mole);

Isomer ratio of products cis:trans = 25:75.

VIII.D.4 Reactions with cis-2-bromo-heptafluorobut-2-ene

(a) At 18°

(i) In dioxane

Cis-$CF_3BrC=CFCF_3$, 0·4 gm., (1·5 m.mole);

Sodium phenoxide solution, 1·5 ml. (1·5 m.mole);

Isomer ratio of products cis:trans = 93:7.

(ii) In D.M.F.

Cis-$CF_3BrC=CCF_3$, 0·45 gm., (1·7 m.mole);

Sodium phenoxide solution, 1·7 ml. (1·7 m.mole);

Isomer ratio of products cis:trans = 73:27.

(iii) In N.M.A.

Cis-$CF_3BrC=CFCF_3$, 0·4 gm., (1·5 m.mole);

Sodium phenoxide solution, 1·5 ml. (1·5 m.mole);

Isomer ratio of products cis:trans = 90:10.

(b) At 80°

(i) In dioxane

Cis-$CF_3BrC=CFCF_3$, 0·5 gm., (1·9 m.mole);

Sodium phenoxide solution, 1·9 ml. (1·9 m.mole);

Isomer ratio of products cis:trans = 92:8.

(ii) In N.M.A.

Cis-$CF_3BrC{=}CFCF_3$, 0·35 gm., (1·3 m.mole);

Sodium phenoxide solution, 1·3 ml. (1·3 m.mole);

Isomer ratio of products cis:trans = 89:11.

VIII.D.5 Reactions with trans-2-bromo-heptafluorobut-2-ene

(a) At 18°

(i) In dioxane

Trans-$CF_3BrC{=}CFCF_3$, 0·4 gm., (1·5 m.mole);

Sodium phenoxide solution, 1·5 ml. (1·5 m.mole);

Isomer ratio of products cis:trans = 12:88.

(ii) In D.M.F.

Trans-$CF_3BrC{=}CFCF_3$, 0·4 gm., (1·5 m.mole);

Sodium phenoxide solution, 1·5 ml. (1·5 m.mole);

Isomer ratio of products cis:trans = 35:65.

(iii) In N.M.A.

Trans-$CF_3BrC{=}CFCF_3$, 0·5 gm., (1·9 m.mole);

Sodium phenoxide solution, 1·9 ml. (1·9 m.mole);

Isomer ratio of products cis:trans = 32:68.

(b) At 80°

(i) In dioxane

Trans-$CF_3BrC{=}CFCF_3$, 0·35 gm., (1·3 m.mole);

Sodium phenoxide solution, 1·3 ml. (1·3 m.mole);

Isomer ratio of products cis:trans = 13:87.

(ii) In N.M.A.

Trans-$CF_3BrC{=}CFCF_3$, 0·4 gm., (1·5 m.mole);

Sodium phenoxide solution, 1·5 ml. (1·5 m.mole);

Isomer ratio of products cis:trans = 35:65.

VIII.D.6 Reactions with perfluoro-trans-4-(2-butenyl)pyridine

(a) At 18°

(i) In dioxane

Olefin, 0·3 gm. (0·90 m.mole);

Sodium phenoxide solution, 0·9 ml. (0·9 m.mole);

Isomer ratio of products cis:trans = 25:75.

(ii) In D.M.F.

Olefin, 0·3 gm., (0·90 m.mole);

Sodium phenoxide solution, 0·9 ml. (0·9 m.mole);

Isomer ratio of products cis:trans = 77:23.

(iii) In N.M.A.

Olefin, 0·3 gm., (0·90 m.mole);

Sodium phenoxide solution, 0·9 ml. (0·9 m.mole);

Isomer ratio of products cis:trans = 77:23.

(b) At 80°

(i) In dioxane

Olefin, 0·35 gm., (1·1 m.mole);

Sodium phenoxide solution, 1·1 ml. (1·1 m.mole);

Isomer ratio of products cis:trans = 24:76.

(ii) In N.M.A.

Olefin, 0·3 gm., (0·90 m.mole);

Sodium phenoxide solution, 0·90 ml. (0·90 m.mole);

Isomer ratio of products cis:trans = 78:22.

VIII.D.7 Control Experiments

These experiments were carried out in order to eliminate the possibility that

(a) products of the reactions with phenoxide are at equilibrium under the conditions of the reactions. To show that this was not operative, pure samples of the isomers (or cis-trans mixtures of known composition) were mixed individually with the three solvents (dioxane, D.M.F., N.M.A.) in the presence of sodium fluoride and sodium phenoxide. The solutions were vigorously stirred for 3 hrs. after which time the isomer composition was determined by ^{19}F n.m.r. spectroscopy. With none of the compounds studied was there any indication of cis-trans isomerization;

(b) a rapid pre-equilibrium was being set up in which cis-trans isomerisation occurred in the presence of phenoxide. To eliminate this possibility pure geometrical isomers of the various olefins (approx. 0·3 gm.) were reacted with a 75% deficiency of sodium phenoxide solution in sealed evacuated Carius tubes. After ½ hr. reaction time the tubes were opened and a small amount of the solution transferred to an n.m.r. tube. With none of the olefins studied in any of the solvents i.e. dioxane, D.M.F., N.M.A., was there any indication of cis-trans equilibration of the starting olefins.

VIII.E Reactions of Sodium Methoxide with Polyfluorobut-2-enes in Methanol

VIII.E.1 Reaction with Perfluoro-trans-4-(2-butenyl)pyridine

Perfluoro-trans-4-(2-butenyl)pyridine (1·0 gm., 3·0 m.mole) and dry methanol (5 ml.) were mixed together in a small flask which was cooled in an ice bath and purged with dry nitrogen. The mixture was stirred and sodium methoxide in methanolic solution (3·0 ml., 1·0M, 3·0 m.mole) was slowly added from a small syringe. Reaction was allowed to proceed for 1 hr. The solution was then poured into water (50 ml.) and the products extracted with ether (2 x 20 ml.). After separation, the ethereal solution was washed with water (20 ml.), dried ($MgSO_4$) and the solvent removed under vacuum to yield a clear liquid (0·7 gm., 70%) which was shown by v.p.c. analysis (di-n-decyl-phthalate, 120°) to contain two compounds with similar retention times. Due to problems of separation of the components the material was characterised as a mixture which was shown to consist of cis- and trans-2-methoxy-3-(4-tetrafluoropyridyl)-hexafluorobut-2-ene. [Found: C, 35·0; H, 0·9; N, 3·9; F, 55·6%; M^+, 343. Calc. for $C_{10}H_3NF_{10}O$: C, 35·0; H, 0·9; N, 4·1; F, 55·4%; M, 343]. The i.r. spectrum was identical with that of a previously prepared sample of the mono-methoxy derivative.[112] Comparison of peak areas from v.p.c. analysis with the integrated peak areas in the n.m.r. spectrum of the mixture indicated that the trans isomer had the lower v.p.c. retention time. Integration of the trifluoromethyl group resonances in the ^{19}F n.m.r. spectrum confirmed a 70:30 ratio of the cis:trans products.

VIII.E.2 Reaction with Perfluorobut-2-ene

(a) At 50°

Perfluorobut-2-ene (2·0 gm., 10·0 m.mole) and sodium methoxide in methanolic solution (3·85 ml., 2·6*M*, 10·0 m.mole) were sealed together in an evacuated Carius tube. The tube was immersed in an oil bath at 50° and vigorously agitated. After 4 hrs. the tube was opened and the reaction mixture analysed by v.p.c. (di-iso-decylphthalate, 40°) which showed a complex reaction mixture the components of which could not be easily resolved. The reaction mixture was not investigated further.

(b) At -15°

Perfluorobut-2-ene (2·0 gm., 10·0 m.mole) was condensed into a small flask at -15° and slowly stirred. Sodium methoxide in methanolic solution (3·85 ml., 2·6*M*, 10·0 m.mole) was pre-cooled to -15° and slowly added to the olefin in the flask over ½ hr. The mixture was left to react for 3/4 hr. Analytical scale v.p.c. again showed the presence of several components which again could not be resolved; the solution was not investigated further.

VIII.E.3 Reaction with trans-2H-heptafluorobut-2-ene

Trans-2H-heptafluorobut-2-ene (1·8 gm., 10·0 m.mole) and sodium methoxide in methanolic solution (3·85 ml., 2·6M, 10·0 m.mole) were sealed together in an evacuated Carius tube. The tube was immersed in an ice bath and was vigorously agitated. After 2 hrs. the tube was opened and the products separated from the solvent by distillation using a column packed with glass helices to yield a clear highly volatile liquid (1·0 gm., 53%). Analytical scale v.p.c. (acetonyl acetone, 0°) showed the presence of a single component which was identified as trans-2H-3-methoxy-hexafluorobut-2-ene, b.p. ≈ 30°. Elemental analysis of this compound proved difficult due to its high volatility, however, satisfactory results were obtained. [Found: C, 30·8; H, 2·3; F, 58·7%; M^+, 194. $C_5H_4F_6O$ requires C, 30·9; H, 2·1; F, 58·8%; M, 194]. Infrared spectrum No. 23.

VIII.E.4 Reaction with a cis-trans mixture of 2-chloro-heptafluorobut-2-ene

A cis-trans mixture of 2-chloro-heptafluorobut-2-ene (4·3 gm., 20·0 m.mole, cis:trans ratio = 60:40) and sodium methoxide in methanolic solution (7·7 ml., 2·6M, 20·0 m.mole) were sealed together in an evacuated glass Carius tube which was placed in an oil bath at 45° and vigorously shaken for 2 hrs. The tube was opened and the contents poured into distilled water (70 ml.), the lower organic layer was separated and dried ($MgSO_4$) to yield a clear liquid (3·4 gm.). Analytical scale v.p.c. showed the presence of four components which were separated by preparative scale v.p.c. (di-n-decylphthalate, 68°) and shown to be (in order of emergence from column); yields being estimated using a Gas Density Balance Chromatogram (di-n-decylphthalate, 75°).

(i) trans-2-chloro-3-methoxy-hexafluorobut-2-ene, b.p. 38° (Siwoloboff), 29%. [Found: C, 26·1; H, 1·6; F, 49·8; Cl, 15·7%; M^+, 228 (Parent), 230 (P+2 corresponding to ^{37}Cl). $C_5H_3F_6ClO$ requires C, 26·3; H, 1·3; F, 50·0; Cl, 15·6%; M, 228 with ^{37}Cl isotope peak at 230]. Infrared spectrum No. 24.

(ii) cis-2-chloro-3-methoxy-hexafluorobut-2-ene, b.p. 40° (Siwoloboff), 28%. [Found: C, 26·3; H, 1·5; F, 50·1; Cl, 15·8%; M^+, 228 (Parent), 230 (P+2 corresponding to ^{37}Cl). $C_5H_3F_6ClO$ requires C, 26·3; H, 1·3; F, 50·0; Cl, 15·6%; M, 228 with ^{37}Cl isotope peak at 230]. Infrared spectrum No. 25.

(iii) 1st diastereomer 2H-2-chloro-3-methoxy-heptafluorobutane, b.p. 43° (Siwoloboff), 8%. [Found: C, 24·0; H, 1·4; F, 53·6; Cl, 14·1%; a parent peak was not present in the mass spectrum, however, peaks corresponding to $[CF_3ClCH]^+$ M, 117 (with ^{37}Cl isotope peak at M, 119) and $[CF_3(OCH_3)FC]^+$ M, 131 were prominent. $C_5H_4F_7ClO$ requires C, 24·2; H, 1·6; F, 53·5; Cl, 14·3%; M, 248 (with Cl isotope pattern)]. Infrared spectrum No. 26.

(iv) 2nd diastereomer 2H-2-chloro-3-methoxy-heptafluorobutane, b.p. 41° (Siwoloboff), 9%. [Found: C, 24·3; H, 1·4; F, 53·4; Cl, 14·3%; a parent peak in the mass spectrum was not present, however, peaks corresponding to $[CF_3ClCH]^+$ M, 117 and $[CF_3(OCH_3)CF]^+$ M, 131 were prominent. $C_5H_4F_7ClO$ requires C, 24·2; H, 1·6; F, 53·5; Cl, 14·3%; M, 248]. Infrared spectrum No. 27.

VIII.E.5 Reaction with a cis-trans mixture of 2-bromo-heptafluorobut-2-ene

A cis-trans mixture (40:60) of 2-bromo-heptafluorobut-2-ene (7·0 gm., 26·8 m.mole) was condensed into a small flask which was cooled to 0°. Sodium methoxide in methanol (10·3 ml., 2·6M, 26·8 m.mole) was slowly added to the solution with stirring over ½ hr. The solution was kept at 0° for 2 hrs. after completion of methoxide addition and then poured into water (100 ml.). The lower organic layer was separated and dried ($MgSO_4$) to yield a clear liquid (6·4 gm.). Analytical scale v.p.c. (di-n-decylphthalate, 100°) showed the presence of five components, the first four of which had very similar retention times and were separated by v.p.c. (di-n-decylphthalate) at 58°. The fifth component had a long retention time and was separated by v.p.c. at 150°. The compounds were identified as, (in order of emergence from column), yields being estimated using a Gas Density Balance Chromatograph (di-n-decylphthalate, 100°).

(i) trans-2-bromo-3-methoxy-hexafluorobut-2-ene, 4%. Insufficient material was obtained to carry out elemental analysis. The mass spectrum showed a parent peak at 272 with an ^{81}Br isotope peak at 274 which corresponds to $C_5H_3F_6BrO$. The ^{19}F n.m.r. spectrum indicates a trans configuration of olefinic trifluoromethyl groups, similarly a weak olefinic ($\rangle C{=}C\langle$) stretching vibration at 6·1µ in the i.r. spectrum is characteristic of a symmetrically substituted trans olefin.[125] Infrared spectrum No. 28.

(ii) cis-2-bromo-3-methoxy-hexafluorobut-2-ene, 3%. This compound was isolated as a mixture with

(iii) 1st diastereomer 2H-2-bromo-3-methoxy-heptafluorobutane, 7%. The mass spectrum of the mixture showed two characteristic splitting patterns, n.m.r. clearly showed the presence of two components. The i.r. spectrum showed a relatively strong olefinic stretching vibration at 6·1µ characteristic of a symmetrically substituted cis olefin.[125] Infrared spectrum No. 29.

(iv) 2nd diastereomer 2H-2-bromo-3-methoxy-heptafluorobutane, b.p. 50° (Siwoloboff), 5%. [Found: C, 20·4; H, 1·2; F, 45·2; Br, 27·2%; a parent peak in the mass spectrum was not present, however, peaks corresponding to $[CF_3BrCH]^+$ M, 161 and $[CF_3(OCH_3)CF]^+$ M, 131 were prominent. $C_5H_4F_7BrO$ requires C, 20·5; H, 1·4; F, 45·4; Br, 27·3%; M, 292]. Infrared spectrum No. 30.

