Novel perfluorocycloalkenr derivatives

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UNIVERSITY OF DURHAM

A THESIS

entitled

NOVEL PERFLUOROCYCLOALKENE DERIVATIVES

submitted by

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(College of St. Hild and St. Bede)

A candidate for the degree of Doctor of Philosophy

1979

To the Memory of my Grandmother

Nancy Louie Simmons Rudland

ACKNOWLEDGEMENTS

I would like to express my gratitude to Professor R.D. Chambers for his continued helpful advice during the course of this work.

I would like to thank the many people at I.C.I. Mond Division for their interest and help, and for the superb hospitality shown to me on several visits. Thanks are due in particular to Dr. R.L. Powell, Dr. G. Whittaker and Dr. H.C. Fielding. I would also like to thank Dr. J.C. Wood for some helpful advice and some n.m.r. spectra.

Thanks are due to the many technical staff for their invaluable assistance: to Mrs. M. Cocks for analyses: to Messrs. W.H. Fettis and R. Hart for their expert glassblowing; and to many others. I would also like to thank: Dr. M. Jones and Mr. D.L. Nevins for the running of mass spectra and for advice thereon; Dr. R.S. Matthews for much helpful assistance with the interpretation of n.m.r. spectra; and Mr. T.F. Holmes for a number of chemicals and much helpful advice.

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Last, but not least, my thanks go to my parents for their endless devotion and encouragement.

MEMORANDUM

The work described in this thesis was carried out at the University of Durham between October 1976 and May 1979. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference. Part of this work has formed the basis of the following publications:-

R.D. Chambers, G. Taylor, and R.L. Powell, JCS Chem. Comm., 1978, 433.

R.D. Chambers, G. Taylor, and R.L. Powell, JCS Perkin I, accepted for publication.

R.D. Chambers, G. Taylor, and R.L. Powell, JCS Perkin I, accepted for publication.

R.D. Chambers, R.S. Matthews, G. Taylor, and R.L. Powell, JCS Perkin I, accepted for publication.

Part of the work has also been filed for patenting:-

UK Patent Appl. No. 7908767 (13/3/79)

"What is now proved was once only imagin'd."

William Blake

The Marriage of Heaven and Hell

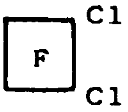
NOMENCLATURE

The following nomenclature is used in this thesis:-

1). A capital F at the beginning of a chemical name means that the compound referred to is totally fluorinated. Thus, for example, F-cyclobutene is equivalent to hexafluorocyclobutene.

2). A capital F in the middle of a name means that all substituents, apart from those named before the F, are fluorine. Thus, for example, 1,2-dichloro-F-cyclobutane is equivalent to 1,2-dichlorohexafluorocyclobutane.

3). The presence of an F in the middle of a ring means that all unmarked substituents are fluorine. Thus, for example, F-cyclobutene and 1,2-dichloro-F-cyclobutane are represented as below:-



SUMMARY

This thesis deals mainly with the preparation and reactions of F-cyclobutene oligomers.

A reinvestigation of the oligomerisation of F-cyclobutene has shown that different trimers are produced by pyridine and by fluoride ion induced reactions. The pyridine induced reaction provides a useful route to the dimers and the trimer, F-1,2-dicyclobutylcyclobutene. Fluoride ion induced reactions of F-cycloalkenes with other F-alkenes are also described. These reactions give an interesting range of products whose structures are explainable in terms of current ring strain theories.

The dimers of F-cyclobutene, and other F-cycloalkyl derivatives, give long-lived, observable carbanions with fluoride ion in a dipolar aprotic solvent.

Nucleophilic substitution reactions of the F-cyclobutene oligomers have been investigated and the products are predictable from a knowledge of the corresponding reactions with F-cyclo-butene. One noticeable difference, however, is the much greater reactivity of the oligomers compared to F-cyclobutene. Thus, for example, the dimers react rapidly at room temperature with neutral alcohols.

Preliminary investigation of the addition reactions of the oligomers indicates that the symmetrical dimer has enhanced reactivity, over formally similar structures, because of its considerable angle strain. Some interesting products are obtained from reactions with diazomethane and from oxidation reactions with potassium permanganate.

Pyrolysis of F-cyclobutenes over fluoride ion has provided a wealth of novel rearrangements which are explainable in terms of cyclobutene ring opening followed by reaction of terminal difluoromethylenes to give trifluoromethyl groups. Thus, for example, F-cyclobutene gives F-2-butyne.

Reaction of F-1,2-dicyclobutylcyclobutene with caesium fluoride in dimethylformamide results in a rearrangement to give a cycloheptene derivative. Pyrolysis of this compound results in initial loss of F-ethene and gives some interesting seven-membered ring compounds.

Photolysis of F-methylenecyclobutanes results in a 1,3-shift of the double bond; the rate of reaction appears to be dependant on angle strain in the initial alkene.

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INTRODUCTION

General Introduction

Over the past few decades there has been a growing tendency in chemistry, both at an industrial and an academic level, to try to find chemicals having special effects and/or novel reactivity. In this context the area of organic fluorine chemistry is of considerable interest since the ability to replace hydrogen, in an organic molecule, either partially or completely, without markedly affecting the geometry of that molecule makes fluorine containing systems quite unusual.

The main difference in properties between fluorocarbon and hydrocarbon systems stems from the difference in electro--negativities of fluorine and hydrogen, and the profound effects arising from the influence of non-bonded electron pairs on the fluorine atoms. Consequently, in fluorocarbons, functional groups are in completely different electronic environments to their hydrocarbon analogues and this leads to a completely different, though often complementary, mode of chemical behaviour.

An important property of many fluorocarbons, particularly from an industrial viewpoint, is their high thermal and chemical stability. For example, polytetrafluoroethylene is an exeptionally useful polymer which, apart from a high degree of chemical and thermal stability, also has a very low coefficient of friction and has been used in the manufacture of dry bearings, as a coating for non-stick cookware, etc..

In the pharmaceutical industry fluorine containing compounds are finding an ever increasing usage. Thus, for example, CF_3-CHBrCl is a very widely used anaesthetic whilst 5-fluorouracil has been used in cancer treatment. Many steroidal compounds containing fluorine have greatly enhanced anti-inflammatory properties, and emulsions containing compounds related to perfluorodecalin are even being proposed as blood substitutes.

Other uses of fluorocarbons include such diverse areas as surfactants, dyes, fire extinguishers, aerosol propellants, refrigerants, coolants for sealed electrical systems, etc..

A particularly interesting area, though much neglected by both the academic and industrial world, is that of small ring compounds. Fluorine tends to stabilise small rings with respect to hydrogen though the reasons for this are not clear. This enhanced stability coupled with easy preparations means that a wealth of interesting chemistry is potentially available from this area.

This thesis illustrates some of the varied and exciting chemistry which is developing with perfluorocycloalkyl derivatives.

CHAPTER 1

THE CHEMISTRY OF POLYFLUORINATED CYCLIC ALKENES

The aim of this chapter is to give a brief survey of one of the many areas of organic fluorine chemistry - that of highly fluorinated, unsaturated, cyclic compounds.

1.A Synthesis

All of the simpler F-cycloalkenes and -cyclic dienes are fairly readily available in the laboratory and in many cases it is possible to prepare analagous polyfluorinated compounds containing one or more atoms other than fluorine (e.g. chlorine or hydrogen). These latter compounds are often useful for helping to deduce reaction mechanisms (see later).

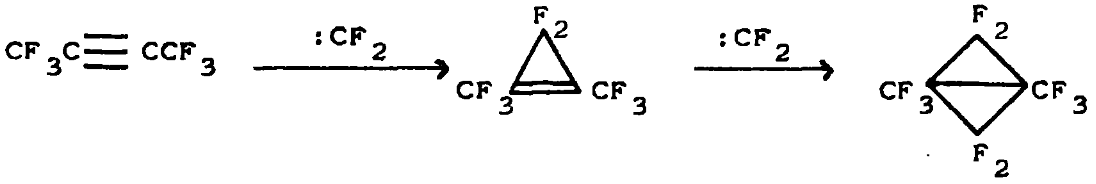
In common with many of their acyclic counterparts, the synthesis of cyclic fluoroalkenes usually involves dehalogenation or dehydrohalogenation at some stage.

1.A.1 Cyclopropenes

F-Cyclopropene can be prepared in about 50% overall yield by addition of difluorocarbene to 1,2-dichlorodifluoroethylene and subsequent dechlorination;[1-3] analagous reactions are used to prepare 1-chloro-F-cyclopropene,[3] tetrachlorocyclopropene [4,5] and F-methylenecyclopropane containing about 5% of F-methylcyclopropene as impurity (scheme 1).[6]

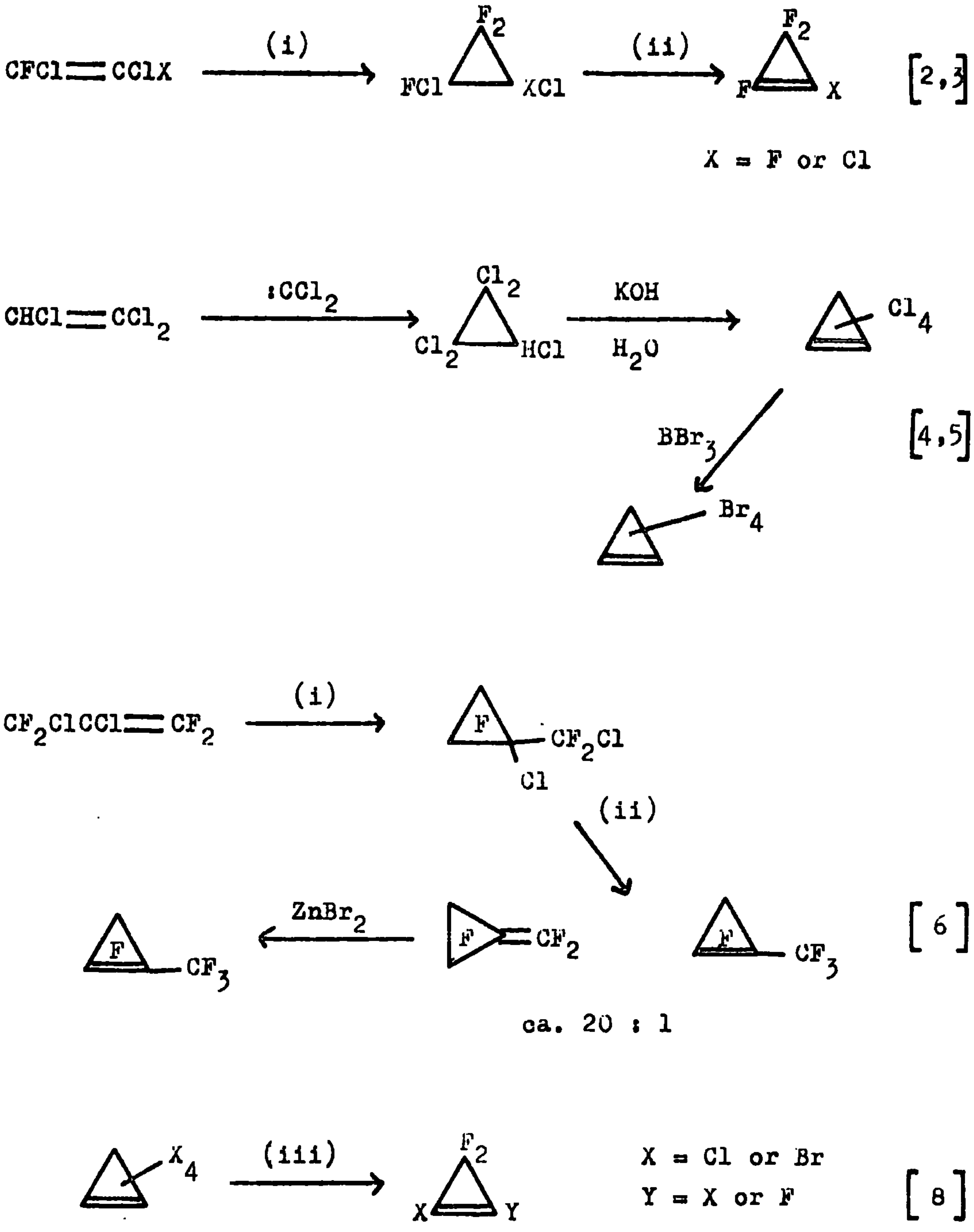
A useful general synthesis of fluorinated alkenes is the replacement of chloride, from the corresponding chlorinated system, by fluoride ion;[7] suprisingly when tetrachloro- or tetrabromo-cyclopropene is reacted with potassium fluoride no F-cyclopropene is obtained,[8] the product being a mixture of di- and tri-fluorocyclopropenes.

An interesting reaction occurs between difluorocarbene and F-2-butyne to give, initially, a cyclopropene which can react further to give a bicyclobutane:-[9]



Scheme 1

Preparation of Fluorinated Cyclopropenes



(i). $:CF_2$ e.g. from F-propene oxide or $(CF_3)_3PF_2$

(ii). $-Cl_2$ e.g. with zinc and dioxan or methanol

(iii). KF, sulpholan, 180°C.

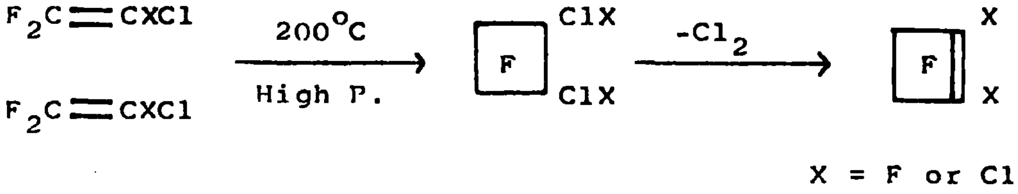
Similar reactions, to give cyclopropenes, occur with other acetylenes, e.g. pentafluoroacetylene.[10]

It is reported that F-cyclopropene is a minor product from the reaction of singlet oxygen with F-1,3-butadiene.[11]

1.A.2 Cyclobutenes

The four-membered ring system is the most readily accessible in organic fluorine chemistry due to the very facile (2+2) cycloadditions which many fluoroethylenes undergo. This is one of the more unusual aspects of fluorocarbon chemistry and has considerable potential synthetic use - the area has been reviewed.[12]

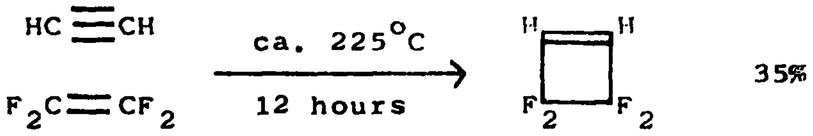
F-Cyclobutene was the first F-cycloalkene to be synthesised and the preparation involves dimerisation of chlorotrifluoro--ethylene and dechlorination of the resultant 1,2-dichloro-F-cyclobutane.[13] 1,2-Dichloro-F-cyclobutene can be prepared by an analagous route and overall yields for both reactions are often as high as 90%.[13]



The dechlorination is usually carried out using zinc dust in a suitable solvent, e.g. methanol.[13] However, it can also be attained thermally in a stream of hydrogen over a suitable catalyst. Unfortunately the high temperatures required for this reaction often result in considerable retro (2+2) addition.[14-16]

F-Cyclobutene can also be prepared by debromination of 1,2-dibromo-F-cyclobutane[17] and by thermal dimerisation of iodotrifluoroethylene in the presence of phosphorus.[18] Low yields (ca. 20%) are obtained by passage of chlorotrifluoro--ethylene through a nickel tube at 680° C,[19] or by passage of hexachloro-1,3-butadiene and hydrogen fluoride over a zinc fluoride/alumina catalyst.[20]

Other polyfluorocyclobutenes made by analagous routes are too numerous to mention, but of particular interest is the cycloaddition of acetylene and F-ethylene to give 3,3,4,4-tetrafluorocyclobutene.[21]

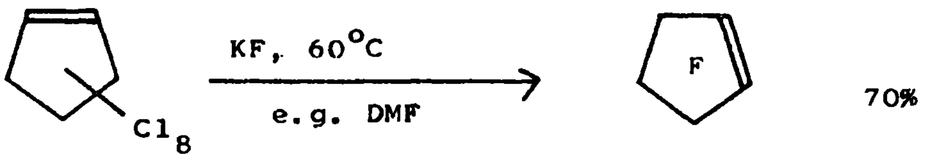


1.A.3 Cyclobutadienes

Both tetrafluoro-[22] and F-tetramethyl-[23] -cyclobutadienes have been generated photochemically, as reactive intermediates, from compounds derived from valence isomers of F-benzenes (scheme 2). F-tetramethylcyclobutadiene can also be made by thermolysis of (1) or by reaction of 3-bromo-F-tetramethylcyclobutene with methyl lithium. In the first case there is some disagreement over the fate of the cyclobutadiene,[24,25] whilst, in the second case, further reaction occurs to give a complex mixture of dimeric products.[26] The spectral data on F-cyclobutadienes has been obtained.[27]

1.A.4 Cyclopentenes

The only perfluoroalkene that can be ob--tained from non-fluorinated starting materials in a one step process is F-cyclopentene, which is made from the reaction of octachlorocyclopentene with fluoride ion in a dipolar aprotic solvent.[7]

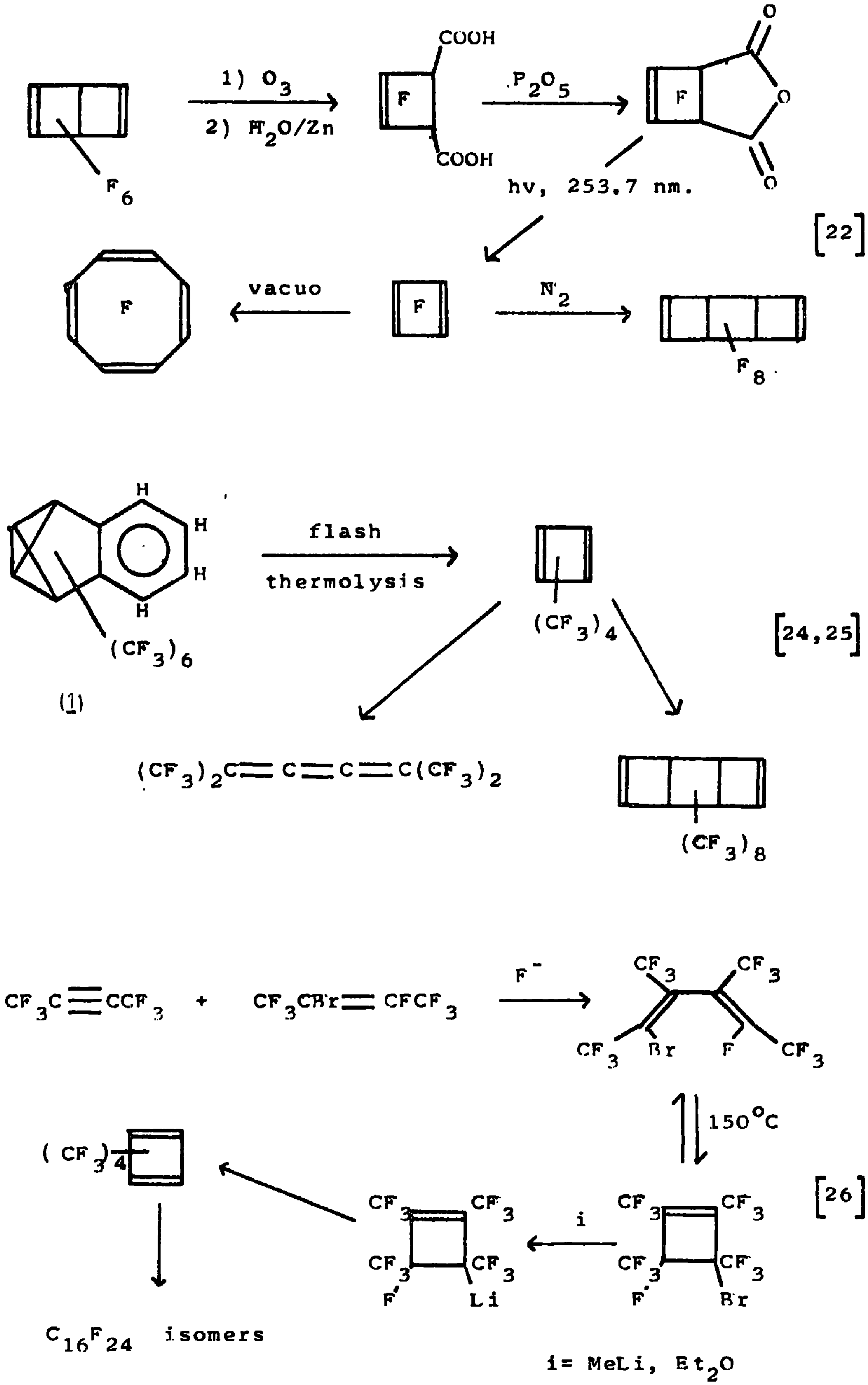


The mechanism involves a series of S_n2' displacements of allylic chlorine. A similar reaction occurs with 1,2-dichloro--F-cyclopentene, which is itself prepared from reaction of octachlorocyclopentene or the readily available hexachloro--cyclopentadiene with antimony pentafluoride.[29,30]

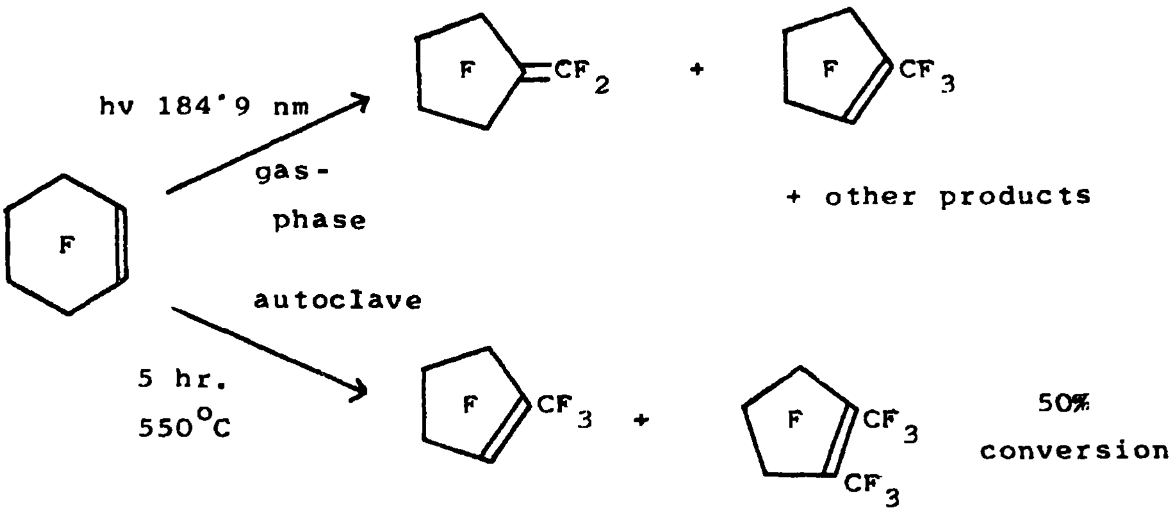
F-Methylenecyclopentane is produced, in low yield, together with some F-methylcyclopentene in a fascinating reaction

Scheme 2

Generation and Fate of F-cyclobutadienes



involving gas-phase photolysis of F-cyclohexene;[31] it is claimed that liquid-phase photolysis gives an 80% yield.[32]

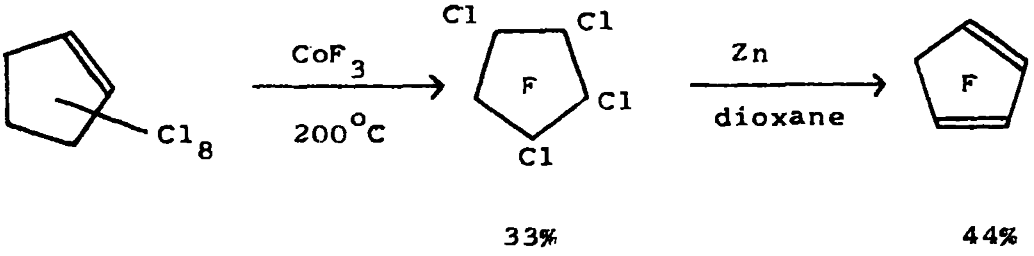


(2) 50%   (3) 20%

A similar reaction occurs thermally; thus in the presence of nickel shavings, at high temperatures, F-cyclohexene gives a good yield of F-1-methylcyclopentene (2) and some F-1,2-dimethylcyclopentene (3).[33] Also, F-cyclopentene was unchanged when heated alone, but in the presence of P.T.F.E. it gave good yields of (2) and (3). The authors took this to mean that the rearrangement of F-cyclohexene involved difluoro--carbene.[33] High pressure thermolysis of P.T.F.E. gives some (2) and (3) together with perfluoroaromatics.[34]

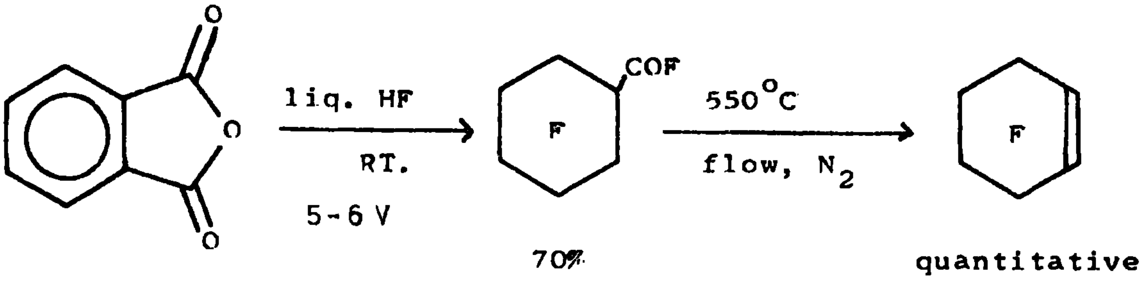
1.A.5 Cyclopentadiene

This is made by cobalt trifluoride fluorination of octachlorocyclopentene followed by zinc dechlorination.[35] The resultant F-cyclopentadiene is very difficult to store - it dimerises even at -10°C.