(v) 2H-2-bromo-3,3-dimethoxy-hexafluorobutane, b.p. 82° (Siwoloboff), 53%. [Found: C, 23·6; H, 2·6; F, 37·4; Br, 26·0%; a parent peak was not observed in the mass spectrum, however, peaks corresponding to $[CF_3C(OCH_3)_2]^+$ M, 143 and $[CF_3HCBr]^+$ M, 161 were prominent. $C_6H_7F_6BrO_2$ requires C, 23·6; H, 2·3; F, 37·4; Br, 26·2%; M, 304]. Infrared spectrum No. 31.

VIII.F Competition Reactions of Polyfluorobut-2-enes for Sodium Phenoxide

(i) General Theory

If two reactants X and Y are competing for a deficiency of a third reactant B, for example

$$X + B \xrightarrow{k_x} \text{products}$$

$$Y + B \xrightarrow{k_y} \text{products}$$

then the rate constant ratio k_x/k_y is defined as[151]

$$\frac{k_x}{k_y} = \frac{\log_{10} C_x/C_x^o}{\log_{10} C_y/C_y^o}$$

where C_x^o and C_y^o are the initial concentrations of X and Y respectively and C_x and C_y are the concentrations at any given time of X and Y respectively. As the volume of the solution remains effectively constant throughout the reaction, concentration can be equated with amounts of compound present (i.e. number of moles). To obtain relative reactivities then molar quantities have to be determined with reasonable accuracy.

It was hoped originally to be able to compete <u>cis</u> and <u>trans</u> isomers of a certain olefin with each other and check the results by crossover experiments. However, for this to be carried out, quantitative analysis had to be carried out by ^{19}F n.m.r. spectroscopy by determining either the quantities of unconverted starting materials or the products. (V.p.c. analysis proved impracticable due to similarity of retention times of the isomeric <u>cis</u> and and <u>trans</u> products). It was found to be impossible to determine accurately the amounts of unreacted olefins present by n.m.r. spectroscopy due to the high volatility of these compounds. Similarly, determination of the quantities of the products by n.m.r. was found to be impracticable due to the very low concentration of the species in solution. The only practical way to determine the relative reactivities was found to be by using pure geometrical isomers of different olefins, carrying out quantitative analysis by v.p.c. By using a Gas Density Balance detector, no previous calibration of the instrument is necessary, and the number of moles of any compound present is directly proportional to its peak area, i.e.

$$n_i = \frac{A_i}{M_i - m}$$

where n_i, A_i and M_i are the number of moles, peak area and molecular weight of the ith component respectively, m is the molecular weight of the carrier gas. Therefore if a known amount of a standard s is introduced into the reaction mixture

$$\frac{n_i}{n_s} + \frac{A_i}{A_s} \frac{(M_s - m)}{(M_i - m)}$$

The number of moles of the ith component (n_i) can then be calculated when A_i and A_s have been measured. As n_i^o is known the rate constant ratio can be calculated.

(ii) <u>Experimental Method</u>

All the competition reactions studied here were carried out using sealed Carius tubes under an atmosphere of dry nitrogen. Approximately 100 mg. of the two olefins were accurately weighed out and were quantitatively transferred into the Carius tube (roughly equimolar amounts were used to minimise errors). The butenyl pyridine (<u>102</u>) was weighed directly into the tube, with the more volatile olefins, however, vacuum line techniques were adopted. After thorough mixing of the olefins the tube was cooled to -180^o and the appropriate volume of sodium phenoxide solution was introduced. Exploratory experiments indicated that accurate quantitative analysis of the products could be achieved if a 75% deficiency of sodium phenoxide was used. In the first series of reactions a 0·25<u>M</u>

solution of sodium phenoxide in dioxane was used. The tube was then sealed under dry nitrogen and placed in a constant temperature bath at 18^{o} with vigorous agitation. After ½ hr. the tubes were opened and a known amount of standard introduced. Quantitative analysis was then carried out using a Griffin and George Gas Density Balance Chromatograph. In all experiments a non-polar column was used (S.G.R.). Reaction mixtures in which the chloro- and bromo-olefins were competed were analysed at 150^{o}, a convenient standard with suitable retention time being a <u>cis</u>:<u>trans</u> mixture of $CF_3(OC_6H_5)C{=}CHCF_3$. Competition reactions between the 2-chloro and butenylpyridine were analysed at 180^{o}, $CF_3(OC_6H_5)C{=}CBrCF_3$ being a convenient standard. Similarly a <u>cis</u>-<u>trans</u> mixture of $CF_3(OC_6H_5)C{=}CClCF_3$ and a temperature of 180^{c} were used to analyse reaction mixtures in which the bromobutenes and butenylpyridine were competed.

It proved impossible to determine the relative reactivity of <u>trans</u>-2H-heptafluorobut-2-ene against the other but-2-enes with any accuracy. The very low reactivity of this olefin and the consequent low concentration of its phenoxy products in the reaction mixture made accurate quantitative analysis impossible.

(iii) Results of Competition Reactions

(a) Cis-$CF_3ClC{=}CFCF_3$ vs. cis-$CF_3BrC{=}CFCF_3$

<u>Cis</u>-$CF_3ClC{=}CFCF_3$, 0·0831 gm., 0·383 m.mole.

<u>Cis</u>-$CF_3BrC{=}CFCF_3$, 0·0885 gm., 0·339 m.mole.

Sodium phenoxide in dioxane, 0·25<u>M</u>, 0·72 ml., 0·18 m.mole.

$CF_3(OC_6H_5)C{=}CHCF_3$, 0·0210 gm., 0·08 m.mole introduced as standard

$$K\ \frac{\underline{cis}\text{-}CF_3BrC{=}CFCF_3}{\underline{cis}\text{-}CF_3ClC{=}CFCF_3} = 1{\cdot}3$$

(b) *Trans*-$CF_3ClC{=}CFCF_3$ vs. *cis*-$CF_3BrC{=}CFCF_3$

Trans-$CF_3ClC{=}CFCF_3$, 0·0777 gm., 0·359 m.mole.

Cis-$CF_3BrC{=}CFCF_3$, 0·0971 gm., 0·0371 m.mole.

Sodium phenoxide in dioxane, 0·25*M*, 0·73 ml., 0·18 m.mole.

$CF_3(OC_6H_5)C{=}CHCF_3$, 0·0240 gm., 0·09 m.mole introduced as standard

$$K\ \frac{\textit{cis}\text{-}CF_3BrC{=}CFCF_3}{\textit{trans}\text{-}CF_3ClC{=}CFCF_3} = 1{\cdot}4$$

(c) *Cis*-$CF_3ClC{=}CFCF_3$ vs. *trans*-$CF_3BrC{=}CFCF_3$

Cis-$CF_3ClC{=}CFCF_3$, 0·0912 gm., 0·421 m.mole.

Trans-$CF_3BrC{=}CFCF_3$, 0·0954 gm., 0·364 m.mole.

Sodium phenoxide in dioxane, 0·25*M*, 0·79 ml., 0·20 m.mole.

$CF_3(OC_6H_5)C{=}CHCF_3$, 0·0250 gm., 0·010 m.mole introduced as standard

$$K\ \frac{\textit{trans}\text{-}CF_3BrC{=}CFCF_3}{\textit{cis}\text{-}CF_3ClC{=}CFCF_3} = 1{\cdot}5$$

(d) *Trans*-$CF_3ClC{=}CFCF_3$ vs. *trans*-$CF_3BrC{=}CFCF_3$

Trans-$CF_3ClC{=}CFCF_3$, 0·0778 gm., 0·360 m.mole.

Trans-$CF_3BrC{=}CFCF_3$, 0·1026 gm., 0·393 m.mole.

Sodium phenoxide in dioxane, 0·25*M*, 0·75 ml., 0·19 m.mole.

$CF_3(OC_6H_5)C{=}CHCF_3$, 0·0250 gm., 0·10 m.mole introduced as standard

$$K\ \frac{\textit{trans}\text{-}CF_3BrC{=}CFCF_3}{\textit{trans}\text{-}CF_3ClC{=}CFCF_3} = 1{\cdot}4$$

(e) Perfluoro-*trans*-4-(2-butenyl)pyridine vs. *trans*-$CF_3ClC{=}CFCF_3$

Trans-$CF_3ClC{=}CFCF_3$, 0·0547 gm., 0·253 m.mole.

Perfluoro-*trans*-4-(2-butenyl)pyridine, 0·0788 gm., 0·238 m.mole.

Sodium phenoxide in dioxane, 0·25*M*, 0·49 ml., 0·12 m.mole.

$CF_3(OC_6H_5)C{=}CBrCF_3$, 0·0229 gm., 0·07 m.mole introduced as standard

$$K\ \frac{\text{perfluoro-}\textit{trans}\text{-4-(2-butenyl)pyridine}}{\textit{trans}\text{-}CF_3ClC{=}CFCF_3} = 11{\cdot}7$$

(f) Perfluoro-trans-4-(2-butenyl)pyridine vs. cis-$CF_3ClC{=}CFCF_3$

Cis-$CF_3ClC{=}CFCF_3$, 0·0473 gm., 0·218 m.mole.

Perfluoro-trans-4-(2-butenyl)pyridine, 0·0764, 0·231 m.mole.

Sodium phenoxide in dioxane, 0·25M, 0·46 ml., 0·12 m.mole.

$CF_3(OC_6H_5)C{=}CBrCF_3$, 0·0239 gm., 0·09 m.mole introduced as standard

$$K \frac{\text{perfluoro-trans-4-(2-butenyl)pyridine}}{\text{cis-}CF_3ClC{=}CFCF_3} = 11{\cdot}5$$

(g) Perfluoro-trans-4-(2-butenyl)pyridine vs. cis-$CF_3BrC{=}CFCF_3$

Cis-$CF_3BrC{=}CFCF_3$, 0·0773 gm., 0·296 m.mole.

Perfluoro-trans-4-(2-butenyl)pyridine 0·0989 gm., 0·299 m.mole.

Sodium phenoxide in dioxane, 0·25M, 0·60 ml., 0·15 m.mole.

$CF_3(OC_6H_5)C{=}CClCF_3$, 0·0193 gm., 0·06 m.mole introduced as standard

$$K \frac{\text{perfluoro-trans-4-(2-butenyl)pyridine}}{\text{cis-}CF_3BrC{=}CFCF_3} = 7{\cdot}5$$

(h) Perfluoro-trans-4-(2-butenyl)pyridine vs. trans-$CF_3BrC{=}CFCF_3$

Trans-$CF_3BrC{=}CFCF_3$, 0·0926 gm., 0·355 m.mole.

Perfluoro-trans-4-(2-butenyl)pyridine, 0·1075 gm., 0·325 m.mole.

Sodium phenoxide in dioxane, 0·25M, 0·68 ml., 0·17 m.mole.

$CF_3(OC_6H_5)C{=}CClCF_3$, 0·0187 gm., 0·06 m.mole introduced as standard

$$K \frac{\text{perfluoro-trans-4-(2-butenyl)pyridine}}{\text{trans-}CF_3BrC{=}CFCF_3} = 7{\cdot}6$$

VIII.G Preparation of Polyfluorobut-2-enes

VIII.G.1 Trans-2H-heptafluorobut-2-ene

The method reported by Maynard[152] was used. Potassium fluoride was dried by heating for 2 days with a bunsen burner and was then stored in a drying oven (120°). N-methyl-2-pyrrolidone was vacuum distilled, the first and last fractions being rejected, and was stored over molecular sieve under an atmosphere of dry nitrogen.

A round bottomed flask (5 l.) fitted with a mercury seal stirrer, reflux condenser and three-necked adaptor with thermometer, dropping funnel and nitrogen inlet was charged with N-methyl-2-pyrrolidone (1500 ml.) and potassium fluoride (540 gm., 9·3 mole). A slow flow of nitrogen was passed through the apparatus and a trap at -180^{o} was placed above the reflux condenser.

Stirring was commenced and the temperature of the slurry was raised to 200^{o} ($\pm 5^{o}$). Hexachlorobutadiene (267 gm., 1·02 mole) was run into the flask over a period of 3 hrs., and the contents gradually became black and viscous. Stirring was continued for a further 3 hrs.

A volatile product was collected in the trap at -180^{o} and was distilled at atmospheric pressure using a vacuum jacketed distillation column to yield a clear highly volatile liquid (116 gm., 62%) which was identified as trans-2H-heptafluorobut-2-ene by comparison of its i.r. and n.m.r. spectra with those of an authentic sample.[126] Infrared spectrum No. 1.

VIII.G.2 Cis- and Trans-2-chloro-heptafluorobut-2-ene

(a) Addition of chlorine to trans-2H-heptafluorobut-2-ene

A sealed evacuated pyrex Carius tube containing trans-2H-heptafluorobut-2-ene (14 gm., 77 m.mole) and chlorine (5·5 gm., 77 m.mole) was irradiated with a 1000 w. Hanovia medium pressure ultraviolet lamp at a distance of approximately 25 cm. for 14 hrs.

The tube was opened and volatile materials allowed to boil off. The product was distilled to yield a colourless liquid (14·8 gm., 76%) which was shown by analytical scale v.p.c. (di-n-decylphthalate, 60^{o}) to contain two major components which were separated by preparative scale v.p.c. and shown to be (in order of emergence from column):

(i) 1st diastereomer of 2H-2,3-dichloro-heptafluorobutane;

(ii) 2nd diastereomer of 2H-2,3-dichloro-heptafluorobutane;

by comparison of their i.r. and n.m.r. spectra with those of authentic samples.[126] Ratio of 1st and 2nd diastereomer = 40:60.

(b) Dehydrochlorination reactions

The reactions were carried out in a three-necked flask (250 ml.) fitted with a reflux condenser, dropping funnel, nitrogen inlet and magnetic stirrer. A trap was placed above the reflux condenser and nitrogen was slowly passed through the apparatus.

(i) 1st diastereomer of 2H-2,3-dichloro-heptafluorobutane

Potassium hydroxide (25 gm., 0·45 mole) was dissolved in water (75 ml.) in the flask and stirring was commenced. 2H-2,3-dichloro-heptafluorobutane (4·2 gm., 16·6 m.mole) was slowly run into the flask and the solution was warmed to 60° on a water bath. The organic layer disappeared and a gas was collected in the trap (3·0 gm., 83%) which was identified as trans-2-chloro-heptafluorobut-2-ene by comparison of its i.r. and n.m.r. spectra with those of an authentic sample.[126]

(ii) 2nd diastereomer of 2H-2,3-dichloro-heptafluorobutane

An identical procedure to that carried out with the 1st diastereomer was followed. Thus the 2nd diastereomer of 2H-2,3-dichloro-heptafluorobutane (5·8 gm., 23·0 m.mole) was dehydrochlorinated to yield cis-2-chloro-heptafluorobut-2-ene (4·4 gm., 83%). Confirmation of the structure was again carried out using i.r. and n.m.r. spectroscopy.