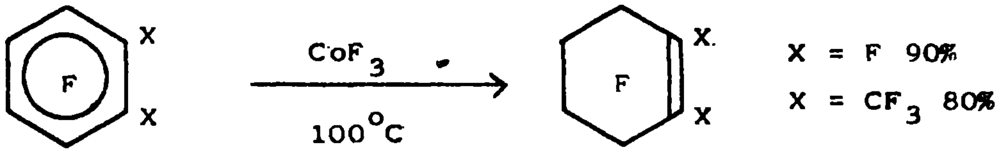


1.A.6 Cyclohexenes

It is claimed that quantitative yields of F-cyclohexene and F-alkylcyclohexenes are obtained by flow pyrolysis of the corresponding carboxylic acids,[36] which are themselves obtained by electrochemical fluorination, in liquid hydrogen fluoride, from hydrocarbon precursors,[37,38]



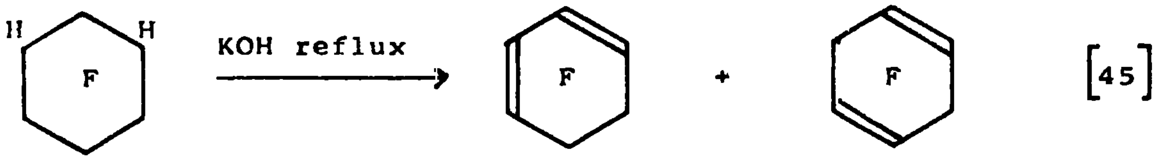
The cobalt trifluoride fluorination of benzene has been studied extensively by Tatlow and co-workers.[39,40] One of the very many products from this reaction is undecafluorocyclohexane which can be dehydrofluorinated with aqueous potassium hydroxide,[39,40] anion exchange resins [41] or thermally to give F-cyclohexene.[42] Low yields are obtained by fluorination of benzene over, for example, silver difluoride.[43] Cobalt trifluoride fluorination of F-benzenes gives very high yields of F-cyclohexenes.[44]

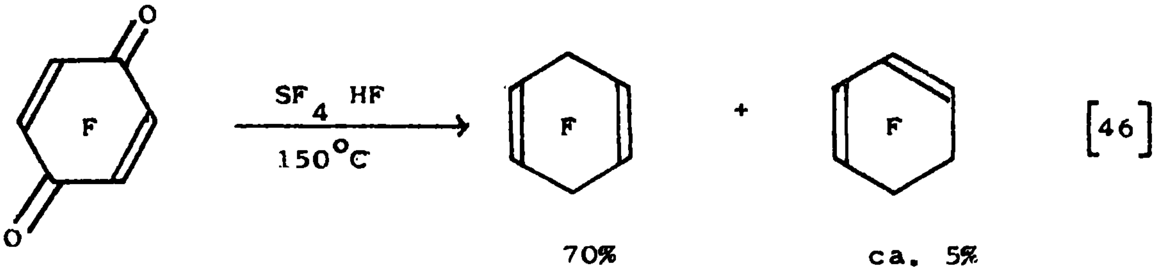


1,2-Dichloro-F-cyclohexene can be obtained in 44% yield by treatment of hexachlorobenzene with antimony pentafluoride.[30]

1.A.7 Cyclohexadienes

These can be prepared from decafluorocyclohexanes [39-41,45] or F-benzenes[44] by similar routes to those used to prepare F-cyclohexenes e.g.

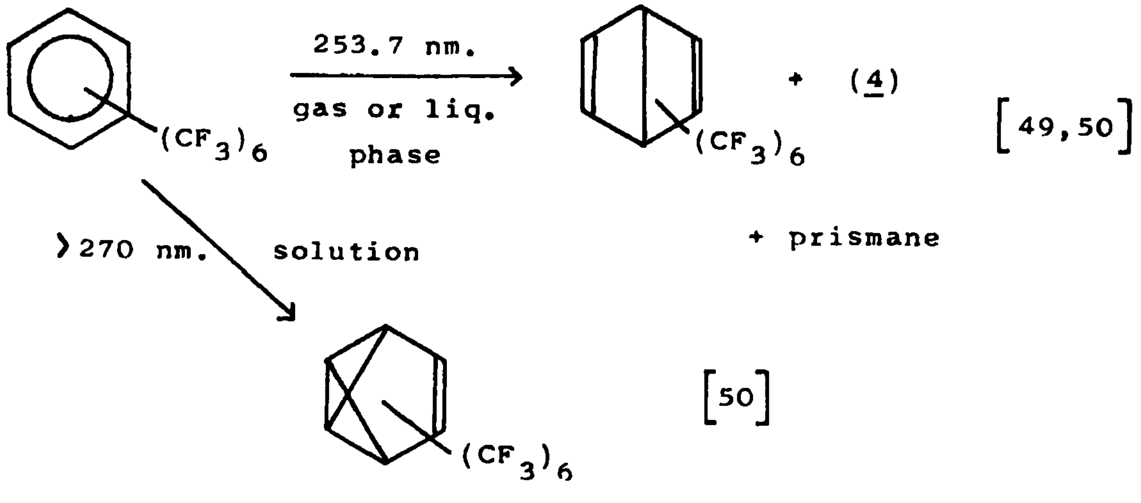




The 1,4-cyclohexadiene can also be obtained, in good yield, by reaction of fluoroanil with sulphur tetrafluoride and hydrogen fluoride [46] or by fluorination of F-benzene with xenon difluoride.[47]

1.A.8 Polycyclic Hexenes

Irradiation of F-benzenes gives good yields of valence isomers. Thus, F-benzene gives F-bicyclo-(2,2,0)hexadiene,[48] whilst F-hexamethylbenzene gives a prismane and benzvalene (4) as well.[49, 50]



(4) 100%

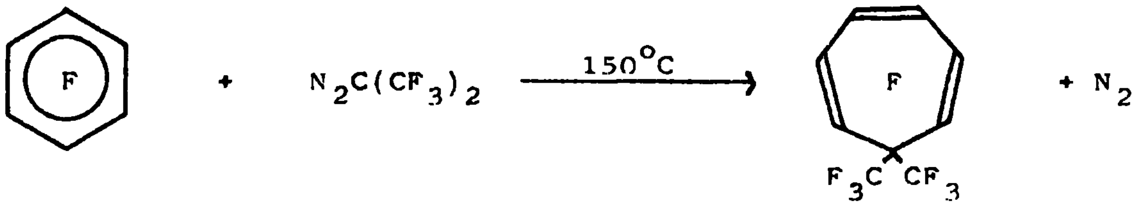
Many other F-benzenes undergo similar rearrangements, e.g. F-toluene.[48] Irradiation of F-1,3-cyclohexadiene gives F-bicyclo(2.2.0)hexene;[51] the reverse reaction occurs thermally and is quantitative.

1.A.9 Cycloheptenes

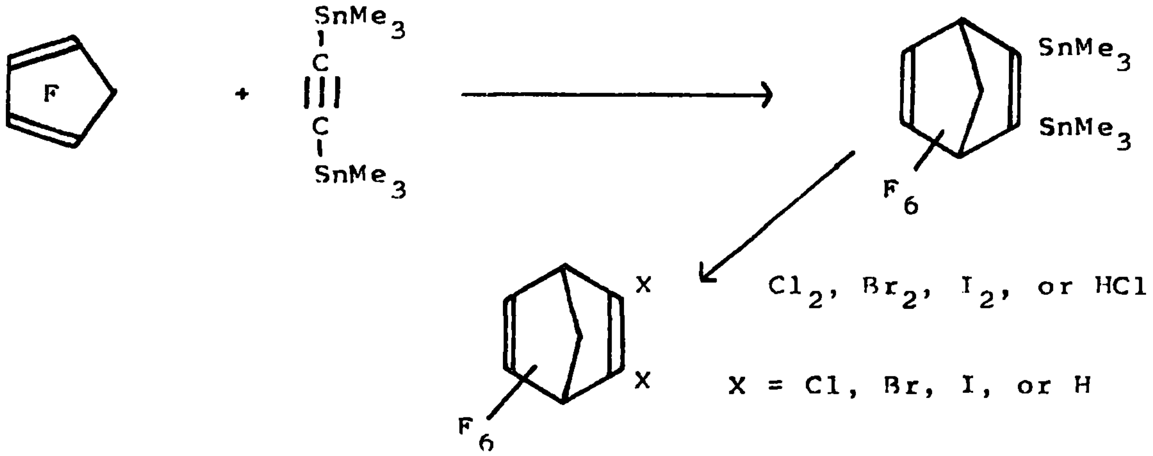
Although a report on the reaction of F-cycloheptene with 1-ethoxy-1-(2-hydroethoxy)ethane has appeared in the literature,[52] the preparation has yet to be published.

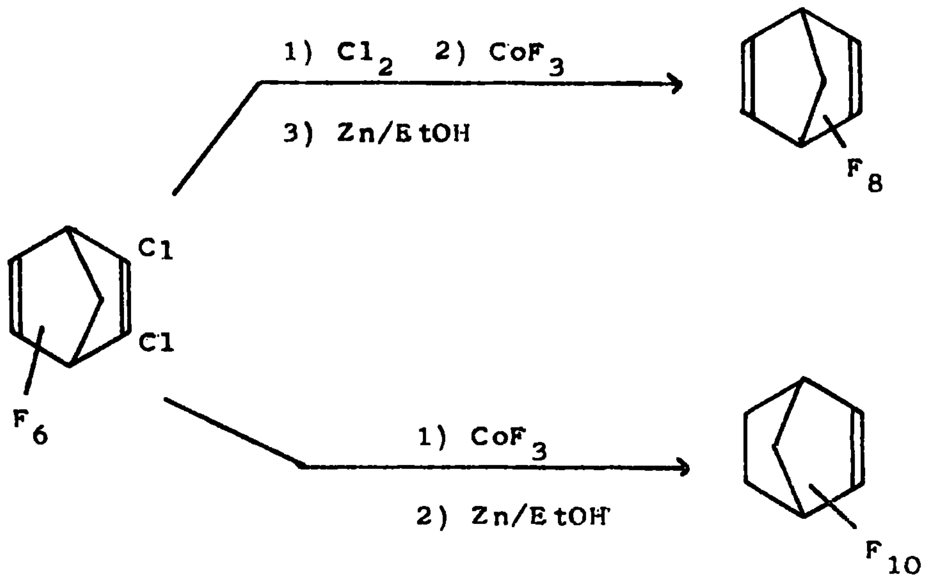
The two isomeric F-cycloheptadienes and F-cycloheptatriene have been obtained, in low yield, by fluorination of cyclo-heptatriene and subsequent dehydrofluorination.[53]

A good general method for preparation of 1,2,3,4,5,6-hexafluorocycloheptatrienes is the addition of carbenes to F-benzenes.[54] Thus, reaction with bistrifluoromethyldiazo-methane gave F-7,7-dimethylcycloheptatriene.[55]



F-Norbornene and F-norbornadiene can be prepared by a lengthy process starting from F-cyclopentadiene.[56] 1,2-Disub-stituted F-norbornadienes (Cl, Br, I, H) can also be obtained by this route.





F-Norbornadiene is a minor product from the pyrolysis of F-bicyclo(2,2,1)heptane-1-carboxylate.[57]

1.B Reactions of Polyfluorocycloalkenes

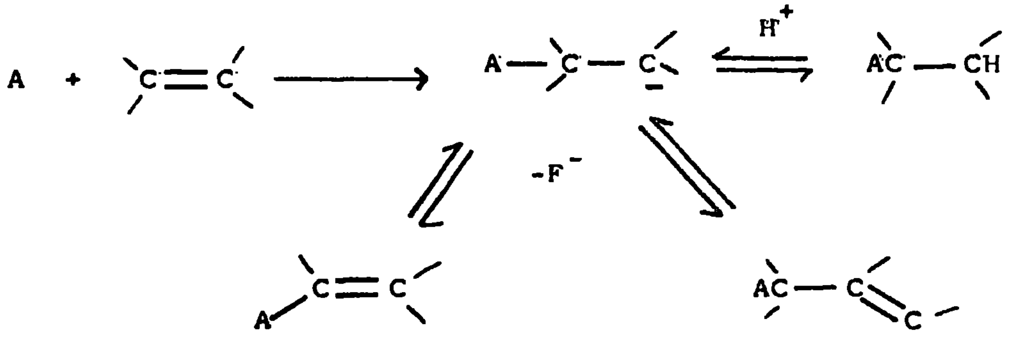
The chemistry of F-alkenes is very wide-ranging but it can be divided into six broad areas:-

1). Reactions with nucleophiles
2). Reactions with electrophiles
3). Additions involving fluoride ion
4). Other addition reactions and polymerisations
5). Cycloaddition reactions
6). Thermal and photochemical reactions

1.B.1 Nucleophilic Attack

This is probably the most studied area of organic fluorine chemistry. Because of the electron withdrawing nature of fluorine and perfluoroalkyl groups the double bonds in F-alkenes are very susceptible to nucleo--philic attack [58] and this is particularly true for compounds containing vinylic fluorines. It is not suprising, therefore, that the simple F-cycloalkenes are very reactive towards nucleophiles although the reactivity decreases with increased ring size.

The initial step in nucleophilic attack on an F-alkene involves formation of an intermediate carbanion which can then either be protonated to give overall addition, or eliminate fluoride ion with overall vinylic or S_n2' displacement. This is shown for a nucleophile A :-



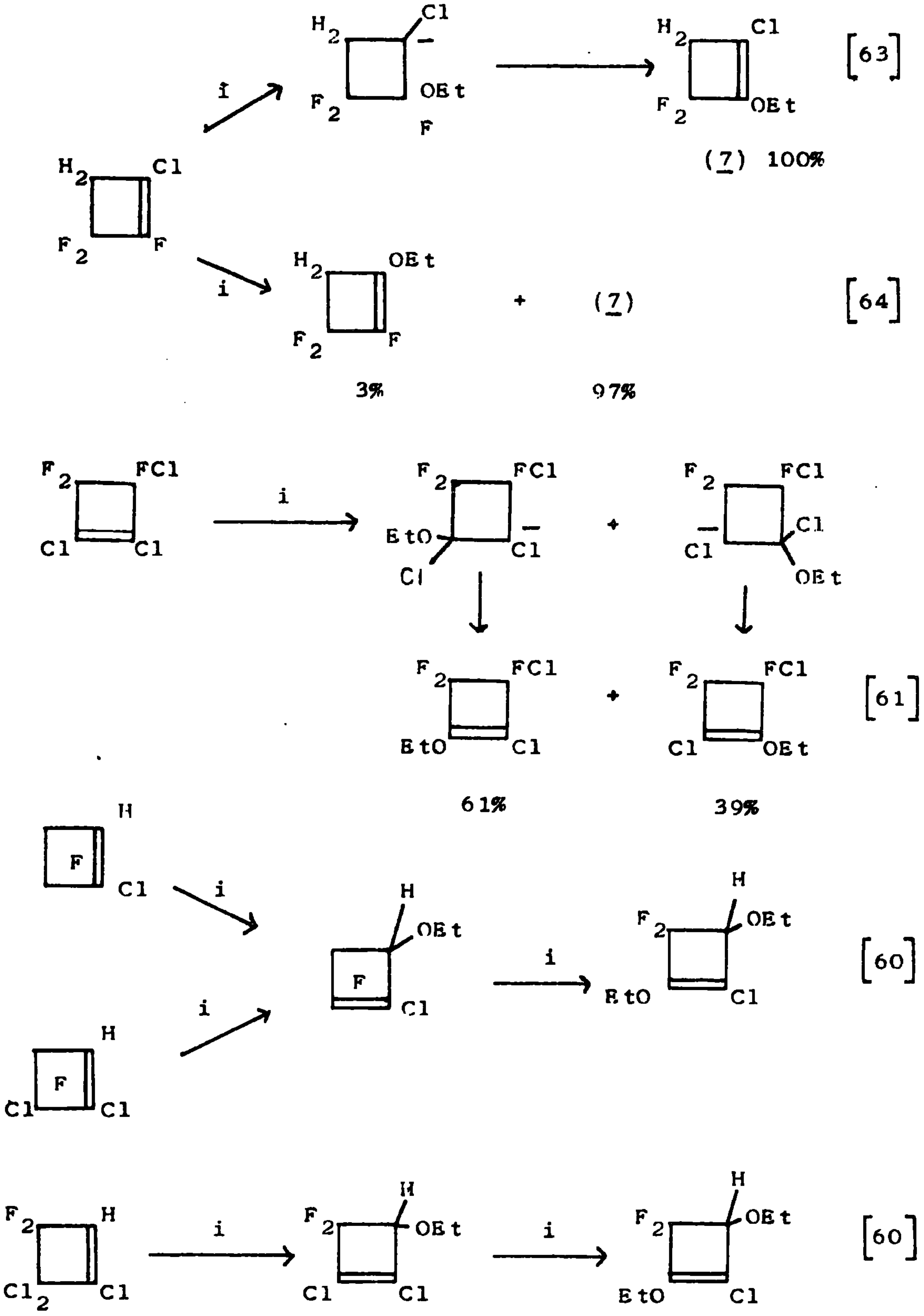
vinylic substitution S_n2' substitution

For cycloalkenes, overall addition of nucleophiles is rarely observed even though this is quite a common reaction for acyclic compounds.[59] As will be seen, the elimination pathway followed (i.e. vinylic or S_n2') is dependant on the substituents on the double bond - vinylic fluorine is usually, but not always, displaced preferentially.[59]

Park has attempted to explain the reactions of polyfluoro-cycloalkenes with nucleophiles in terms of the stability of the intermediate carbanions. Thus, initially, nucleophilic attack occurs to give the most stable carbanion, the order for alpha stabilisation being I ∼ Br > Cl > F > OR. The carbanion then decomposes with elimination of the least basic beta-substituent, the leaving group ability thus being I > Br > Cl > F > OR > H.[60] If attack of the nucleophile at either carbon of the double bond gives an anion with the same alpha-substituent then both possible anions will be formed, but the one preferred will be that with the greatest beta-stabilisation, the order being gem-dichloro > gem-fluorochloro > gem-ethoxychloro > gem-diethoxy > gem-difluoro.[61] Unfortunately, Park used only alkoxide ion as a nucleophile in reactions with polyfluorocyclobutenes and whilst his rationale is broadly correct for this system (scheme 3) and

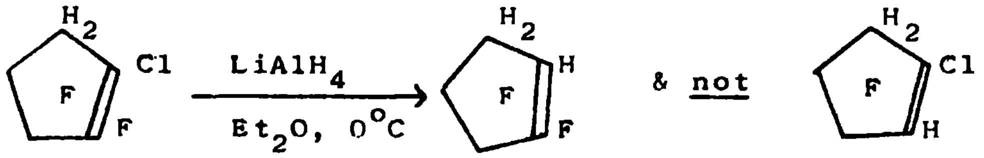
Scheme 3

Reactions of Polyfluorocyclobutenes with Alkoxide



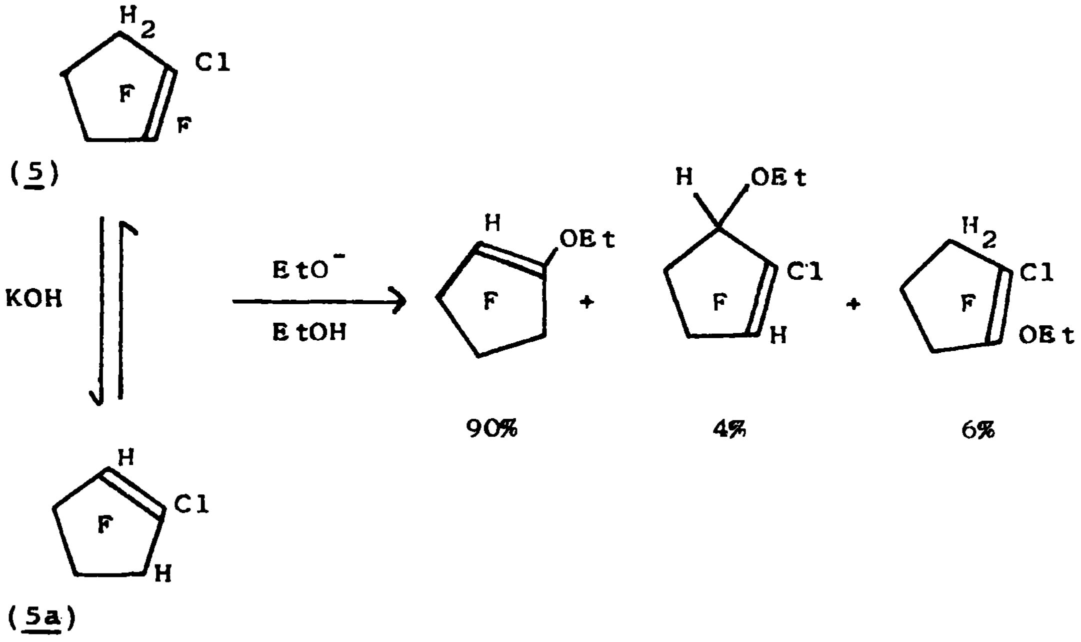
i = KOH, 25°C ethanol

can often be applied succesfully to other systems, it is not universally applicable. For example, reaction of 1-chloro-5H,5H-pentafluorocyclopentene (5) with lithium aluminium hydride results in replacement of the chlorine[62] and not the vinylic fluorine as predicted by Park's theory.

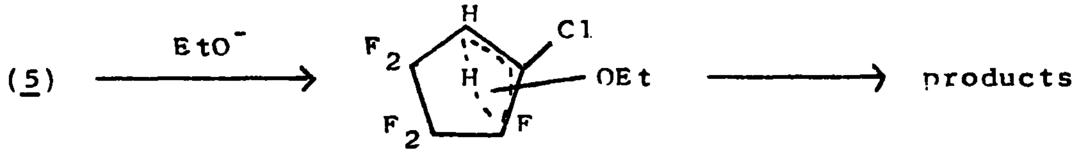


(5)

In view of the far greater reactivity of vinylic fluorine over vinylic chlorine towards nucleophiles [58] this reaction is highly intriguing but as yet has not been satisfactorily explained. The reaction of (5) and its cyclohexene analogue with ethoxide ion has been investigated by Burton.[64] He found that (5) was in equilibrium with its isomer (5a), and that the major substitution product arose from attack on (5a) rather than (5), i.e. (5a) appears to be more reactive towards ethoxide than (5). Deuterium labelling experiments showed that the isomerisation was, at least in part, intramolecular.



Burton explained this apparently anomalous behaviour by postulating an alkoxide bridged intermediate in which the alkoxide ion is situated above the vinylic chlorine thus making it inherently more probable that substitution will occur at this site:-



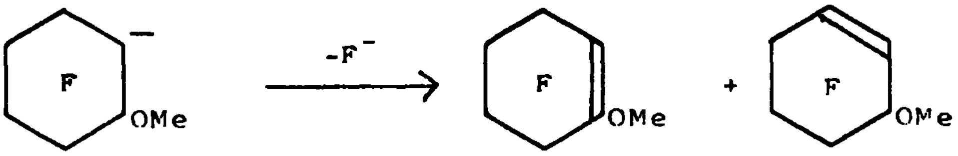
A reinvestigation of the reaction of 1-chloro-3H,3H-trifluorocyclobutene, (6), with ethoxide ion indicated a small amount (3%) of a product, (8), arising from replacement of the chlorine rather than the fluorine [64]- this was not observed by Park [63] (scheme 3). Formation of (8) cannot be explained in terms of an alkoxide-bridged intermediate nor in terms of Park's theory and the reason for it's formation remains a mystery. Burton concluded from the preceding reactions that for compounds containing allylic gem-dihydro groups the reaction with alkoxide is dominated by conformational changes arising from ring size effects.[64] Contrary to this, Park holds that the dominating effects are electronic in nature,[60] and that ring size is not important, at least for reactions of cyclo-butenes and -pentenes with nucleophiles.[65] As will be seen shortly, in some systems the products cannot be predicted by a consideration of electronic effects in intermediate carbanions, nor are they dependant on ring size.

Thus it is apparent that there is no single unifying postulate to predict, a priori, the exact product formation from reaction of a polyfluorocycloalkene with a nucleophile. This is not suprising in view of the diversity of halo-alkenes and attacking nucleophiles, which probably precludes a single working hypothesis. It seems probable that product identity depends not just on intermediate carbanion stability but also on such factors as ring-strain, nucleophilicity, steric hindrance, polarity of reaction medium, etc..

1.B.1a Oxygen Nucleophiles

These reactions are summarised in Table 1.

With alkoxide ion the major initial product for F-cyclo-alkenes results from replacement of vinylic fluorine and this is the only reaction observed for F-cyclo-butene [66,67] and -propene.[68] However, with F-cyclo-pentene and -hexene small amounts of products arising from S_n2' displacement are obtained. This has been explained by trans addition to the alkene [67] - thus, for addition of methoxide to F-cyclo-hexene the negative charge is situated, in the carbanion, on the opposite side of the ring to the methoxy group. This means that loss of fluoride ion from the carbon bearing the methoxy group is electronically preferred but loss from the adjacent difluoromethylene sterically so.



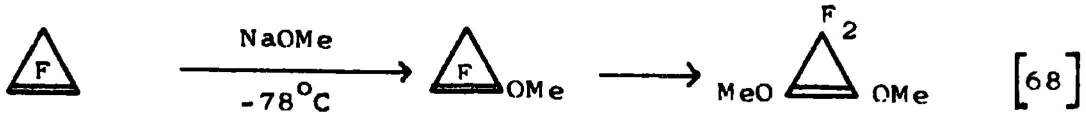
Replacement of one of the vinylic fluorines by, for example, a methyl group results in a much greater amount of S_n2' displacement.[67] In cyclo- pentenes and -butenes the steric opposition to syn-coplanar eliminations is not so large.

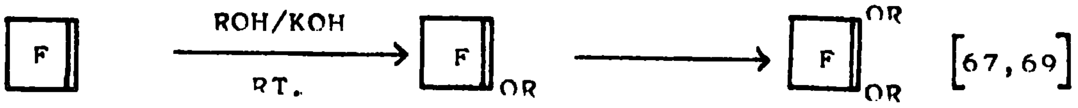
The initial products from nucleophilic substitution can react further and, once again, the major product(s) results from replacement of vinylic fluorine.[68-70] The exception is the cyclohexyl system where S_n2' displacement is the main reaction pathway.[67]

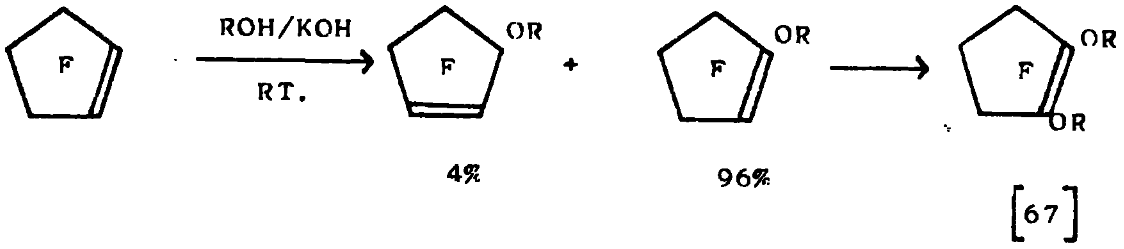
With diols the products appear to be dependant on the chain length of the nucleophile. Thus ethane diol [71] and 1,3-propane diol [72] give complex mixtures with F-cyclohexene, arising from attack by both hydroxy groups - this may be a function of the reaction conditions (see chapter 4). In contrast, 1,4-butane diol apparentely behaves as a monohydric