VIII.G.3 Cis- and Trans-2-bromo-heptafluorobut-2-ene

(a) Addition of bromine to trans-2H-heptafluorobut-2-ene

A sealed evacuated pyrex Carius tube containing trans-2H-heptafluorobut-2-ene (6·8 gm., 37·4 m.mole) and bromine (6·0 gm., 37·5 m.mole) was irradiated with a 1000 w. Hanovia medium pressure ultraviolet lamp at a distance of approximately 25 cm. for 17 hrs.

The tube was opened and the contents shaken with aqueous sodium metabisulphite solution. The organic layer was separated to yield a clear liquid (11·9 gm., 93%), analytical scale v.p.c. (di-n-decylphthalate, 70°) showed the presence of two components which were separated by preparative scale v.p.c. and were identified as (in order of emergence from column):

(i) <u>1st diastereomer 2H-2,3-dibromo-heptafluorobutane</u>;

(ii) <u>2nd diastereomer 2H-2,3-dibromo-heptafluorobutane</u>;

by comparison of their i.r. and n.m.r. spectra with those of authentic samples.[126] Ratio of 1st and 2nd diastereomer = 35:65.

(b) <u>Dehydrobromination reactions</u>

Identical apparatus and conditions were used as for the previous dehydrochlorination reactions (VII.G.2(b)).

(i) <u>1st diastereomer of 2H-2,3-dibromo-heptafluorobutane</u>

2H-2,3-dibromo-heptafluorobutane (5·3 gm., 16 m.mole) potassium hydroxide (27 gm., 0·48 mole) and water (30 ml.) were stirred together at 60° for 12 hrs. The lower organic layer in the flask and material collected in the cold trap (3·0 gm., 75%) were combined and was found to consist of a single compound by analytical scale v.p.c. (di-n-decylphthalate, 25°) which was identified as <u>trans</u>-2-bromo-heptafluorobut-2-ene by comparison of its i.r. and n.m.r. spectra with those of an authentic sample. Infrared spectrum No. 4.

(ii) <u>2nd diastereomer of 2H-2,3-dibromo-heptafluorobutane</u>

2H-2,3-dibromoheptafluorobutane (7·1 gm., 20·7 m.mole) potassium hydroxide (27 gm., 0·48 mole) and water (30 ml.) were stirred together at 60° for 12 hrs.

The lower organic layer in the flask and the material collected in the cold trap were combined to yield a clear liquid (4·5 gm., 83%) which was shown by analytical scale v.p.c. to contain a single compound which was identified as cis-2-bromo-heptafluorobut-2-ene by comparison of its i.r. and n.m.r. spectra with those of an authentic sample. Infrared spectrum No. 5.

VIII.G.4 Perfluoro-trans-4-(2-butenyl)pyridine

(a) Preparation of perfluoro-4-sec-butylpyridine

In a typical reaction, pentafluoropyridine (12 gm., 71 m.mole), octafluorobut-2-ene (15·6 gm., 78 m.mole), sulpholan (15 ml.) and caesium fluoride (6 gm., 39 m.mole) were sealed in a nickel tube under dry nitrogen which was rotated in an oil bath at 160°. After 48 hrs. the tube was cooled and volatile materials were vacuum transferred into a cold trap to yield a clear liquid (20·2 gm.). Analytical scale v.p.c. (S.G.R., 110°) showed the presence of two components which were separated by distillation at atmospheric pressure using a spinning band column and were identified as:

(i) perfluoro-4-sec-butylpyridine (15·1 gm., 58%);

(ii) perfluoro-2,4-di-sec-butylpyridine (5·0 gm., 12%);

by comparison of their i.r. and n.m.r. spectra with those of authentic samples.

(b) Defluorination of perfluoro-4-sec-butylpyridine

In a typical experiment perfluoro-4-sec-butylpyridine (5·8 gm., 15·7 m.mole) was passed through a silica tube (24" x $\frac{1}{2}$") packed with coarse iron filings using a flow of dry nitrogen. The tube was heated to 440°, volatile materials were collected in a trap at -78° (4·2 gm.).

Analytical scale v.p.c. (di-n-decylphthalate, 100°) showed the presence of two components which were separated by preparative scale v.p.c. and identified as (in order of emergence from column):

(i) perfluoro-trans-4-(2-butenyl)pyridine, (3·6 gm., 69%);

(ii) perfluoro-4-sec-butylpyridine, (0·6 gm.);

by comparison of their i.r. and ^{19}F n.m.r. spectra with those of authentic samples.

VIII.G.5 Perfluoro-2,3-diethylbut-2-ene

Octafluorobut-2-ene (2·0 gm., 10·0 m.mole), caesium fluoride (2 gm., 13·1 m.mole) and sulpholan were sealed together in a nickel tube, under an atmosphere of dry nitrogen, which was rotated in an oil bath at 100° for 24 hrs. The tube was opened and volatile materials allowed to boil off. The remaining material was vacuum distilled to yield a clear liquid (1·0 gm., 50%) which was identified as perfluoro-2,3-diethylbut-2-ene. [Found: C, 24·2; F, 75·8%; M^+, 400. Calc. for C_4F_{16}: C, 24·0; F, 76·0%; M, 400]. Comparison of the i.r. and ^{19}F n.m.r. spectra with those of an authentic sample further confirmed the structure. Infrared spectrum No. 7.

CHAPTER IX

Organometallic Chemistry

IX.A Organolithium Derivatives

IX.A.1 Perfluoro-2-butenyl-lithium

All the reactions of n-butyl-lithium with these 2-butenes were carried out in a 250 ml. flask fitted with nitrogen inlet and outlet, and a dropping funnel. Agitation was effected using a magnetic stirrer.

In a typical reaction a cis-trans mixture of 2-bromo-heptafluorobut-2-ene (5 gm., 19·2 m.mole) which had been previously dried over P_2O_5 was added to dry diethyl ether (70 ml.) in the flask. A slow flow of dry nitrogen was passed through the apparatus and the flask cooled to -78^o in a cardice/acetone bath. A solution of n-butyl-lithium in hexane (8·0 ml., 2·5M, 20 m.mole) was slowly added to the flask from the dropping funnel with vigorous stirring. On standing the solution for 3 hrs. at -78^o a deep brown solution was produced. HCl gas in excess was passed into the apparatus and the solution was allowed to warm to room temperature. A trap at -180^o was placed on the outlet from the flask, however, no volatile material was collected. The reaction solution was hydrolysed with dilute acid and then filtered to yield a brown amorphous solid (3·3 gm.) which was identified by i.r. and E.S.C.A. as being polymeric material of general structure $\text{-(}C(CF_3)=C(CF_3)\text{)-}_n$. Material of this nature has been previously reported as being formed in fluoride ion-initiated reactions of hexafluorobut-2-yne.

A similar experiment in which 2-bromo-heptafluorobut-2-ene (5·4 gm., 20·7 m.mole) was reacted with n-butyl-lithium (8·6 ml., 2·5M, 21·5 m.mole) in ether (70 ml.) for ½ hr. followed by attempted quenching with trimethylchlorosilane (2·3 gm., 21·2 m.mole) and subsequent work up again produced only polymeric material (3·6 gm.).

Numerous reactions were carried out in which the conditions were varied, using different trapping agents ($HgCl_2$ or diethylcarbonate), reaction times and pre-cooling the butyl-lithium solution to -78°, but in all cases only polymeric material was obtained.

IX.A.2 Reaction of Tetrafluoropyridyl-lithium with Octafluorobut-2-ene

4-Bromo-tetrafluoropyridine (2·3 gm., 10 m.mole) and ether (25 ml.) were placed in a 100 ml. flask fitted with nitrogen inlet and outlet, and a dropping funnel fitted with a drying tube. A slow flow of nitrogen was passed through the apparatus which was cooled to -78° in a cardice/acetone bath; n-butyl-lithium in hexane (10·5 ml., 1·0M, 10·5 m.mole) was slowly added to the flask from the dropping funnel. The exchange reaction was allowed to proceed for $^3/_4$ hr. Octafluorobut-2-ene (2·1 gm., 10·5 m.mole) was condensed into the flask and the reaction was allowed to proceed for $\frac{1}{2}$ hr. at -78°. The apparatus was allowed to slowly attain room temperature and the solution was hydrolysed with dilute HCl. The ethereal layer was removed and the aqueous layer washed with ether (20 ml.), the organic phases were combined and dried ($MgSO_4$) and the solvent evaporated under vacuum to yield a brown solid which was recrystallised from ether to yield a white crystalline solid (1·8 gm., 78%) which was identified as a <u>cis-trans</u> mixture of <u>perfluoro-2,3-di-(4-pyridyl)-but-2-ene</u>, m.p. 121-124°. [Found: C, 36·2; N, 6·1; F, 57·4%; M^+, 462. $C_{14}N_2F_{14}$ requires C, 36·4; N, 6·0; F, 57·6%; M, 462]. Integration of the trifluoromethyl group resonances in the ^{19}F n.m.r. spectrum indicated a 4:1 ratio of the geometrical isomers, however, due to the absence of couplings unambiguous assignments could not be made. Infrared spectrum No. 32.

A similar reaction using identical quantities of reactants was carried out, however, the solution of tetrafluoropyridyl-lithium at -78° was added to octafluorobut-2-ene in the flask. Identical work up afforded again the cis-trans mixture of perfluoro-2,3-di-(4-pyridyl)-but-2-ene in similar yield.

IX.B Organomagnesium Derivatives

The apparatus used for these reactions consisted of a 250 ml. flask fitted with nitrogen inlet and outlet, and a dropping funnel. A slow flow of nitrogen was passed through the apparatus and the reactions were carried out at room temperature.

Thus when 2-bromo-heptafluorobut-2-ene (5·0 gm., 19·2 m.mole) was slowly added to magnesium (0·5 gm., 20·5 m.mole) in dry T.H.F. (150 ml.), a reaction was seen to take place by observing the disappearance of the metal. The solution was poured over crushed cardice and was hydrolysed with dilute HCl. The organic layer was separated, work up yielded only tarry material (3·0 gm.).

A similar reaction in which attempted trapping of the organomagnesium derivative with tetrafluoropyridazine followed by a similar work up yielded only the unreacted perfluoroheterocycle.

IX.C Organocopper Derivatives

IX.C.1 Reaction of 2-Iodo-heptafluorobut-2-ene with Iodobenzene and Copper Bronze in D.M.F.

A cis-trans mixture of 2-iodo-heptafluorobut-2-ene (1·25 gm., 4·1 m.mole; cis-trans ratio = 68:32), iodobenzene (0·85 gm., 3·1 m.mole), copper bronze (0·6 gm., 9·4 m.mole) and D.M.F. (15 ml.) were sealed together in a small Pyrex Carius tube which was heated to 120° for 8 hrs. The tube was opened and the unreacted copper filtered off. The resulting solution was poured into water (50 ml.) and was extracted with ether (2 x 20 ml.). The ethereal solution was dried ($MgSO_4$) and the solvent evaporated under vacuum to yield a clear liquid (0·7 gm., 70%) which was identified as a cis-trans mixture of 2-phenyl-heptafluorobut-2-ene. [Found: C, 46·5; H, 2·1; F, 51·3%; M^+ 258. Calc. for $C_{10}H_5F_7$:[118] C, 46·5; H, 1·9; F, 51·5%; M, 258]. Integration of the trifluoromethyl group resonances confirmed a 55:45, cis-trans ratio.

IX.C.2 Attempted Preparation of Perfluoro-2-butenyl-copper by Exchange

Pentafluorobenzene (3·5 gm., 20·8 m.mole) and T.H.F. (50 ml.) were mixed together in the apparatus previously described (IX.A.1) which was cooled to -78°. n-Butyl-lithium in hexane (21·5 ml., 1·0M, 21·5 m.mole) was slowly added to the solution and the reaction allowed to proceed for 45 min. Cuprous iodide (4·0 gm., 21·0 m.mole) was added to the solution which was stirred for 11 hrs. at -78°, 2-bromo-heptafluorobut-2-ene (5·4 gm., 20·7 m.mole) was added to the flask and the solution was left for 11 hrs. at -78°. The solution was allowed to warm up to room temperature and was left for 3 hrs. Benzoyl chloride (3·0 gm., 21·3 m.mole) was added slowly to the solution which was left for ½ hr. The solution was concentrated under vacuum and was hydrolysed with dilute HCl and extracted with ether (2 x 25 ml.). Evaporation of the ether under vacuum produced a clear liquid (3·8 gm., 68%) which was shown by v.p.c. analysis to contain a single component which was identified as pentafluorobenzophenone by comparison of its n.m.r. and i.r. spectra with those of an authentic sample.

A further reaction was carried out using a similar procedure to that previously described, however, the apparatus was fitted with a reflux condenser and the solution was left at 55° for 4½ hrs. after the addition of 2-bromo-heptafluorobut-2-ene. After work up only pentafluorobenzophenone was again isolated.

APPENDIX 1

^{19}F and ^{1}H N.m.r. Spectra

N.M.R. Data

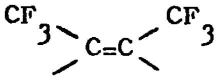
Both the ^{19}F and ^{1}H spectra were recorded using a Varian A56/60D spectrometer.

Fluorine chemical shifts were measured from external $CFCl_3$, positive shifts being to high field. External T.M.S. was used as reference for proton spectra with positive values of the shifts indicating lower field.

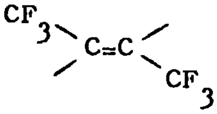
Geometrical isomers of the various 2-butenes have been distinguished by the CF_3-CF_3 coupling constant. It has been shown that in these systems, the cis-CF_3 coupling has a value of approximately 12 Hz. whilst trans-CF_3 couplings have a characteristic value of approximately 1·5 Hz.

In cases where a vinylic fluorine was present, the CF_3-F coupling across the double bond was used to provide additional confirmation of the structure. This has a value of approximately 23 Hz. when the groups are cis and approximately 9 Hz. when trans.[118]

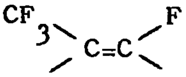
Characteristic Coupling Constants



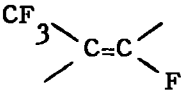
J = 11 → 13 Hz.



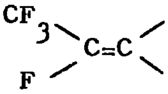
J = 1 → 2 Hz.



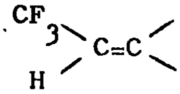
J = 18 → 25 Hz.



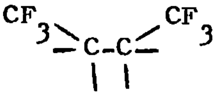
J = 8·5 → 11 Hz.



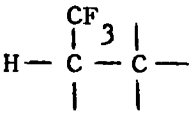
J = 4 → 8 Hz.



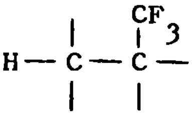
J = 7 → 9 Hz.