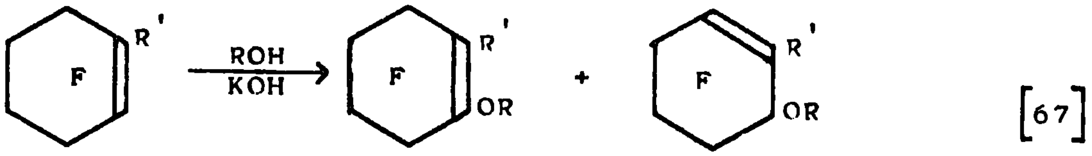
Table 1

Reactions of Polyfluorocycloalkenes with Oxygen Nucleophiles

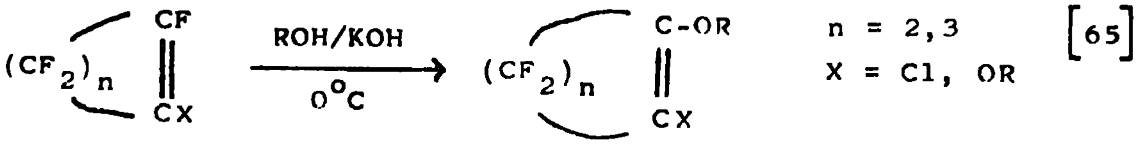


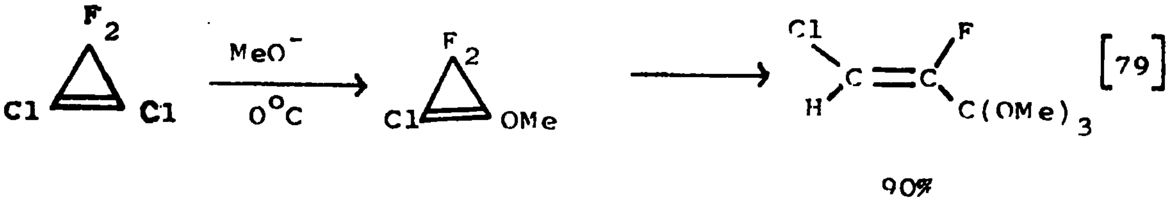






R' = F, OMe, Me, H





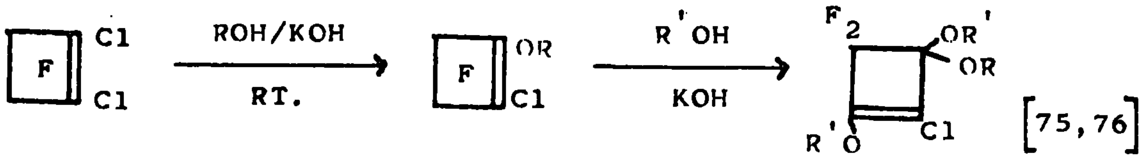
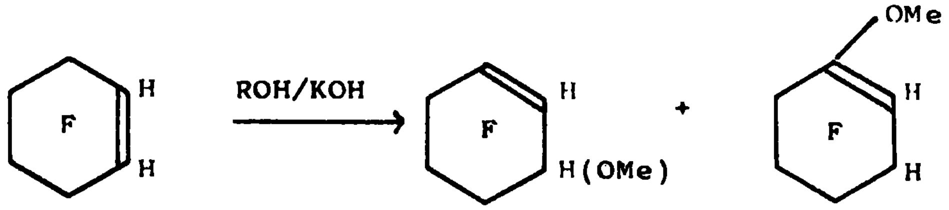
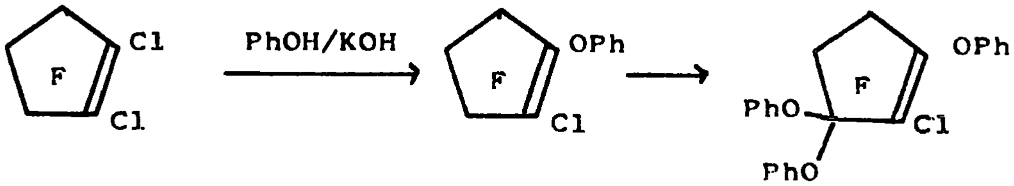


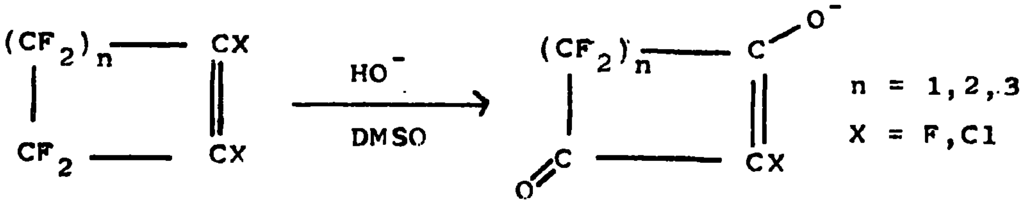
Table 1 - continued



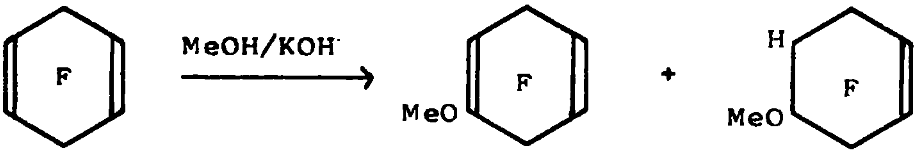
[80]



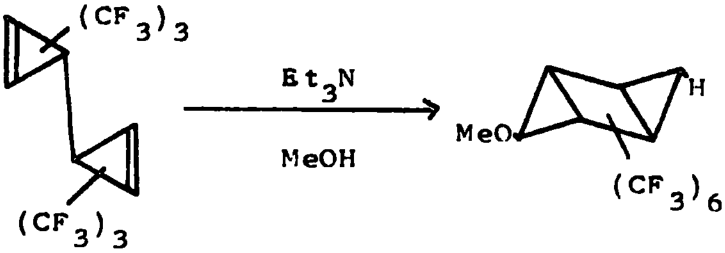
[81]



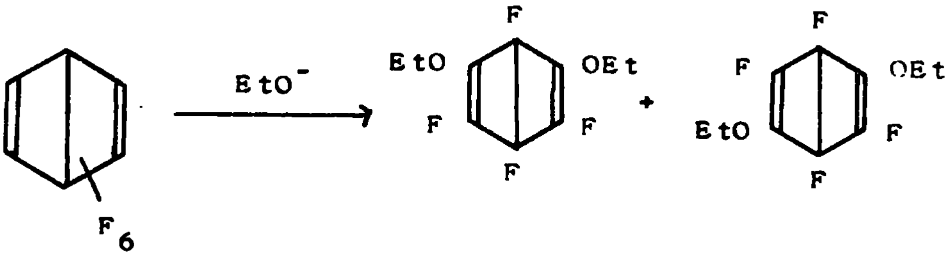
[82]



[85]

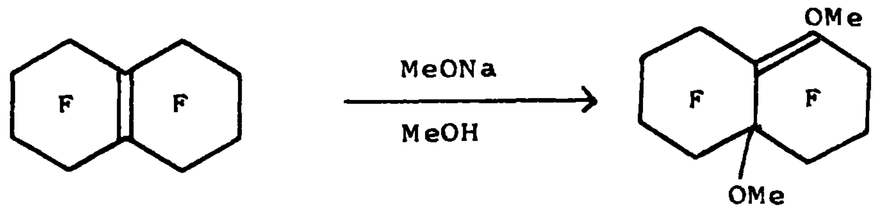


[86]



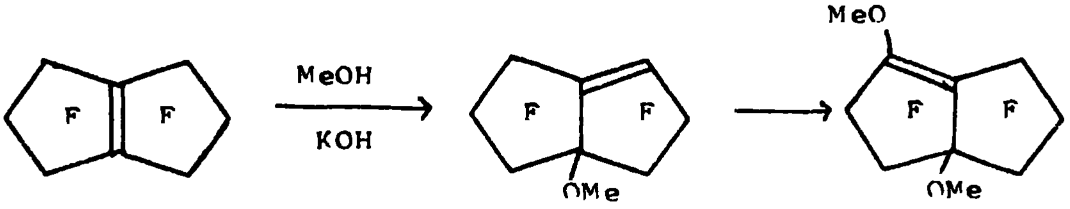
[87]

Table 1 - continued



(9)

[90]



(10)

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alcohol.[72]

In cyclic alkenes containing only one vinylic fluorine the major reaction is displacement of this fluorine,[65,73] although, once again, the cyclohexyl systems undergo S_n2' displacement of fluorine as well.[67,74]

1,2-Dichloro-F-cycloalkenes undergo initial vinylic chlorine substitution, and then further reaction can occur to displace two of the allylic fluorines.[75-78] With 1,2-dichloro-difluorocyclopropene, however, the mono-methoxy adduct reacts further to give cis-3,3,3-trimethoxy-1-chloro-2-fluoro-propene, presumably via an intermediate carbonium ion[79] (Table 1). Reaction of 1,2-dichloro-F-cyclopentene with ethane diol gave only two products but these were not rigorously identified.[77]

1,2-Dihydro-F-cycloalkenes undergo reactions with alkoxides to displace two allylic fluorines; with the cyclo-pentene and -hexene systems some alcohol addition is also observed.[80]

Phenols behave very similarly to alcohols,[66,81] but the following points should be borne in mind: phenols are generally weaker bases than alcohols; phenoxy substituents will be less capable of promoting further substitution; it is possible that the increased size of phenols may be important in some cases.

Hydroxide ion reacts with F-cycloalkenes or 1-substituted F-cycloalkenes to give salts of 1-hydroxycycloalken-3-ones.[83] Thus, reaction of F-methylcyclopentene with potassium hydroxide gives the potassium salt of 1-hydroxy-F-2-methylcyclopent-3--one.[84]

F-Cyclohexadienes undergo similar reactions with nucleo--philes but some addition of alcohol is observed.[85] Addition also occurs in the reaction of methanol with F-hexamethyl--3,3'-dicyclopropene and involves a fascinating ring closure.[86]

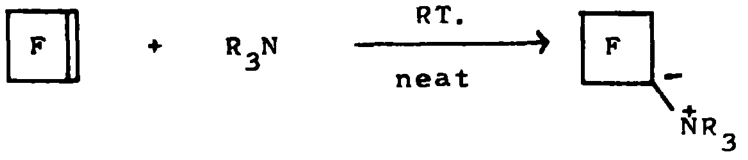
The reactions of F-Dewar benzenes have been extensively investigated,[87-89] and with nucleophiles the reactivity and products are as expected for very strained F-cycloalkenes.

It is reported that F-tropone and methoxide ion give a symmetrical dimethoxy adduct.[53]

Evidence that steric effects may be of importance in nucleophilic reactions is illustrated by the lower reactivity of the internal alkene (9) compared to its analogue (10) (Table 1); this has been attributed to a less accessible double bond.[90]

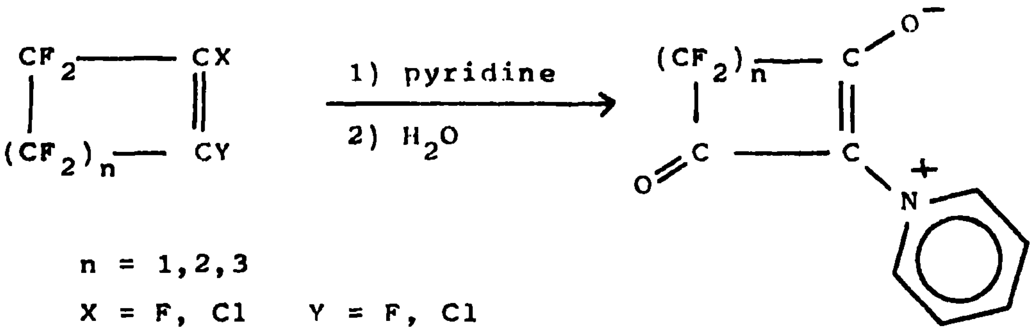
1.B.1b Nitrogen Nucleophiles

In striking contrast to their lack of reactivity with acyclic F-alkenes, tertiary amines react with F-cyclobutene to give stable, isolable ylides.[91-93] These will be discussed more fully in chapter 3.



R = Et, ^{n}Bu [92,93]

A similar reaction occurs with pyridine and it's derivatives but in this case the ylides have not been isolated.[94] However, the hydrolysis products, stable betaines, can be obtained in good yield by reaction of F-cycloalkenes or their 1,2-dichloro-analogues with pyridine followed by water.[95]



[95]

n = 1,2,3

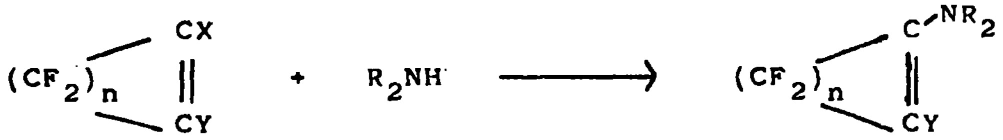
X = F, Cl Y = F, Cl

In the absence of water oligomerisation occurs in the case of F-cyclobutene[94] - this will be discussed in chapter 2.

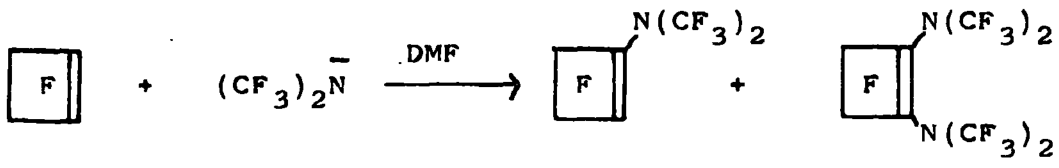
The reaction with secondary amines parallels that with alkoxides[73,88,90,96,97] except that the resultant mono-adduct is deactivated to further substitution by more amine, but not by alkoxide, for example.[98] This is, of course, a function of the base strengths of the two nucleophiles as is the failure of F-cyclobutene and diphenylamine to react at all.[96]

1,2-Dichloro-F-cycloalkenes also react as with alkoxides i.e. by replacement of vinylic chlorine.[97,98]

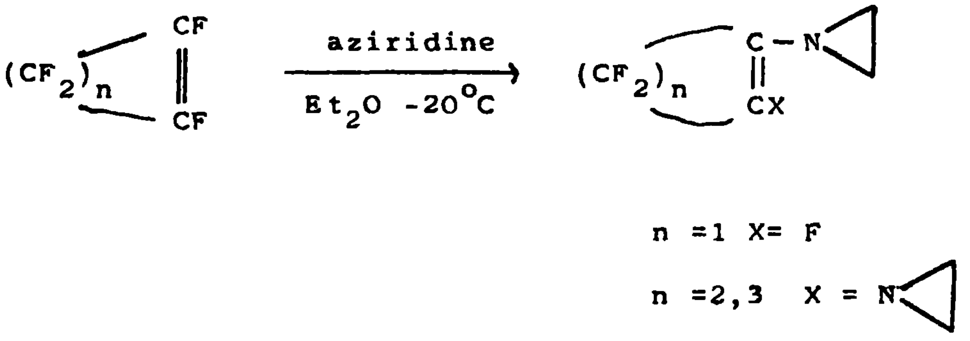
n =1,2,3 Y=X=Cl



[97]



[99]