J = 0 → 18 Hz.

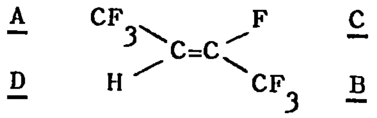


J = 2 → 29 Hz.



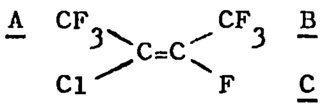
J = 0 → 1·6 Hz.

Trans-2H-heptafluorobut-2-ene



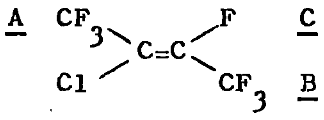
Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
60·4	J_{AC} = 17·7, J_{AD} = 6·9 J_{AB} = 1·5	3	A-C$\underline{F}_3$
74·6	J_{BC} = 8·9, J_{AB} = 1·5	3	B-C$\underline{F}_3$
117·2	Complex multiplet	1	C-$\underline{F}$

Cis-2-chloro-heptafluorobut-2-ene



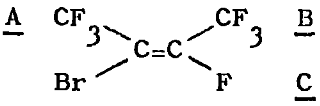
Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
62·2	Doublet of Quartets $J_{AC} = 8·7$, $J_{AB} = 11·5$	3	A-C$\underline{F}_3$
66·3	Doublet of Quartets $J_{BA} = 11·3$, $J_{BC} = 7·7$	3	B-C$\underline{F}_3$
106·8	Broad Multiplet $J_{CB} = 7·7$, $J_{CA} = 8·7$	1	C-$\underline{F}$

Trans-2-chloro-heptafluorobut-2-ene



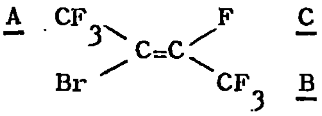
Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
64·8	Doublet of Quartets $J_{AC} = 24·7$, $J_{AB} = 1·5$	3	A-C$\underline{F}_3$
68·4	Doublet of Quartets $J_{BA} = 1·5$, $J_{BC} = 5·5$	3	B-C$\underline{F}_3$
113·7	Broad Multiplet $J_{CA} = 24·7$, $J_{CB} = 5·5$	1	C-$\underline{F}$

Cis-2-bromo-heptafluorobut-2-ene



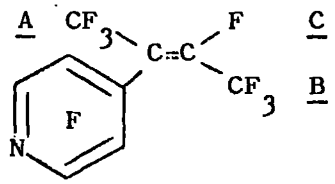
Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
59·8	Doublet of Quartets J_{AC} = 9·0, J_{AB} = 11·5	3	A-C$\underline{F}_3$
66·2	Doublet of Quartets J_{BA} = 11·5, J_{BC} = 7·2	3	B-C$\underline{F}_3$
95·6	Complex multiplet J_{CB} = 7·2, J_{CA} = 9·0	1	C-$\underline{F}$

Trans-2-bromo-heptafluorobut-2-ene



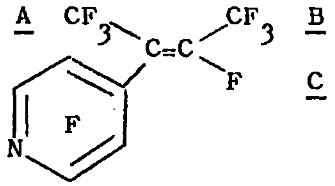
Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
62·6	Doublet of Quartets J_{AC} = 25·5, J_{AB} = 1·5	3	A-C$\underline{F}_3$
68·1	Doublet of Quartets J_{BC} = 4·0, J_{BA} = 1·5	3	B-C$\underline{F}_3$
102·4	Complex Multiplet J_{CB} = 4·0, J_{CA} = 25·5	1	C-$\underline{F}$

Perfluoro-*trans*-4-(2-butenyl)pyridine



Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
61·3	Doublet of Quartets $J_{AC} = 21$, $J_{AB} = 1\cdot5$	3	$\text{A-C}\underline{\text{F}}_3$
69·0	Doublet of Quartets $J_{BC} = 7\cdot5$, $J_{BA} = 1\cdot5$	3	$\text{B-C}\underline{\text{F}}_3$
88·0	Broad Multiplet	2	2,6 Ring F's
103·9	Multiplet $J_{CA} = 21$, $J_{CB} = 7\cdot5$	1	$\text{B-}\underline{\text{F}}$
140·0	Broad Multiplet	2	3,5 Ring F's

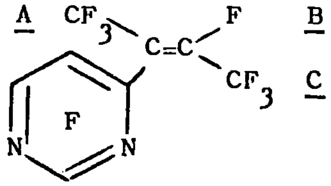
Perfluoro-*cis*-4-(2-butenyl)pyridine



Spectrum carried out on a 20:80, *cis*:*trans* mixture

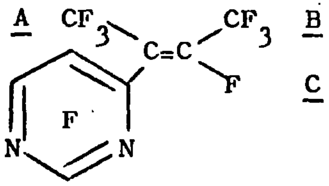
Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
57·4	Doublet of Quartets $J_{AB} = 11\cdot0$, $J_{AC} = 6\cdot5$	3	$\text{A-C}\underline{\text{F}}_3$
67·3	Doublet of Quartets $J_{BA} = 11\cdot0$, $J_{BC} = 7\cdot0$	3	$\text{B-C}\underline{\text{F}}_3$
88·0	Broad Multiplet	2	2,6 Ring F's
100·4	Broad Resonance	1	$\text{C-}\underline{\text{F}}$
140·0	Broad Multiplet	2	3,5 Ring F's

Perfluoro-trans-4-(2-butenyl)pyrimidine



Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
48·2	Doublet $J_{25} \approx 26$	1	2 Ring F
62·8	Doublet of Quartets $J_{AB} = 22$, $J_{AC} = 1{\cdot}5$	3	A-CF_3
72·3	Doublet of Quartets $J_{CA} = 1{\cdot}5$, $J_{CB} = 7{\cdot}5$	3	C-CF_3
74·0	Doublet $J_{65} = 22$	1	6 Ring F
109·4	Overlapping Quartet of Quartets $J_{BA} = 22$, $J_{BC} = 7{\cdot}5$	1	B-F
154·4	Broad Triplet $J \approx 25$	1	5 Ring F

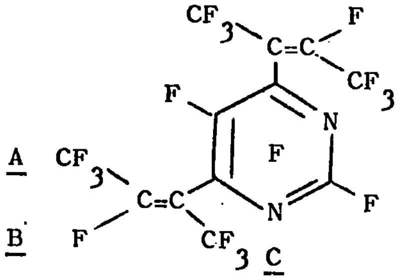
Perfluoro-cis-4-(2-butenyl)pyrimidine



Spectrum carried out on a 11:89 cis:trans mixture

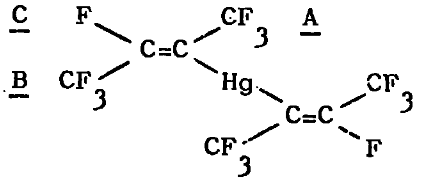
Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
48·2	Doublet $J_{25} \approx 26$	1	2 Ring F
59·3	Doublet of Quartets $J_{AB} = 11{\cdot}0$, $J_{AC} = 8{\cdot}5$	3	A-CF_3
70·8	Doublet of Quartets $J_{BA} = 11{\cdot}0$, $J_{BC} = 7{\cdot}0$	3	B-CF_3
74·0	Doublet $J_{65} = 22$	1	6 Ring F
105·6	Broad Resonance	1	C-F
154·4	Broad Triplet $J \approx 25$	1	5 Ring F

Perfluoro-*trans*-4,6-di-(2-butenyl)pyrimidine



Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
49·5	Broad Resonance	1	2 Ring $\underline{F}$
62·9	Doublet of Quartets $J_{CB} = 20$, $J_{CA} = 1{\cdot}5$	6	$\text{C-C}\underline{\text{F}}_3$
72·4	Doublet of Quartets $J_{AC} = 1{\cdot}5$, $J_{AB} = 7$	6	$\text{A-C}\underline{\text{F}}_3$
109·5	Broad Resonance	2	$\text{B-}\underline{\text{F}}$
136·0	Broad Doublet $J \approx 30$	1	5 Ring $\underline{F}$

Perfluoro-*trans*-bis-(2-butenyl)mercury

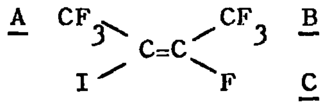


in ether

Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
52·2	Doublet of Quartets $J_{AB} = 1{\cdot}5$, $J_{AC} = 18$	3	$\text{A -C}\underline{\text{F}}_3$
71·4	Doublet of Quartets $J_{BA} = 1{\cdot}5$, $J_{BC} = 9$	3	$\text{B-C}\underline{\text{F}}_3$
96·1	Broad Resonance	1	$\text{C-}\underline{\text{F}}$

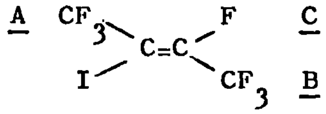
The low field trifluoromethyl group at 52·2 p.p.m. shows a large Hg-F coupling of 136 Hz. of 16% intensity relative to the major resonances.

Cis-2-iodo-heptafluorobut-2-ene



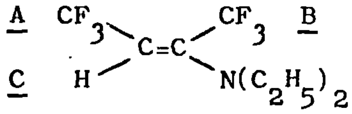
Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
57·5	Overlapping Multiplet J_{AB} = 12 approx., J_{AC} = 9·0	3	A-$C\underline{F}_3$
67·4	Complex Multiplet J_{BA} = 12, $J_{BC} \approx 8$	3	B-$C\underline{F}_3$
78·5	Complex Multiplet	1	C-$\underline{F}$

Trans-2-iodo-heptafluorobut-2-ene



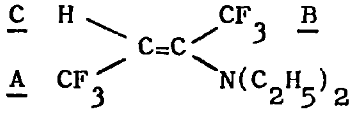
Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
60·3	Doublet of Quartets J_{AB} = 1·5, J_{AC} = 24·5	3	A-$C\underline{F}_3$
68·5	Doublet of Quartets J_{BA} = 1·5, J_{BC} = 4·0	3	B-$C\underline{F}_3$
87·9	Quartet of Quartets J_{CB} = 4·0, J_{CA} = 24·5	1	C-$\underline{F}$

Cis-2H-3-N,N-diethylamino-hexafluorobut-2-ene



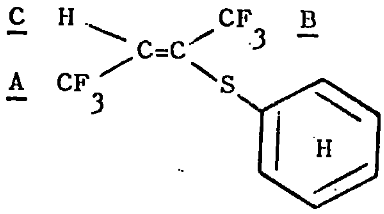
Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
54·4	Overlapping Doublet of Quartets J_{AB} = 12·5, J_{AC} = 8·5	1	A-C$\underline{F}_3$
63·2	Quartet J_{BA} = 12·5	1	B-C$\underline{F}_3$
Proton Spectrum			
0·85	Triplet J = 7	3	C$\underline{H}_3$-CH$_2$
2·97	Quartet J = 7	2	CH$_3$-C$\underline{H}_2$
4·6	Quartet J_{CA} = 8·5	1	C-$\underline{H}$

Trans-2H-3-N,N-diethylamino-hexafluorobut-2-ene



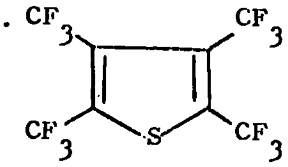
Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
58·4	Doublet of Quartets J_{AB} = 1·5, J_{AC} = 8·0	1	A-C$\underline{F}_3$
67·7	Quartet J_{BA} = 1·5	1	B-C$\underline{F}_3$
Proton Spectrum			
0·85	Triplet J = 7	3	C$\underline{H}_3$-CH$_2$
2·97	Quartet J = 7	2	CH$_3$-C$\underline{H}_2$
5·17	Quartet J_{CA} = 8·0	1	C-$\underline{H}$

Trans-2H-3-thiophenoxy-hexafluorobut-2-ene



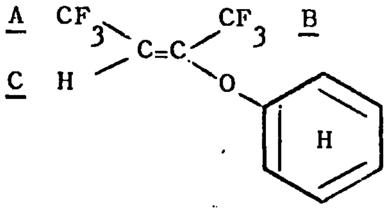
Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
59·9	Doublet of Quartets $J_{AB} = 1{\cdot}5$, $J_{AC} = 7{\cdot}0$	1	A-C$\underline{F}_3$
65·2	Quartet $J_{BA} = 1{\cdot}5$	1	B-C$\underline{F}_3$
Proton Spectrum			
6·3	Quartet $J_{CA} = 7{\cdot}0$	1	C-$\underline{H}$
6·95	Complex Multiplet	5	Ring H's

Tetrakis-trifluoromethyl-thiophene



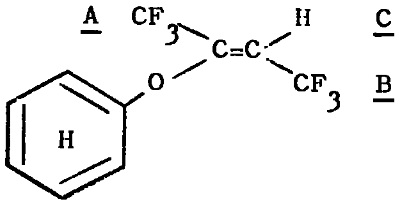
Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
57·4	Broad Singlet	1	3,4-C$\underline{F}_3$ groups
59·1	Broad Singlet	1	1,5-C$\underline{F}_3$ groups

Cis-2H-3-phenoxy-hexafluorobut-2-ene



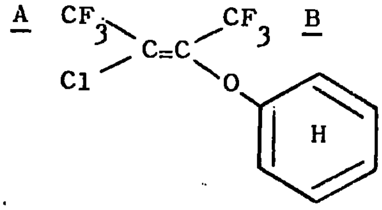
Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
56·0	Overlapping Doublet of Quartets J_{AB} = 11·0, J_{AC} = 9·0	1	A-C$\underline{F}_3$
69·8	Quartet J_{BA} = 11·0	1	B-C$\underline{F}_3$
Proton Spectrum			
4·7	Quartet J_{CA} = 9·0	1	C-$\underline{H}$
6·75	Complex Multiplet	5	Ring H's

Trans-2H-3-phenoxy-hexafluorobut-2-ene



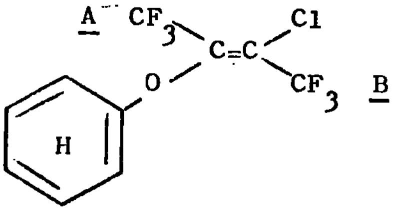
Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
61·5	Doublet of Quartets J_{BA} = 1·5, J_{BC} = 8·0	1	B-C$\underline{F}_3$
71·0	Quartet J_{AB} = 1·5	1	A-C$\underline{F}_3$
Proton Spectrum			
5·5	Quartet J_{CB} = 8·0	1	C-$\underline{H}$
6·5	Complex Multiplet	5	Ring H's

Cis-2-chloro-3-phenoxy-hexafluorobut-2-ene



Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
62·9	Quartet J_{AB} = 12·0	1	A-$C\underline{F}_3$
63·5	Quartet J_{BA} = 12·0	1	B-$C\underline{F}_3$

Trans-2-chloro-3-phenoxyhexafluorobut-2-ene

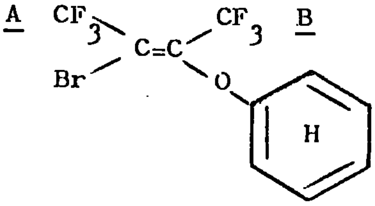


Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
65·1	Quartet J_{BA} = 1·5	1	B-$C\underline{F}_3$
65·5	Quartet J_{AB} = 1·5	1	A-$C\underline{F}_3$

Proton Spectrum

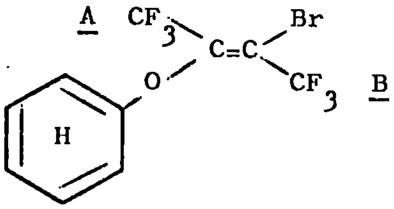
Both cis and trans isomers show a broad multiplet at approximately 6·9 p.p.m. assigned to the protons of the aromatic rings

Cis-2-bromo-3-phenoxy-hexafluorobut-2-ene



Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
60·1	Quartet J_{AB} = 12·5	1	A-CF$_3$
62·7	Quartet J_{BA} = 12·5	1	B-CF$_3$

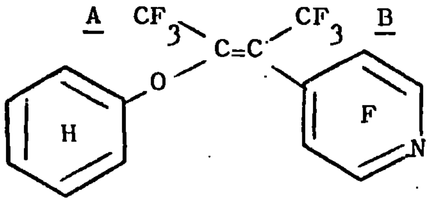
Trans-2-bromo-3-phenoxy-hexafluorobut-2-ene



Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
62·3	Quartet J_{AB} = 1·5	1	A-CF$_3$
64·7	Quartet J_{BA} = 1·5	1	B-CF$_3$

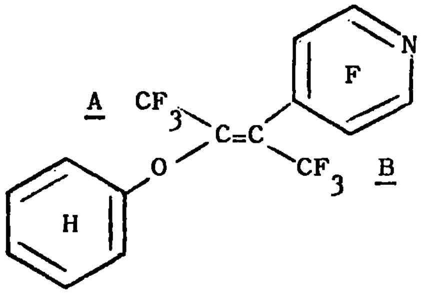
The ^{1}H n.m.r. spectrum of the mixture consists of a broad complex multiplet at 6·85 p.p.m. assigned to the protons of the aromatic rings.

Cis-2-phenoxy-3-(4-tetrafluoropyridyl)-hexafluorobut-2-ene



Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
58·9	Quartet J_{BA} = 12	3	B-CF_3
66·0	Quartet J_{AB} = 12	3	A-CF_3
90·7	Complex Multiplet	2	2,6 Ring F's
141·0	Complex Multiplet	2	3,5 Ring F's

Trans-2-phenoxy-3-(4-tetrafluoropyridyl)-hexafluorobut-2-ene

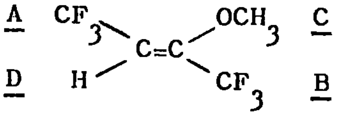


Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
64·9	Quartet J_{AB} = 1·5	3	A-CF_3
62·3	Quartet J_{BA} = 1·5	3	B-CF_3
90·7	Complex Multiplet	2	2,6 Ring F's
141·0	Complex Multiplet	2	3,5 Ring F's

Proton Spectra

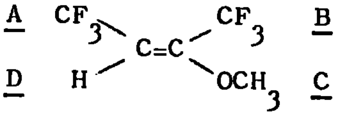
Both the _cis_ and _trans_ isomers show a broad multiplet at 6·9 p.p.m. assigned to the protons of the aromatic rings.

Trans-2H-3-methoxy-hexafluorobut-2-ene



Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
59·9	Doublet of Quartets J_{AB} = 1·5, J_{AD} = 7·0	3	A-C$\underline{F}_3$
73·1	Quartet J_{BA} = 1·5	3	B-C$\underline{F}_3$
Proton Spectrum			
3·5	Singlet	3	-O-C$\underline{H}_3$
5·3	Quartet J_{DA} = 7·0	1	D-$\underline{H}$

Cis-2H-3-methoxy-hexafluorobut-2-ene

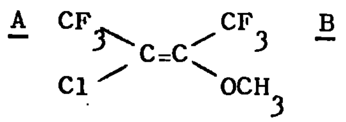


Characterised as a component in a 10:90 *cis*:*trans* mixture

Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
56·2	Doublet of Quartets J_{AB} = 12, J_{AD} = 7	1	A-C$\underline{F}_3$
71·0	Quartet J_{BA} = 12	1	B-C$\underline{F}_3$
Proton Spectrum			
3·6	Singlet		O-C$\underline{H}_3$

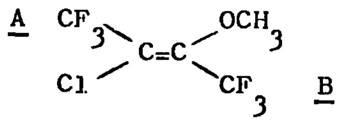
Due to the extremely low concentration of this compound in the mixture, the chemical shift of the hydrogen atom at position-2 could not be determined.

Cis-2-chloro-3-methoxy-hexafluorobut-2-ene



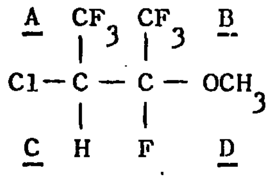
Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
62·5	Quartet $J_{AB} = 12{\cdot}5$	1	A-$\underline{\text{CF}}_3$
65·3	Quartet $J_{BA} = 12{\cdot}5$	1	B-$\underline{\text{CF}}_3$
Proton Spectrum			
3·65	Singlet		O-$\underline{\text{CH}}_3$

Trans-2-chloro-3-methoxy-hexafluorobut-2-ene



Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
64·7	Quartet $J_{AB} = 1{\cdot}0$	1	A-$\underline{\text{CF}}_3$
66·5	Quartet $J_{BA} = 1{\cdot}0$	1	B-$\underline{\text{CF}}_3$
Proton Spectrum			
3·47	Singlet		O-$\underline{\text{CH}}_3$

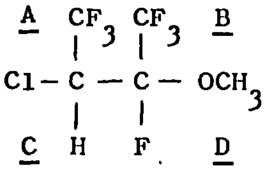
1st diastereomer 2H-2-chloro-3-methoxy-heptafluorobutane



$$\mathrm{Cl{-}\overset{CF_3}{\underset{H}{C}}{-}\overset{CF_3}{\underset{F}{C}}{-}OCH_3}$$

Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
69·9	Complex Multiplet $J_{AB} = 6$, $J_{AC} = 6$ $J_{AD} = 9{\cdot}0$	3	A-C$\underline{F_3}$
78·5	Quartet $J_{BA} = 6$	3	B-C$\underline{F_3}$
133·4	Overlapping Doublet of Quartets $J_{DA} = 9{\cdot}0$, $J_{DC} = 8{\cdot}5$	1	D-$\underline{F}$
Proton Spectrum			
2·8	Singlet	3	O-C$\underline{H_3}$
3·7	Overlapping Doublet of Quartets $J_{CA} = 6$, $J_{CD} = 8{\cdot}5$	1	C-$\underline{H}$

2nd diastereomer 2H-2-chloro-3-methoxy-heptafluorobutane



$$\mathrm{Cl-\underset{H}{\overset{CF_3}{C}}-\underset{F}{\overset{CF_3}{C}}-OCH_3}$$

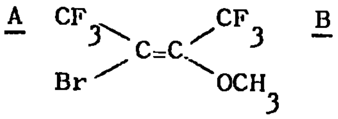
Due to the very low concentration of this component in the mixture only a very small amount of pure material was isolated, consequently the n.m.r. spectrum was poorly resolved.

Chemical Shift (p.p.m.)	Coupling Constant (H .)	Relative Intensity	Assignment
70·4	Broad resonance apparently containing 15 Hz. and 6 Hz. couplings	3	A-$\underline{CF_3}$
77·3	Broad resonance	3	B-$\underline{CF_3}$
130·0	Quartet J_{DA} = 15	1	D-$\underline{F}$

Proton Spectrum

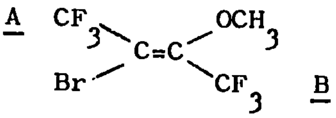
2·8	Singlet	3	O-$\underline{CH_3}$
3·7	Broad resonance	1	C-$\underline{H}$

Cis-2-bromo-3-methoxy-hexafluorobut-2-ene



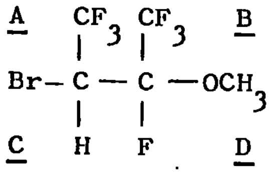
Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
60·0	Quartet J_{AB} = 13	1	A-C$\underline{F}_3$
64·5	Quartet J_{BA} = 13	1	B-C$\underline{F}_3$
Proton Spectrum			
3·3	Singlet	–	O-C$\underline{H}_3$

Trans-2-bromo-3-methoxy-hexafluorobut-2-ene



Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
61·2	Quartet J_{AB} = 1·5	1	A-C$\underline{F}_3$
65·0	Quartet J_{BA} = 1·5	1	B-C$\underline{F}_3$
Proton Spectrum			
3·8	Singlet	–	O-C$\underline{H}_3$

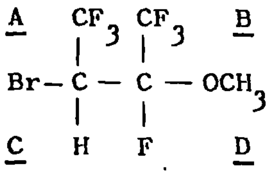
1st diastereomer 2H-2-bromo-3-methoxy-heptafluorobutane



$$\begin{array}{ccccc} & CF_3 & & CF_3 & \\ & | & & | & \\ Br- & C & - & C & -OCH_3 \\ & | & & | & \\ & H & & F & \end{array}$$

Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
67·4	Doublet of Doublets $J_{AD} = 14$, $J_{AC} = 7$	3	$A\text{-}C\underline{F}_3$
76·4	Broad Singlet	3	$B\text{-}C\underline{F}_3$
128·4	Quartet $J_{DA} = 14$	1	$D\text{-}\underline{F}$
Proton Spectrum			
3·1	Singlet	3	$O\text{-}C\underline{H}_3$
3·8	Quartet $J_{CA} = 7$	1	$C\text{-}\underline{H}$

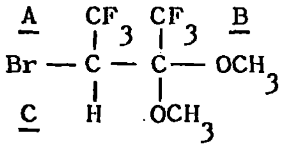
2nd diastereomer 2H-2-bromo-3-methoxy-heptafluorobutane



$$Br-\overset{CF_3}{\underset{H}{C}}-\overset{CF_3}{\underset{F}{C}}-OCH_3$$

Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
67·4	Overlapping Doublet of Doublets of Quartets (Sextet) $J = 8$	3	A-$C\underline{F}_3$
77·4	Quartet $J_{BA} = 8$	3	B-$C\underline{F}_3$
124·8	Overlapping Doublet of Quartets $J_{DA} = 8$, $J_{DC} \approx 8$	1	D-$\underline{F}$
Proton Spectrum			
3·6	Singlet	3	O-$C\underline{H}_3$
4·4	Overlapping Doublet of Quartets $J_{CA} \approx 8$, $J_{CD} \approx 8$	1	C-$\underline{H}$

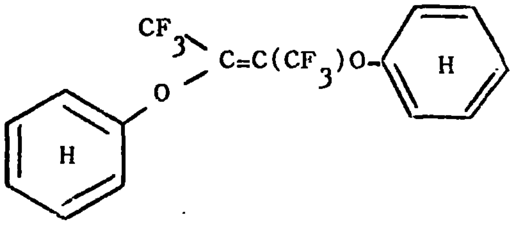
2H-2-bromo-3,3-dimethoxy-hexafluorobutane



$BrC(CF_3)(H){-}C(CF_3)(OCH_3)OCH_3$

Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
65·2	Overlapping Doublet of Quartets $J_{AB} = 7$, $J_{AC} = 7$	1	A-C$\underline{F}_3$
73·5	Quartet $J_{BA} = 7$	1	B-C$\underline{F}_3$
Proton Spectrum			
3·5	Singlet	6	O-C$\underline{H}_3$
4·4	Quartet $J_{CA} = 7$	1	C-$\underline{H}$

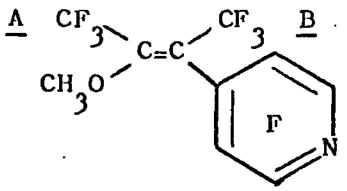
2,3-Diphenoxy-hexafluorobut-2-ene



probably trans in ether

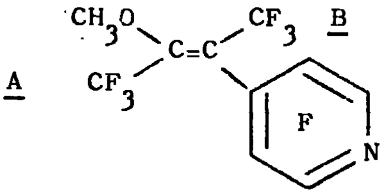
Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
57·0	Singlet	-	C$\underline{F}_3$ groups
Proton Spectrum			
6·8	Broad Multiplet	-	Protons of aromatic rings

Cis-2-methoxy-3-(4-tetrafluoropyridyl)hexafluorobut-2-ene



Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
58·4	Quartet J_{BA} = 12·0	3	B-CF_3
65·9	Quartet J_{AB} = 12·0	3	A-CF_3
92·4	Complex Multiplet	2	2,6 Ring F's
142·6	Complex Multiplet	2	3,5 Ring F's

Trans-2-methoxy-3-(4-tetrafluoropyridyl)hexafluorobut-2-ene

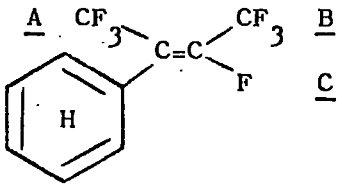


Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
62·4	Quartet J_{BA} = 1·5	3	B-CF_3
66·8	Quartet J_{AB} = 1·5	3	A-CF_3
92·4	Complex Multiplet	2	2,6 Ring F's
142·6	Complex Multiplet	2	3,5 Ring F's

Proton Spectra

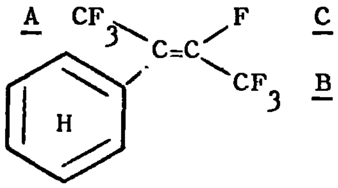
Both cis and trans isomers show a singlet at 3·5 p.p.m. assigned to the methyl groups.

Cis-2-phenyl-heptafluorobut-2-ene



Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
59·7	Overlapping Doublet of Quartets J_{AB} = 12·0, J_{AC} = 11·0	3	A-C$\underline{F}_3$
68·4	Overlapping Doublet of Quartets J_{BA} = 12·0, J_{BC} = 7·0	3	B-C$\underline{F}_3$
113·8	Complex Multiplet J_{CA} = 11·0, J_{CB} = 7·0	1	C-$\underline{F}$

Trans-2-phenyl-heptafluorobut-2-ene

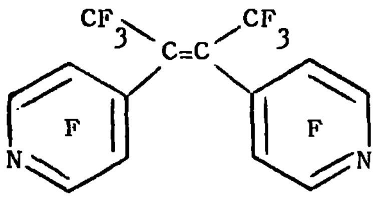


Chemical Shift (p.p.m.)	Coupling Constant (Hz.)	Relative Intensity	Assignment
63·1	Doublet of Quartets J_{AB} = 1·5, J_{AC} = 26	3	A-C$\underline{F}_3$
68·0	Doublet of Quartets J_{BA} = 1·5, J_{BC} = 7·0	3	B-C$\underline{F}_3$
118·1	Complex Multiplet J_{CA} = 26, J_{CB} = 7·0	1	C-$\underline{F}$

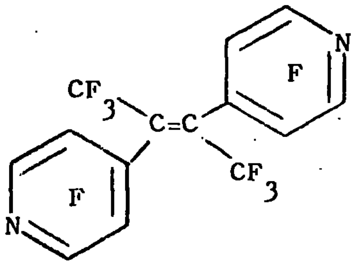
Proton Spectra

Both the *cis* and *trans* isomers show a broad multiplet at 6·8 p.p.m. assigned to the protons of the aromatic rings.