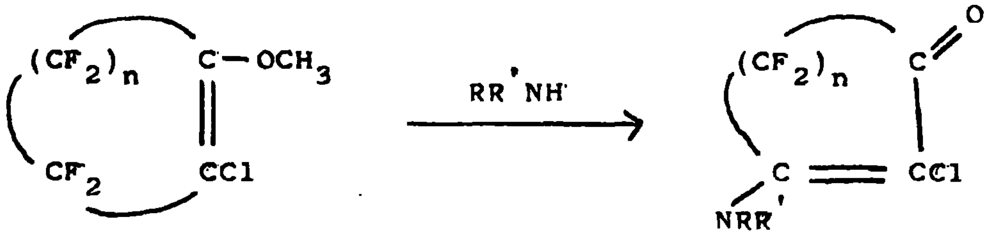


[100]

n =1 X= F

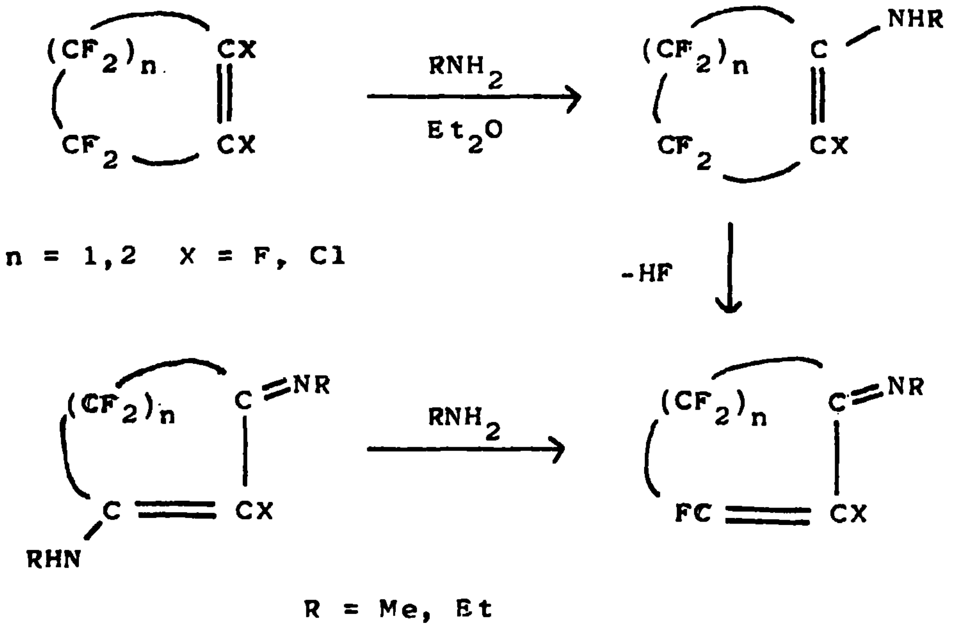
n =2,3 X = N

Both vinylic fluorines of F-cyclobutene are replaced by caesium bistrifluoromethyl amide [99] and by aziridine.[100] An interesting reaction occurs, to give a cycloalken-3-one, when 1-chloro-2-methoxy-F-cycloalkenes are treated with secondary amines.[101] The reaction also occurs, very slowly, for the corresponding ethoxy compounds but yields are poor.



n = 1,2

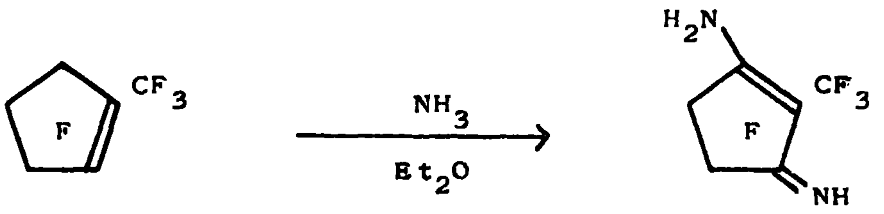
Primary amines and ammonia react with F-cycloalkenes and their 1,2-dichloro analogues to give 1-amino-3-imino-cyclo-alkenes.[84,90,96,98,102,103] Presumably the initially formed product undergoes 1,4-elimination of hydrogen fluoride and subsequent reaction with more amine.



[103]

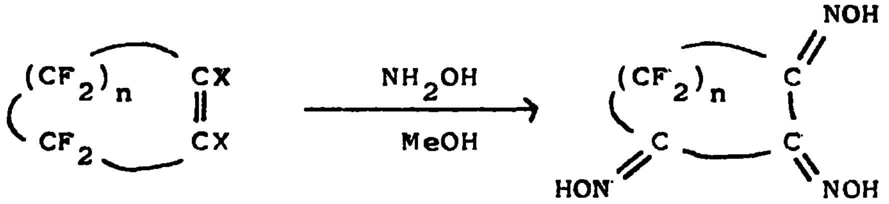
n = 1,2 X = F, Cl

R = Me, Et



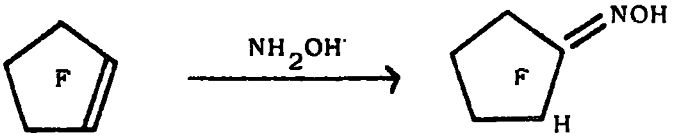
[84]

It is claimed that reaction with hydroxylamine gives 1,2,3-trioximinocycloalkanes [103] but a recent Russian report appears to be at variance with this observation.[104] However, the conditions for the latter reaction were not reported and it is possible that the oximinocyclopentane (11) could react further under different conditions with initial elimination of hydrogen fluoride.

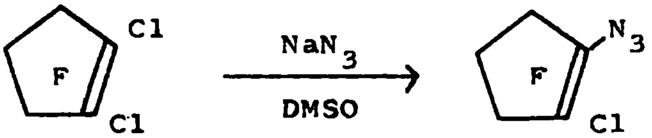


[103]

X = F, Cl n = 1,2



(11) [104]

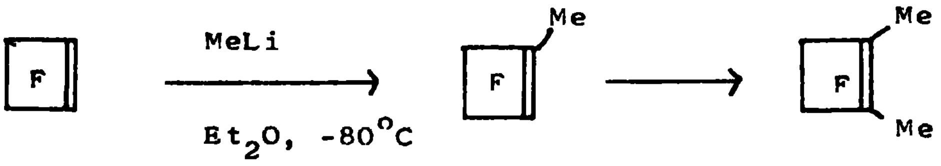


[98]

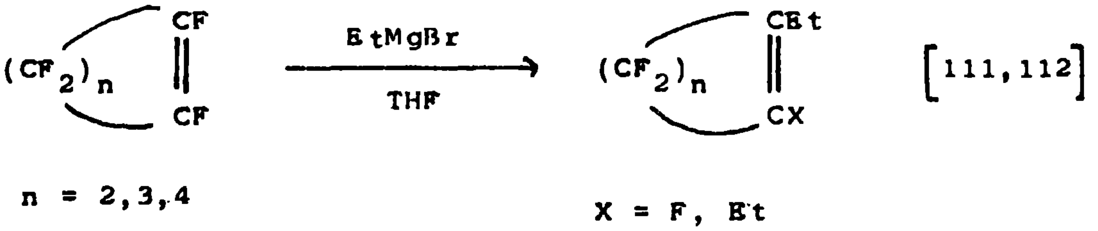
1,2-Dichloro-F-cyclopentene reacts with azide ion to give the mono-substituted product.[98]

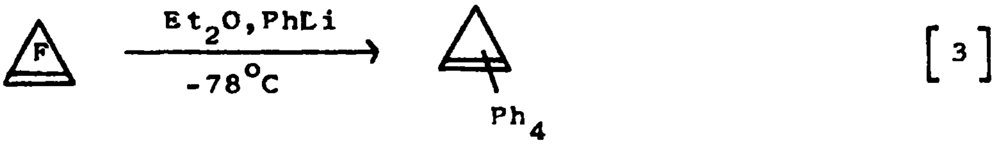
1.B.1c Carbon Nucleophiles

The major reaction of alkyl lithiums [87,88,105-109] and Grignard reagents [110-112] is replacement of one or both of the vinylic fluorines. Displacement of allylic fluorine is rarely observed, a noticeable example being the reaction of F-cyclopropene with



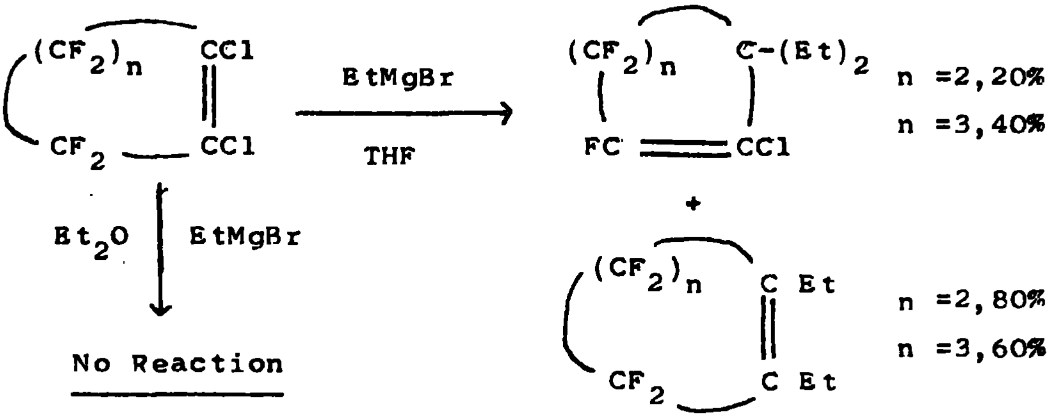
[105]



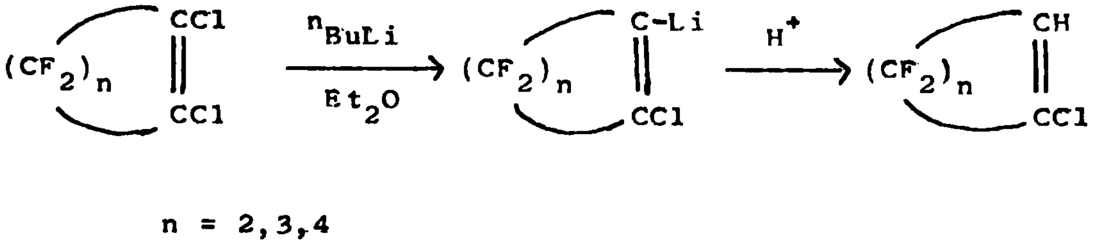


phenyl lithium to give tetraphenylcyclopropene.[3]

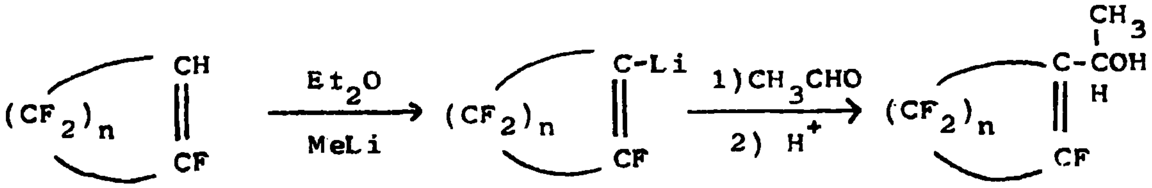
In the reaction of Grignards with 1,2-dichloro-F-cyclo-alkenes there is competition, in the second substitution step, between displacement of chlorine and allylic fluorine; the solvent has a profound effect in this system.[111]



This behaviour is in contrast to that with alkyl lithiums where, with methyl lithium, substitution of chlorine occurs, whilst with ^{n}butyl lithium lithiation of the alkene occurs.[113]

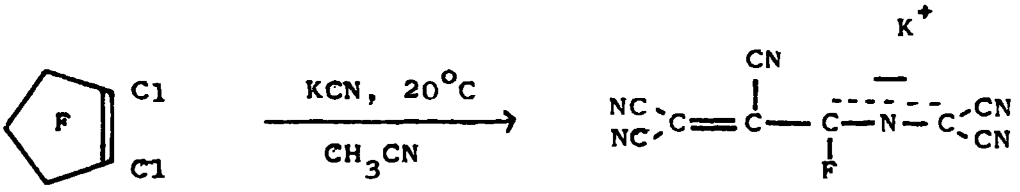


Lithium exchange also occurs in the reaction of 1-H-F-cyclo--alkenes with methyl lithium to give the synthetically useful lithium perfluoroalkenyl reagents, (12).[114]



(12)

n = 2,3,4



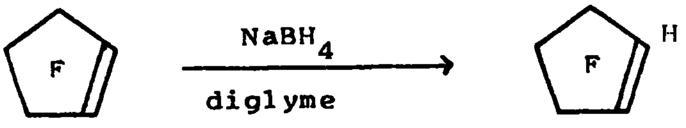
[115]

(13) 30%

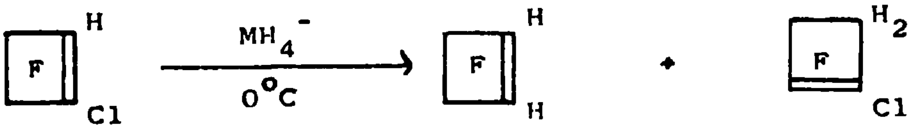
Cyanide ion has been little used as a nucleophile in organic fluorine chemistry since it activates systems to further nucleophilic attack thus resulting in polysubstitution e.g. the reaction of 1,2-dichloro-F-cyclopentene with potassium cyanide to give (13).[115]

1.B.1d Complex Hydrides

The reaction of F-cycloalkenes with sodium borohydride[87,88,107,116] and lithium aluminium hydride [62,117,118] is analagous to that with alkoxides. 1-Chloro- and 1,2-dichloro-F-cycloalkenes react as with alkoxide in the first step but in subsequent substitutions there is competition between displacement of chlorine and allylic fluorine.[119] The ratio of products is greatly dependant on the nature of the hydride ion; this suggests a steric and/or solvent effect.



[116]



[119]

M = Al (Et_2O) 37% 63%

M = B (diglyme) 80% 20%

The anomalous behaviour of 2-chloro-3H,3H-F-cycloalkenes with lithium aluminium hydride [62] (and nucleophiles in general [64]) has already been mentioned.

Diborane does not react with F-cycloalkenes except in the presence of fluoride ion when it behaves as borohydride.[120]

1.B.1e Other Nucleophiles

These reactions are summarised in Table 2.

Thiols react with F-cycloalkenes [121,122] or the corresponding 1,2-dichloro compounds [81,122,123] by replacement of one, or both, of the vinylic substituents; S_n2' displacement is not observed.

Reaction of potassium sulphide with a variety of polyfluorochlorocycloalkenes led to low yields of p-dithiins.[124]

Trialkyl phosphines behave similarly to trialkylamines e.g. reaction of F-cyclobutene and triphenylphosphine gives a stable ylide [125,126] whose ^{19}F n.m.r. spectrum is very similar to that of the ylide from triethylamine.[93]

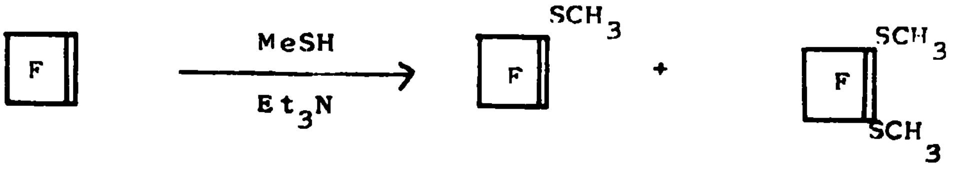
Dialkyl phosphines behave like thiols[122,127,128] i.e. one or two vinylic displacements of fluorine or chlorine occur. However, a solvent appears to be important,[127] since in the absence of one, complex mixtures are obtained.

Treatment of 1-halo- [73,131] or 1,2-dihalo-[129,130] F-cycloalkenes with trialkyl phosphites gives phosphonic esters via phosphorane intermediates.[131] Similar reactions occur with phosphonous [129] and phosphinous [129] esters. However, with F-cycloalkenes the product is a mixture of phophinic esters and phosphoranes.[131]

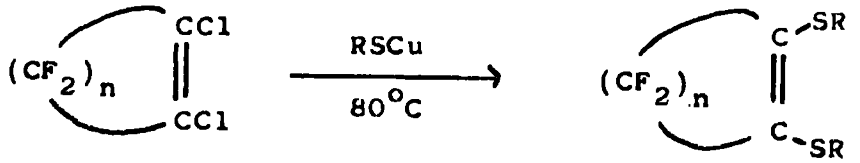
Arsines also act as nucleophiles [97,132,133] and reaction

Table 2

Polyfluorocycloalkenes with Various Nucleophiles

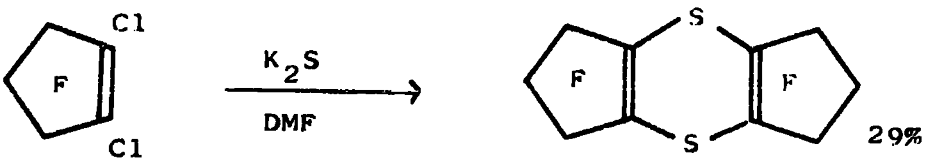


[122]

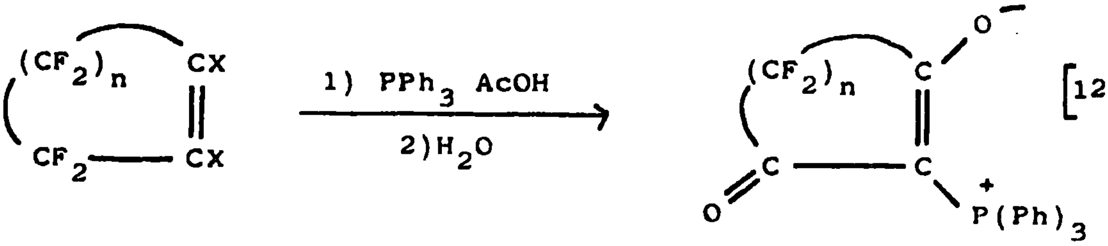


[123]

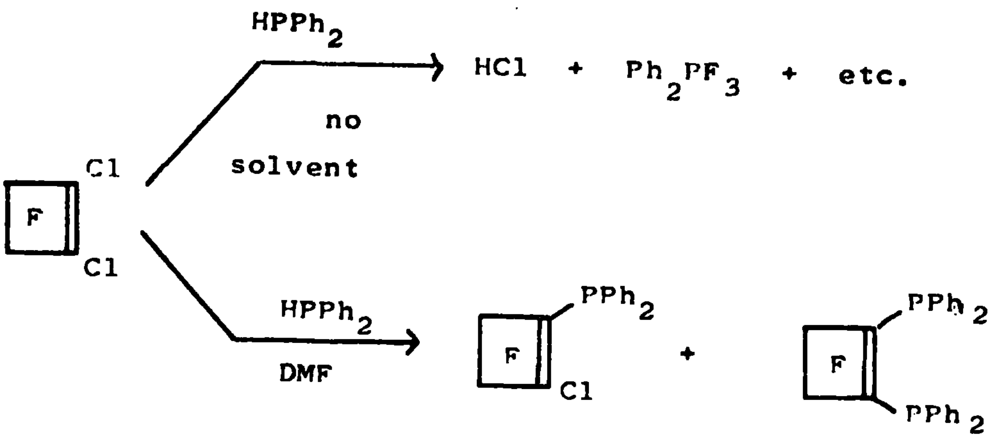
R = Ph, $PhCH_2$



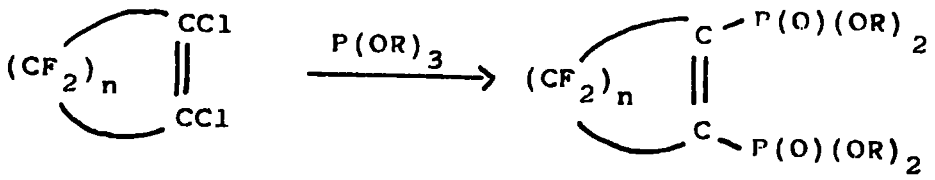
[124]



[125]

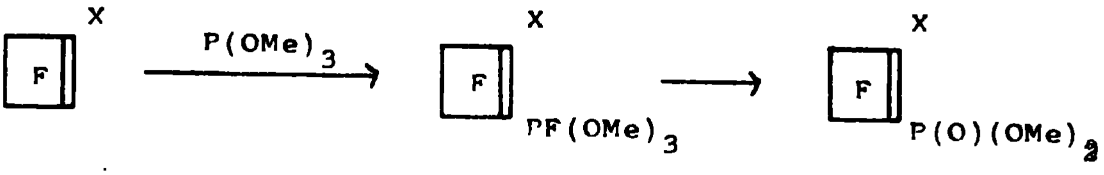


[122]

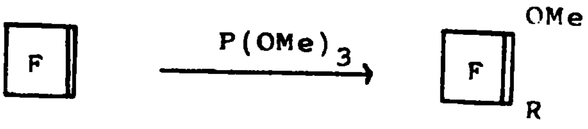


[129]

Table 2 - continued

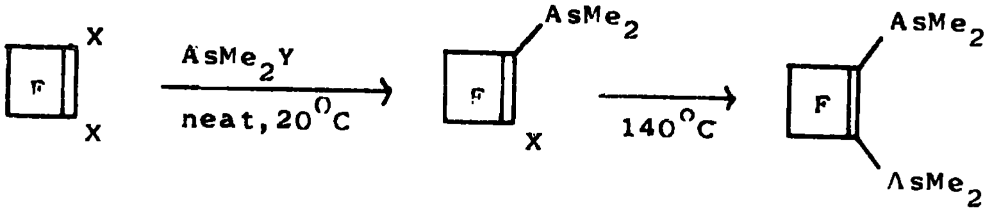


[131]



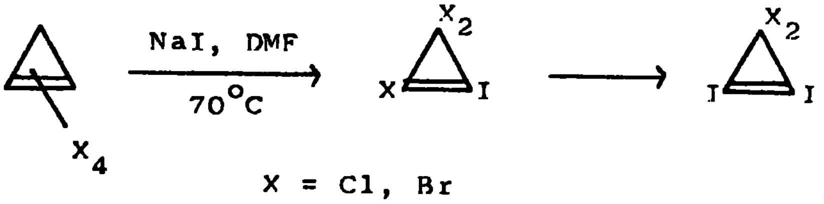
$R = PF_n(O)(OMe)_{2-n}$

$n = 1,2$ or 0



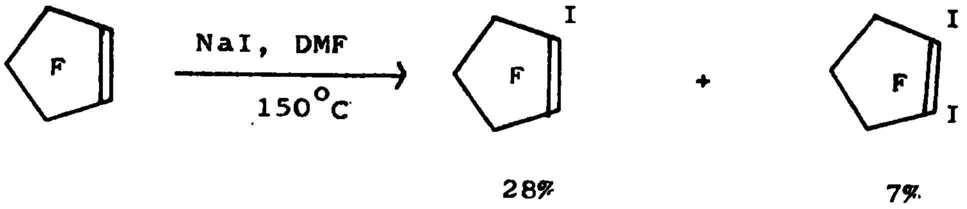
[131]

$Y = AsMe_2$, H, MgBr X = F, Cl

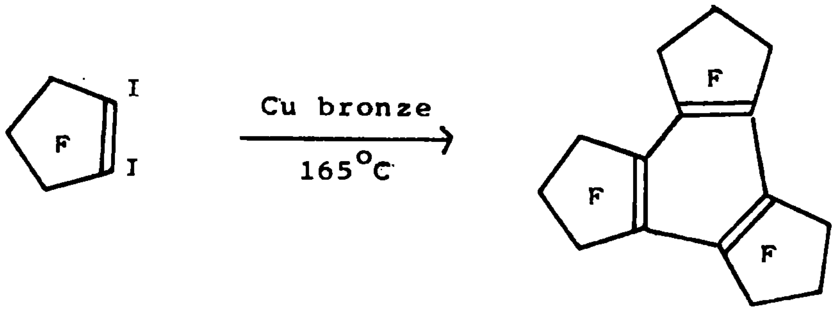


[4]

X = Cl, Br



[133]



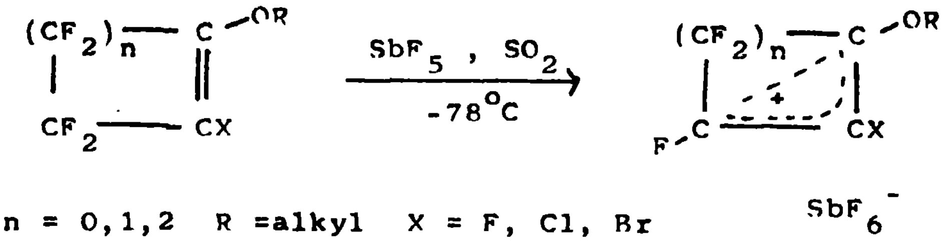
leads to vinylic displacement for cycloalkenes, c.f. their reaction with, for example, F-propene where addition occurs.

Iodide ion in an aprotic dipolar solvent replaces vinylic halide ion [5,134-136] and the ease of reaction, and yield, decreases with increasing ring size. The resultant 1-iodo- and 1,2-diiodo-F-cycloalkenes give a range of highly novel compounds when coupled with copper.[134,136] Similar displacements, of fluoride ion, have been observed using chloride ion.[134] Exchange of vinylic chlorine for bromine occurs over a calcium sulphate/charcoal bed at 250°C in the presence of hydrogen bromide.[135]

The many and varied reactions of F-cycloalkenes with metal carbonyls and metal carbonyl anions will not be discussed here; excellent reviews on this interesting area are available.[137]

1.B.2 Electrophilic Attack

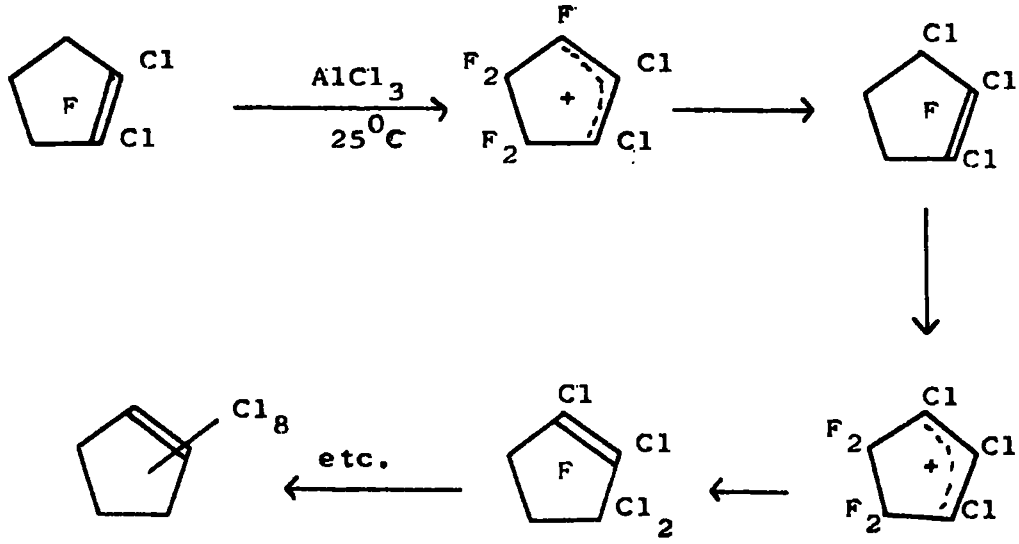
Generally, highly fluorinated alkenes are relatively resistant to attack by electrophiles. With strongly electrophilic species, however, reaction can occur, usually by initial loss of allylic fluorine to give an intermediate cation which can often be isolated. For example, treatment of 1,2-dihalodifluorocyclopropenes,[2,8] 1,2-disubstituted-F-cyclobutenes [138,139] or 1-alkyl-F-cyclo-alkenes [139] give cationic species which can be separated or observed in solution by ^{19}F n.m.r..