Cis- and trans-2,3-di-(4-tetrafluoropyridyl)hexafluorobut-2-ene



and



in ether

The n.m.r. spectrum was carried out on a mixture of the cis and trans isomers and due to the absence of coupling between the trifluoromethyl groups assignment of these resonances proved impossible.

Chemical Shift (p.p.m.)	Coupling Constant (Hz).	Assignment
Isomer 1; relative abundance 4		
62·7	Broad Singlet	$-C\underline{F}_3$ groups
87·3	Broad Complex Multiplet	2,6 Ring F's
134·6	Broad Resonance	3,5 Ring F's
Isomer 2; relative abundance 1		
59·6	Broad Singlet	$-C\underline{F}_3$ groups
87·3	Broad Complex Multiplet	2,6 Ring F's
134·6	Broad Resonance	3,5 Ring F's

APPENDIX 2

Infrared Spectra

INFRARED SPECTRA

1. *Trans*-2H-heptafluorobut-2-ene
2. *Trans*-2-chloro-heptafluorobut-2-ene
3. *Cis*-2-chloro-heptafluorobut-2-ene
4. *Trans*-2-bromo-heptafluorobut-2-ene
5. *Cis*-2-bromo-heptafluorobut-2-ene
6. Perfluoro-*trans*-4-(2-butenyl)pyridine
7. Perfluoro-2,3-diethylbut-2-ene
8. Hexafluorobut-2-yne
9. *Cis*- and *trans*-perfluoro-4-(2-butenyl)pyrimidine
   (*cis*:*trans* ratio = 11:89)
10. Perfluoro-*trans*-4,6-di-(2-butenyl)pyrimidine
11. Perfluoro-*trans*-bis-(2-butenyl)mercury
12. *Cis*- and *trans*-2-iodo-heptafluorobut-2-ene
    (*cis*:*trans* ratio = 68:32)
13. *Trans*-2H-3-thiophenoxy-hexafluorobut-2-ene
14. *Cis*- and *trans*-2H-3-N,N-diethylamino-hexafluorobut-2-ene
    (*cis*:*trans* ratio = 76:24)
15. Tetrakis-trifluoromethyl-thiophene
16. *Cis*- and *trans*-2-phenoxy-3-(4-tetrafluoropyridyl)-hexafluorobut-2-ene
    (*cis*: *trans* ratio = 25:75)
17. 2,3-Diphenoxy-hexafluorobut-2-ene
18. *Trans*-2H-3-phenoxy-hexafluorobut-2-ene
19. *Cis*-2H-3-phenoxy-hexafluorobut-2-ene
20. *Trans*-2-chloro-3-phenoxy-hexafluorobut-2-ene
21. *Cis*-2-chloro-3-phenoxy-hexafluorobut-2-ene
22. *Cis*- and *trans*-2-bromo-3-phenoxy-hexafluorobut-2-ene
    (*cis*:*trans* ratio = 63:37)
23. *Trans*-2H-3-methoxy-hexafluorobut-2-ene

24. Trans-2-chloro-3-methoxy-hexafluorobut-2-ene

25. Cis-2-chloro-3-methoxy-hexafluorobut-2-ene

26. 1st Diastereomer 2H 2-chloro-3-methoxy-heptafluorobutane

27. 2nd Diastereomer 2H-2-chloro-3-methoxy-heptafluorobutane

28. Trans-2-bromo-3-methoxy-hexafluorobut-2-ene

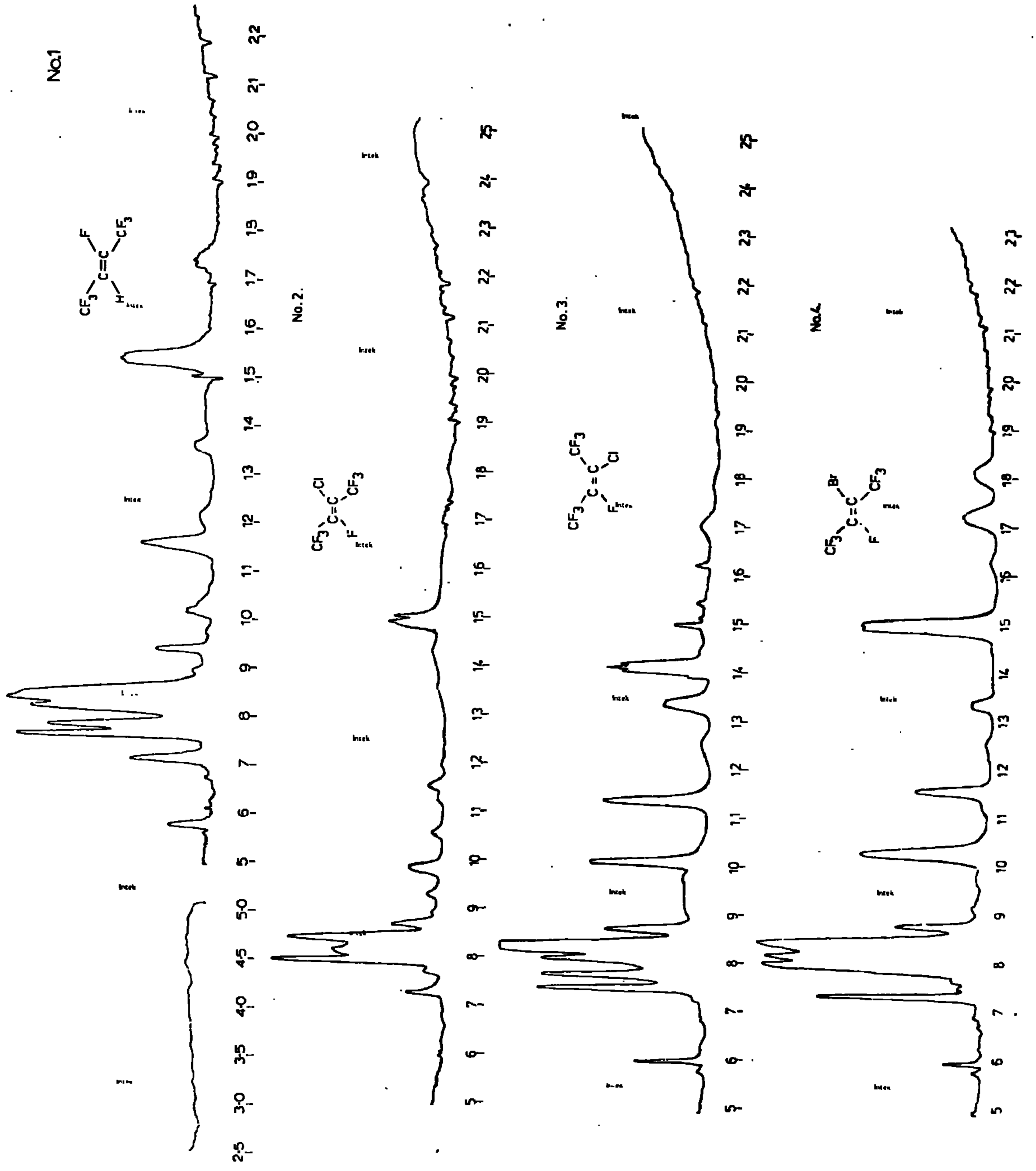
29. A mixture of cis-2-bromo-3-methoxy-hexafluorobut-2-ene and the 1st diastereomer of 2H-2-bromo-3-methoxy-heptafluorobutane

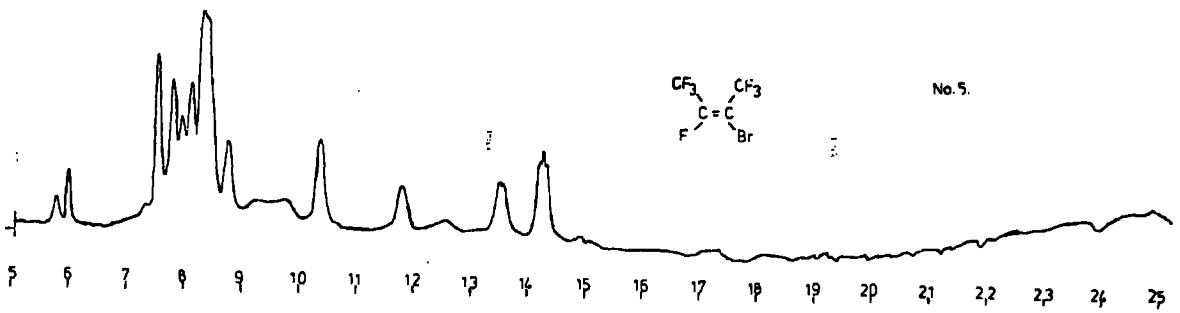
30. 2nd Diastereomer 2H-2-bromo-3-methoxy-heptafluorobutane

31. 2H-2-Bromo-3,3-dimethoxy-hexafluorobutane

32. Perfluoro-cis- and -trans-2,3-di-(4-pyridyl)-but-2-ene

33. Cis- and trans-2-phenyl-heptafluorobut-2-ene


No.1
CF3 C=C F CF3 H
2.5 3.0 3.5 4.0 4.5 5.0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22
No. 2.
CF3 C=C Cl CF3 F
5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
No. 3.
CF3 C=C CF3 Cl F
5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
No. 4.
CF3 C=C Br CF3 F
5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23



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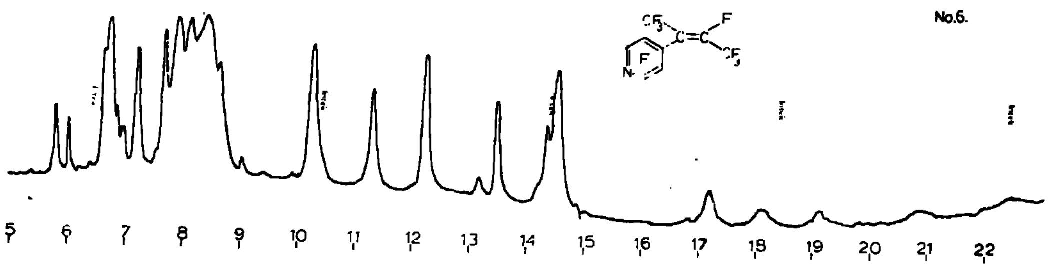

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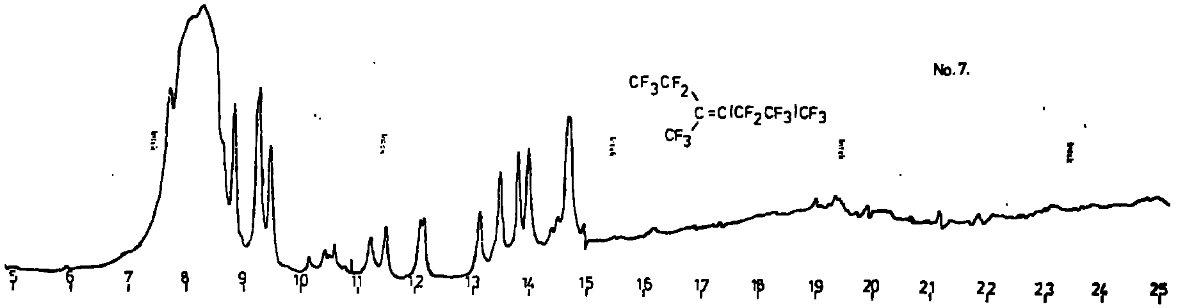

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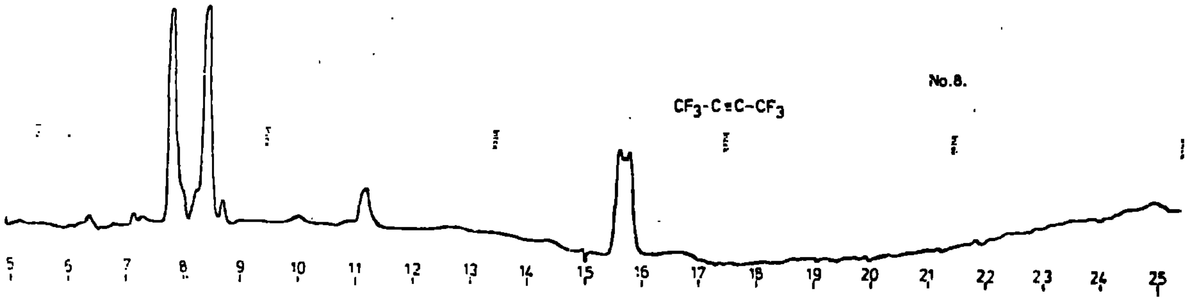

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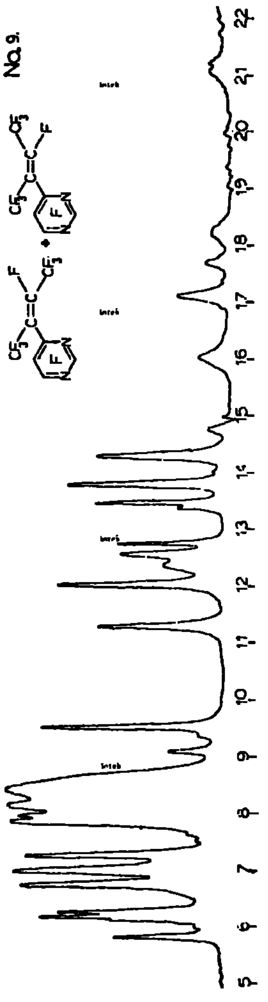
No. 9.



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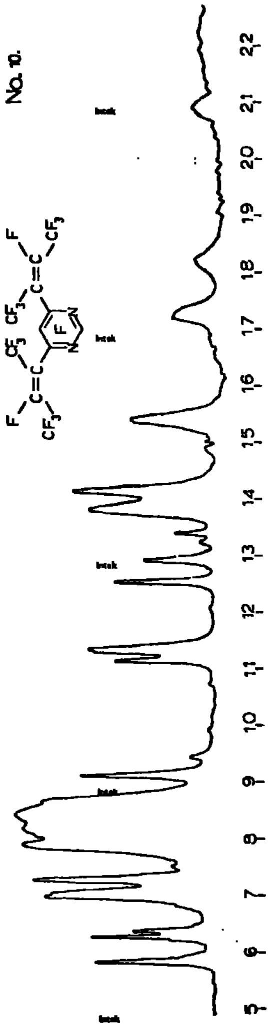

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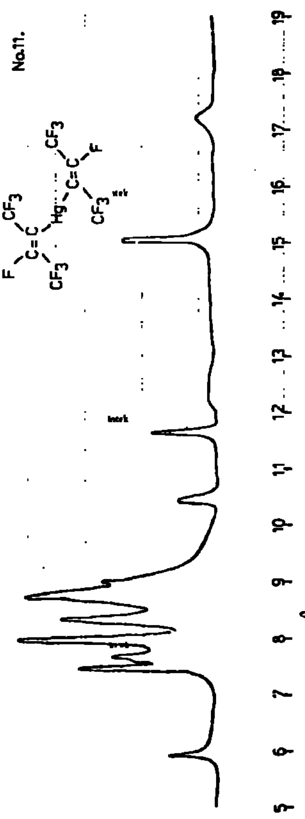

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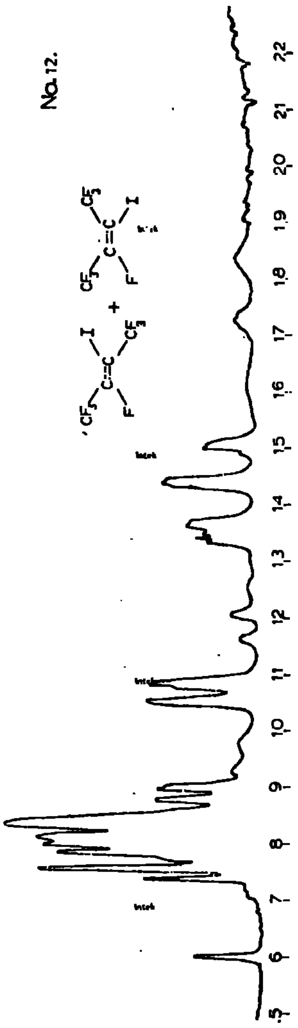

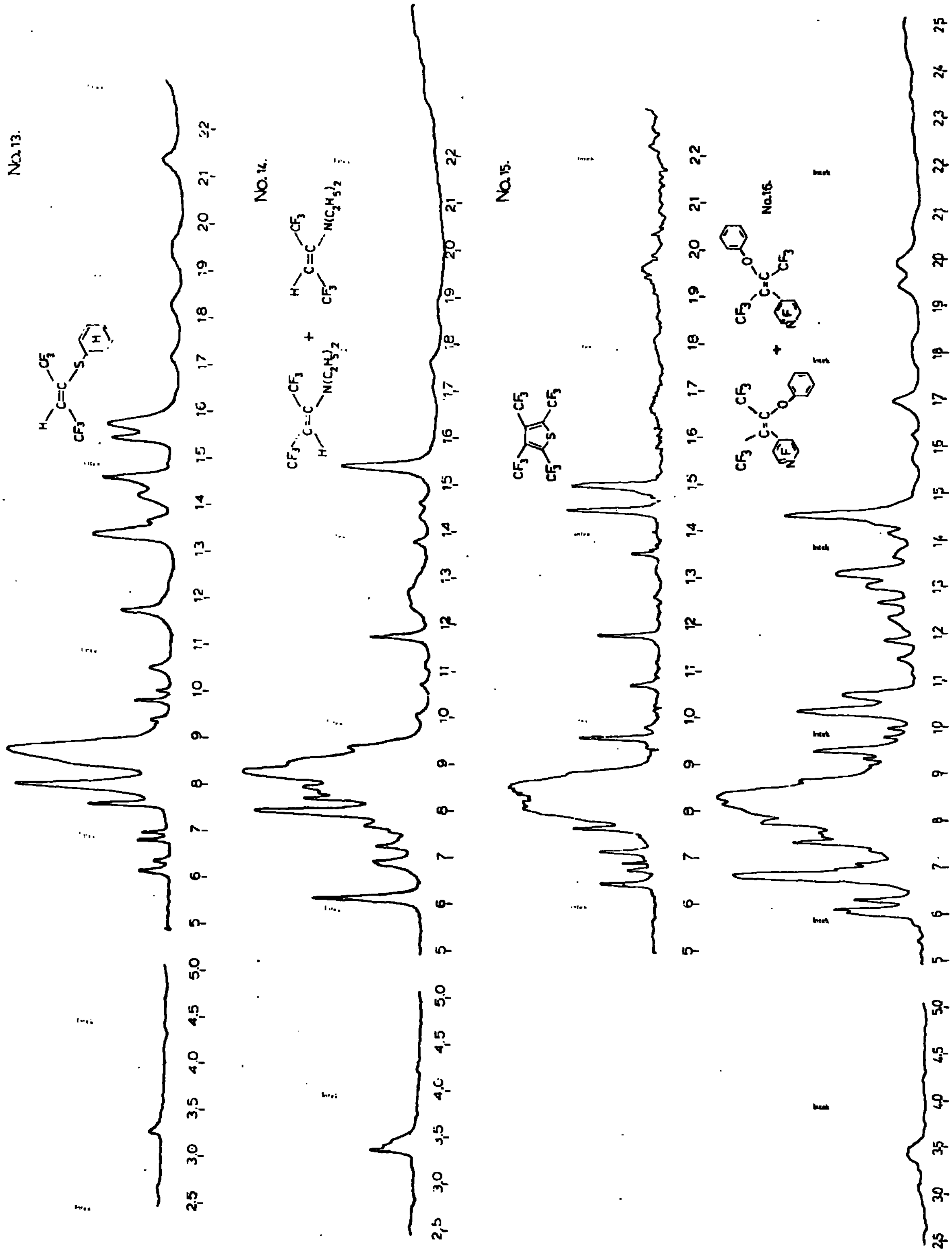
No.13.
No.14.
No.15.
No.16.
2,5
3,0
3,5
4,0
4,5
5,0
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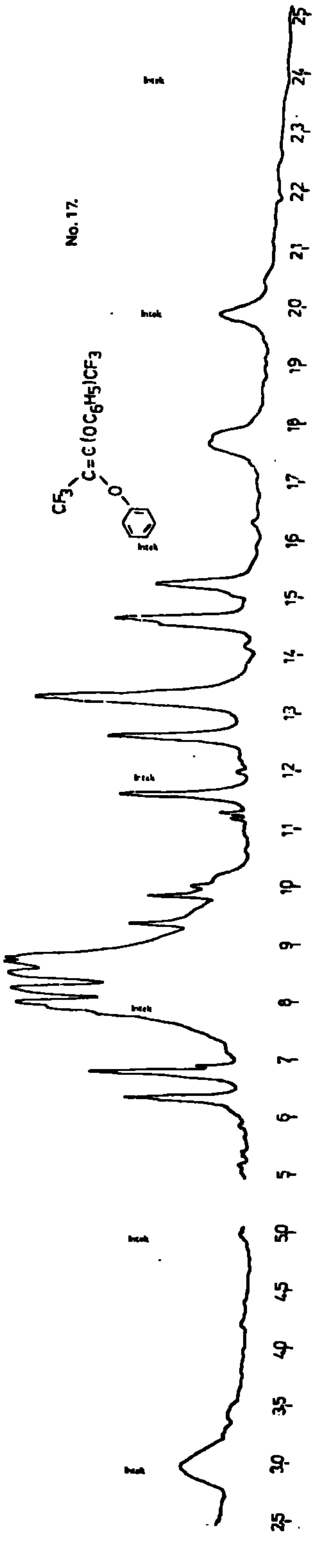
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CF3-C=C(OC6H5)CF3
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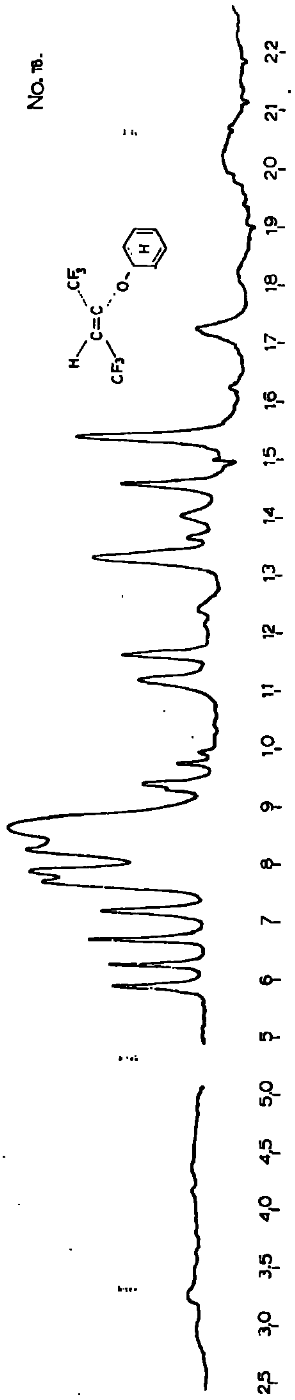
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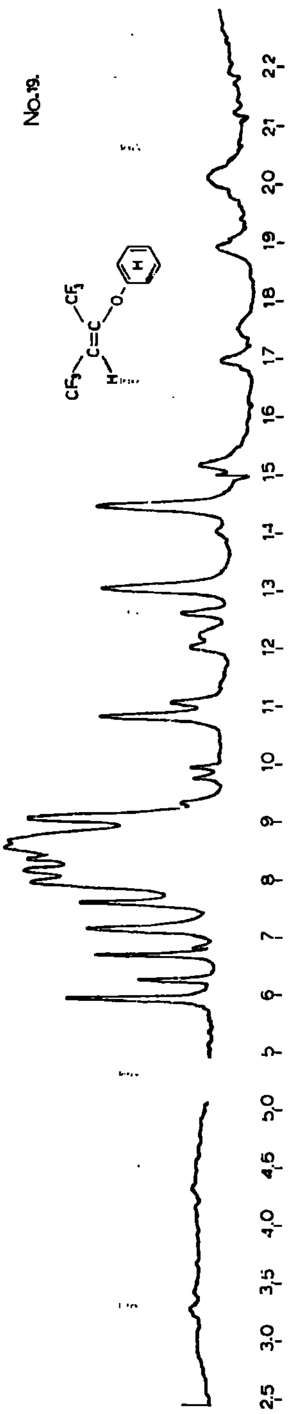
2,5 3,0 3,5 4,0 4,5 5,0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22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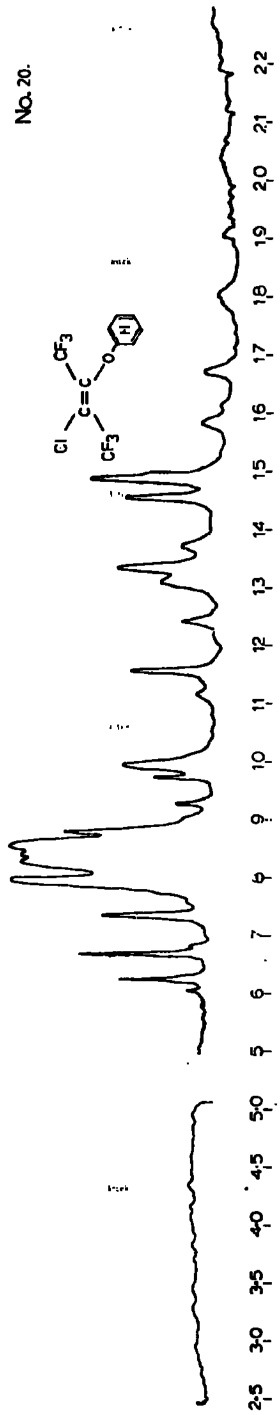
2,5 3,0 3,5 4,0 4,5 5,0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22


No. 20.
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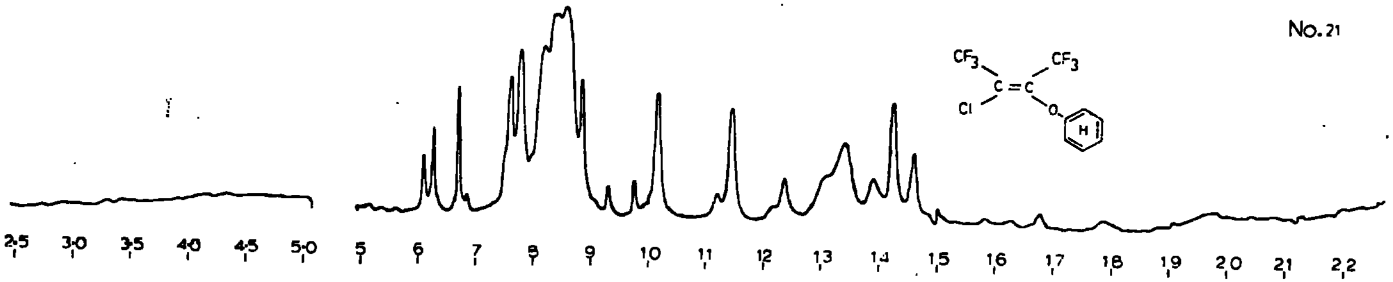
No. 21



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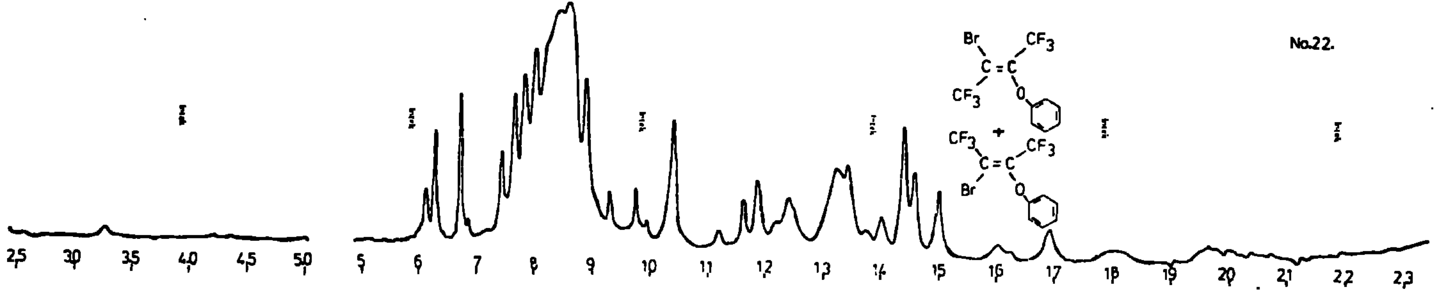

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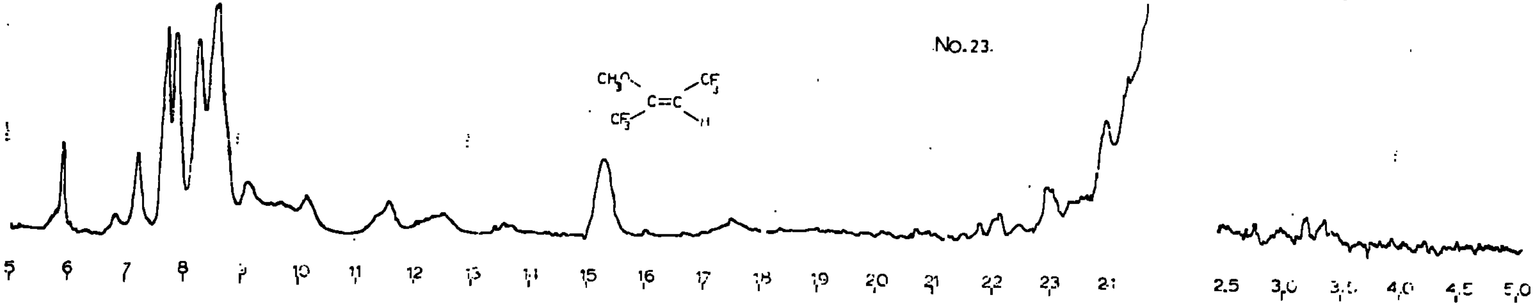

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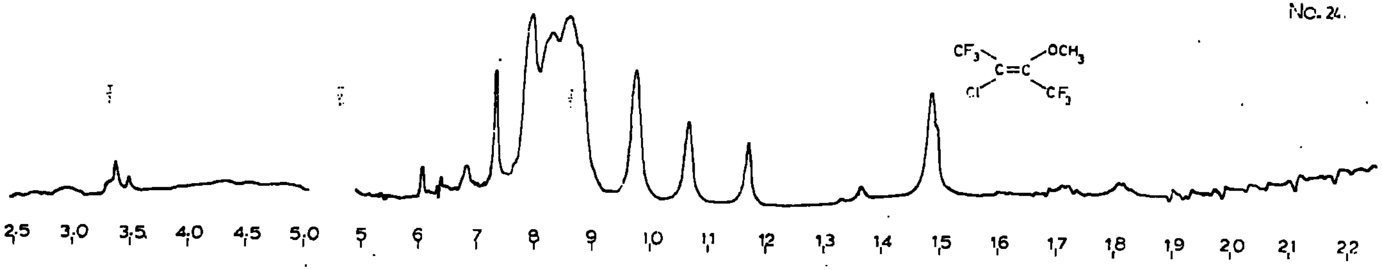

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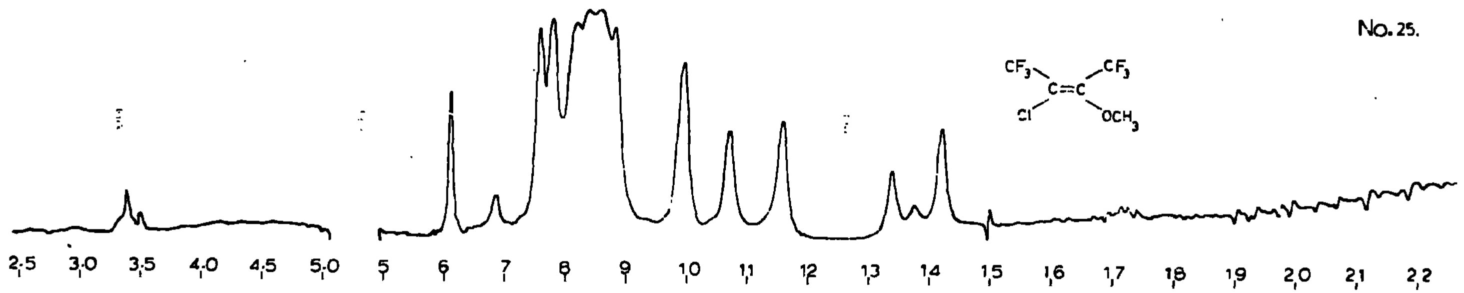

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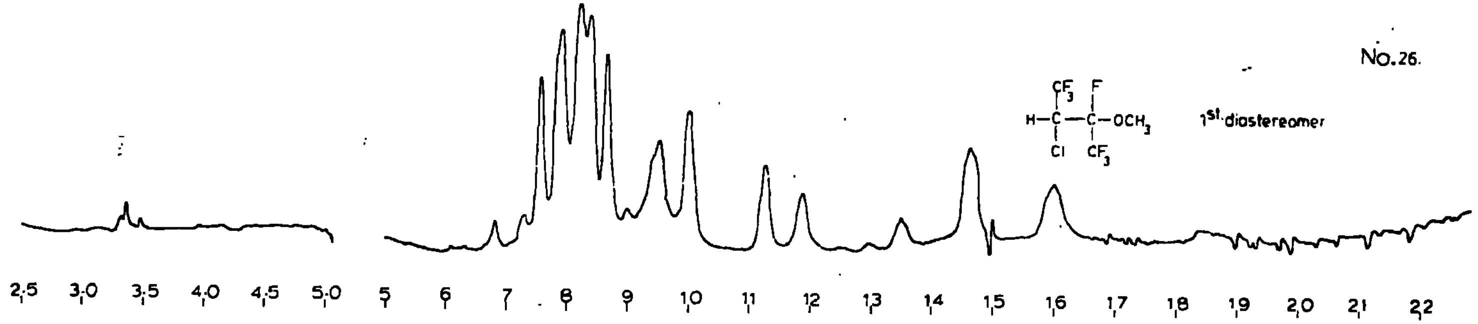

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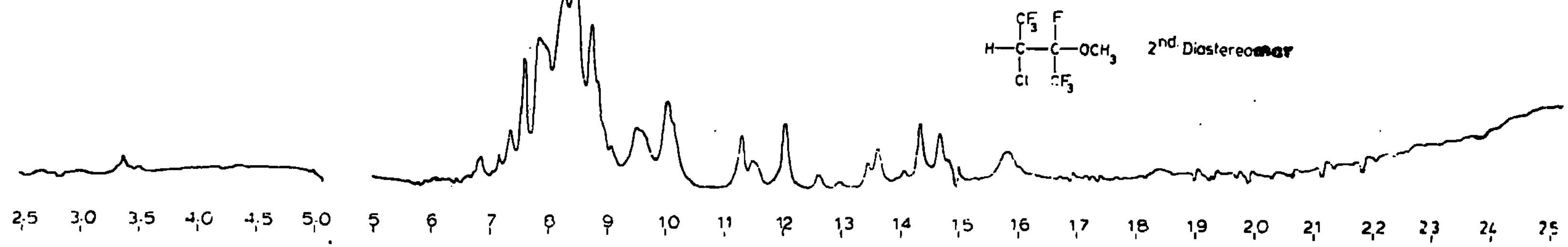

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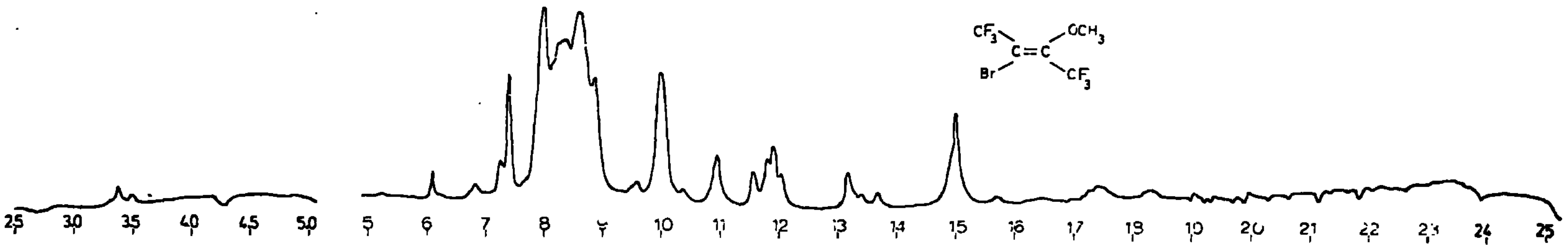

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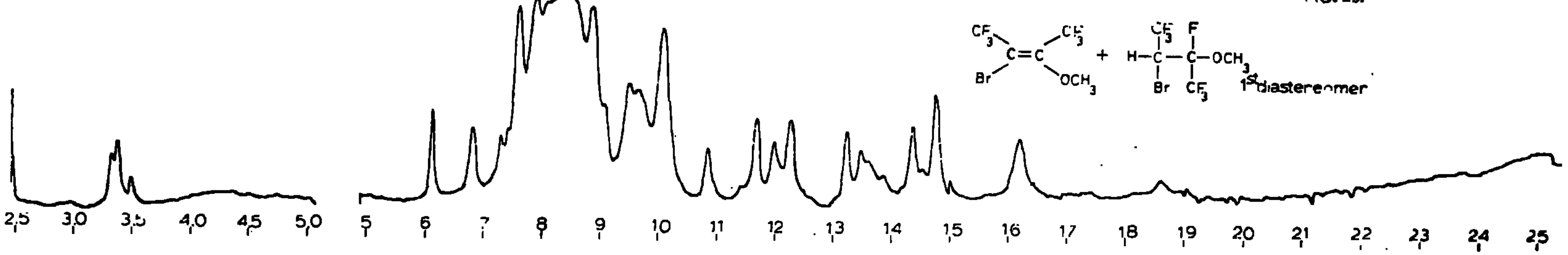

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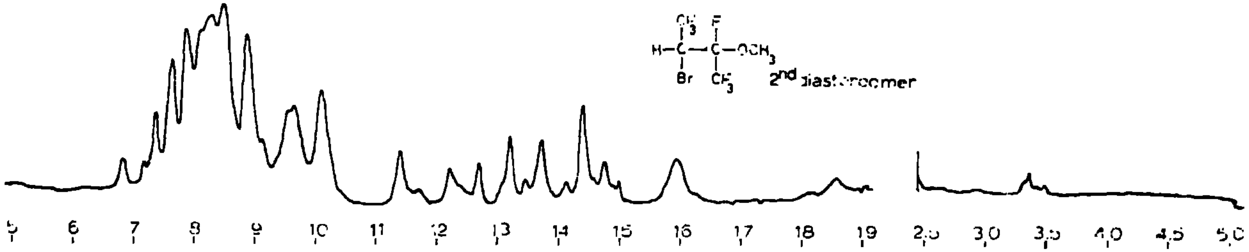

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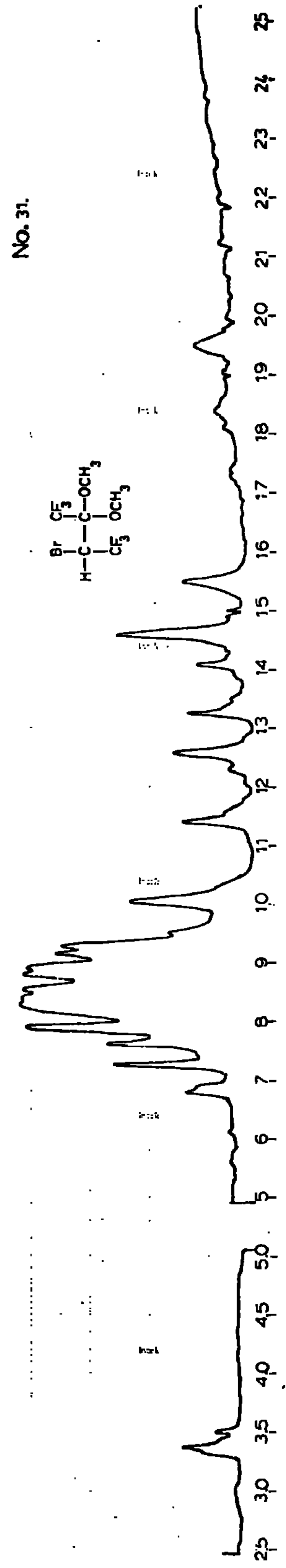

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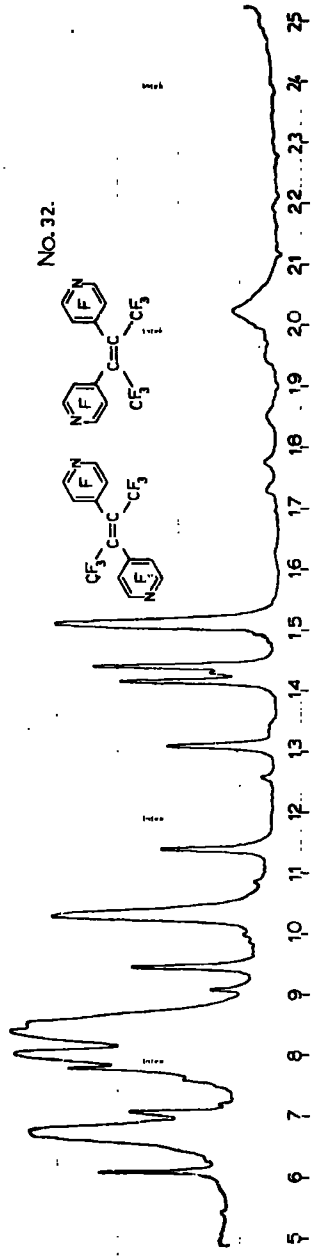

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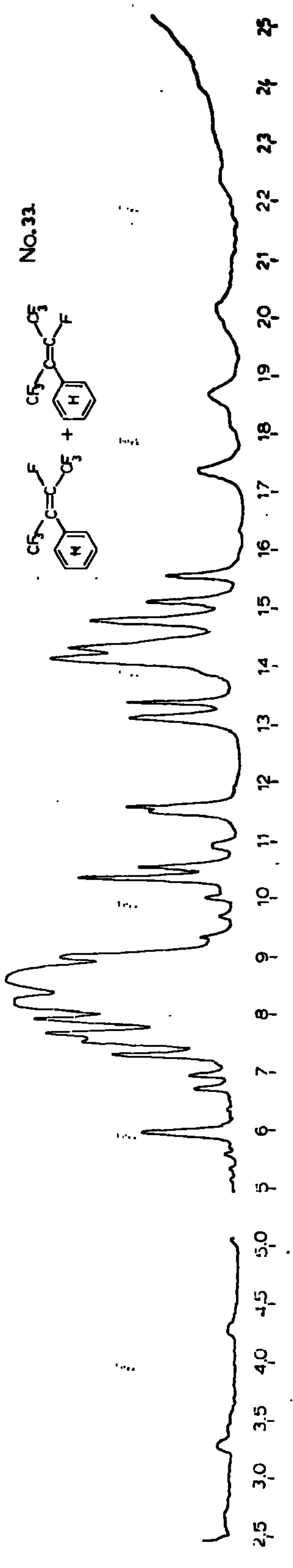

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