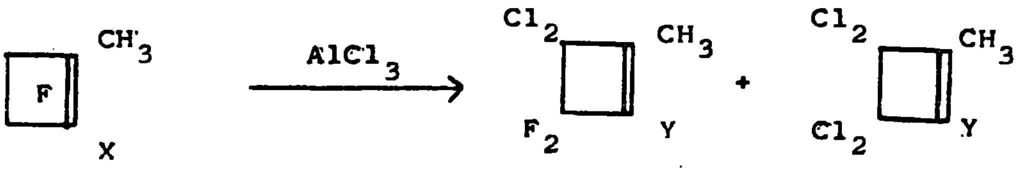
n = 0,1,2 R =alkyl X = F, Cl, Br

[139]

Treatment of 1,2-dichloro-F-cycloalkenes with aluminium trichloride results in replacement of the fluorines by chlorine.[140] Presumably all the fluorines in the ring become potentially allylic as a result of double bond migrations. Similar reactions occur for F-cycloalkenes.However, with F-cyclohexene, hexachlorobenzene is obtained.[140]



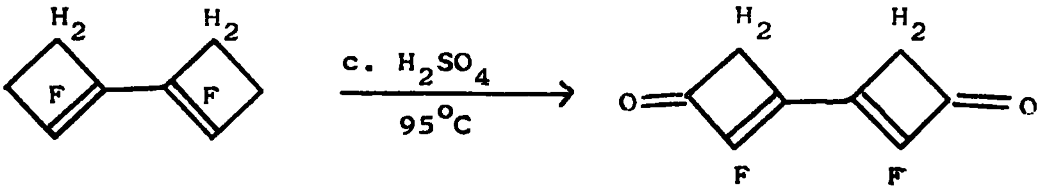
[140]



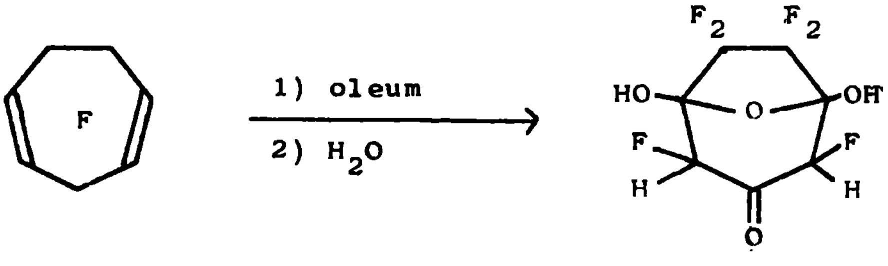
[141]

X = Y = CH_3 X = F, Y = Cl

Concentrated sulphuric acid is a useful reagent for converting allylic difluoromethylenes into keto functions:-



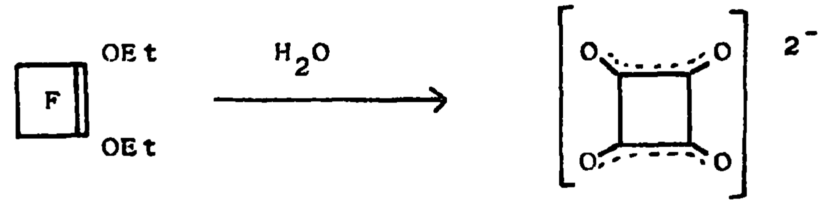
[142]



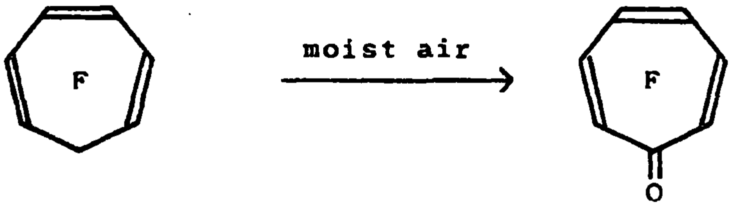
[143]

(<u>14</u>)

The second example is particularly fascinating and production of (14) can be rationalised by a series of intermediate carbocations. In a few cases, e.g. production of squaric acid [144] and hydrolysis of F-cycloheptatriene,[53] the allylic fluorines are very readily hydrolysed to give keto functions, even by water. However, these are special cases since the products are highly conjugated systems.

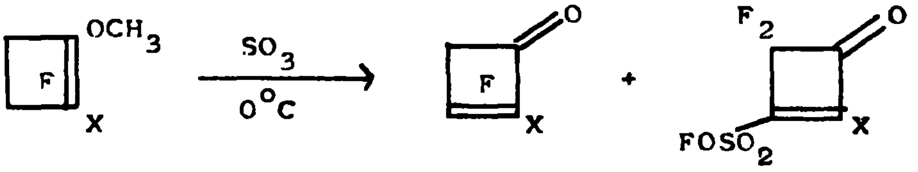


[144]



[53]

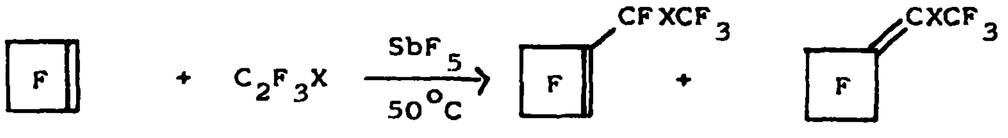
Treatment of 1-methoxy-F-cyclopentene with sulphur tri-oxide results in 1,4-elimination of methyl fluoride.[145] The reaction also occurs for the corresponding cyclobutene system but in this case the major product is the fluoro-sulphate (15). Three fluorosulphates were obtained on treat-ment of F-cyclobutene with sulphur trioxide.[146]



[145]

25%

(15) 30%



[147]

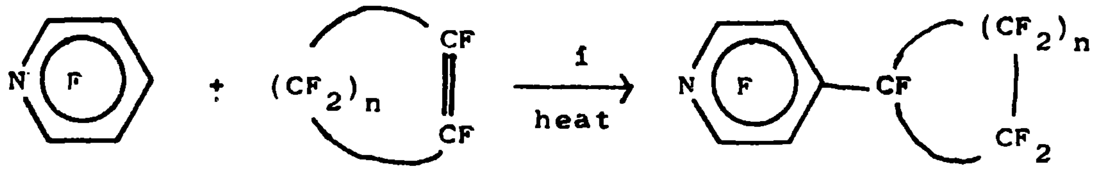
X = F, CF_3, H   X = H

Although F-cyclobutene is not dimerised by antimony penta-fluoride [138] it will react with tetra- and tri-fluoroethenes and F-propene to give 1:1 adducts.[147] Under the same conditions F-cyclopentene is unreactive.

1.B.3 Additions Involving Fluoride Ion

In the presence of fluoride ion, F-cycloalkenes, in common with their acyclic analogues, give small concentrations of the corresponding anions. These anions can be trapped by suitably electro-philic species to give overall addition to the original double bond. One obvious reaction is for the anion to attack the alkene itself to give dimers - this reaction will be considered in chapter 2.

These anions can be used to alkylate activated fluoro-aromatics in a nucleophilic equivalent of the Friedel-Crafts reaction.[148]



i) KF, sulpholan   n = 2,3,4

Examples of other trapping reactions are given in Table 3. Of particular interest is the reaction of F-cyclobutyl anion with sulphur since it is thought that radical intermediates may be involved.[149]

1.B.4 Addition Reactions

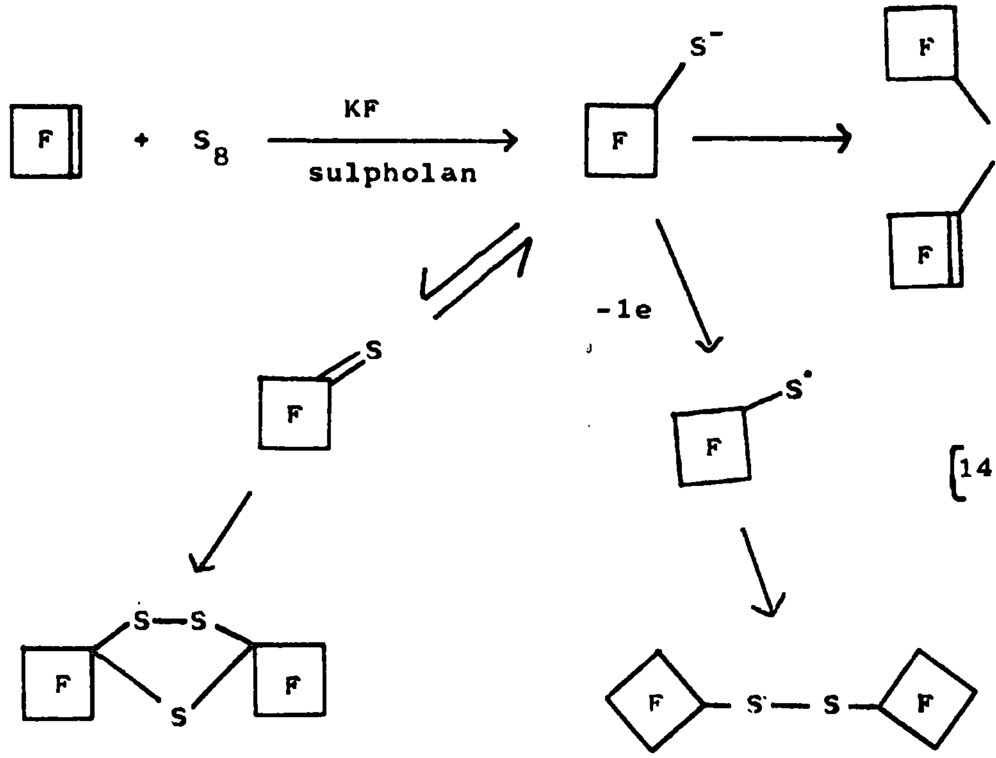
This encompasses free radical additions, polymerisations and oxidation reactions.

1.B.4a Free Radical Addition

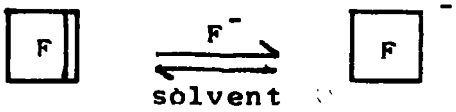
Alcohols, aldehydes and ethers can readily be added across the double bond of F-cycloalkenes by gamma-ray or peroxide induced reaction.[156,157] The products obtained are cis- and trans-isomer mixtures although

Table 3

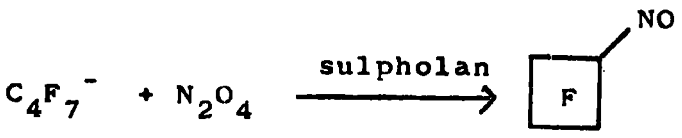
Trapping of Perfluorocyclobutyl Anion



[149]



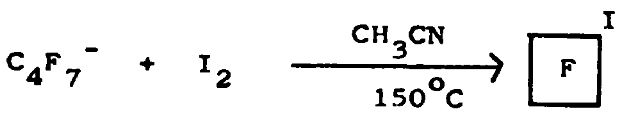
= $C_4F_7^-$



[150,151]

50%

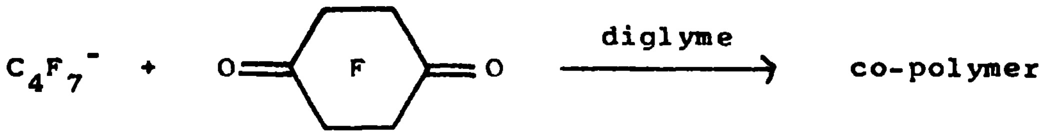
[152]



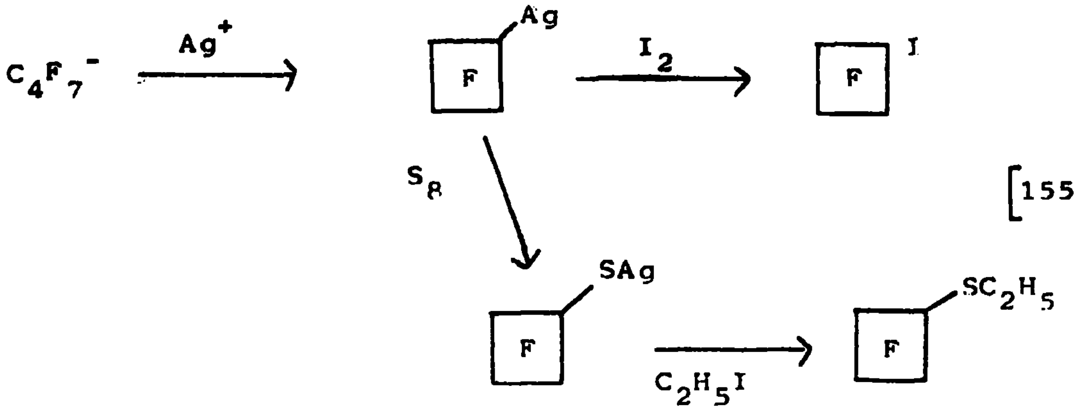
27%

[153]

Table 3 - continued



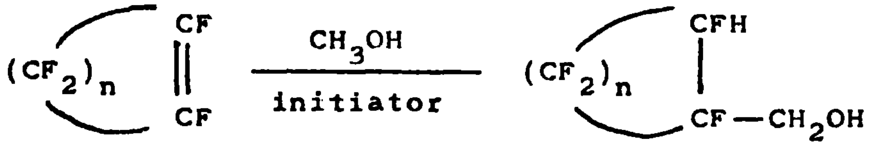
[154]



[155]

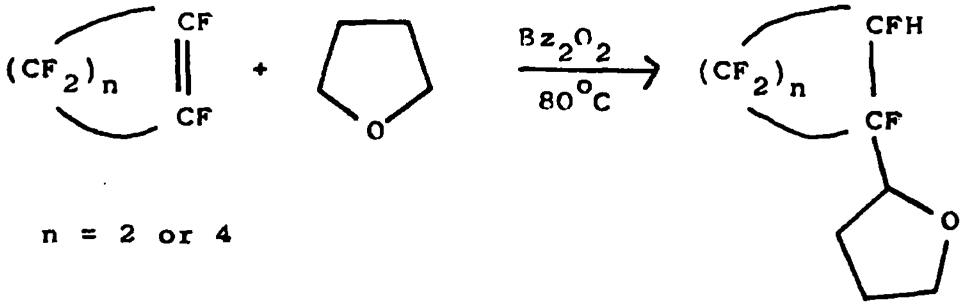
---

there is a tendency for the cis-isomer to predominate with increasing ring size: it is the only product observed for gamma-ray induced addition of acetaldehyde to F-cyclohexene.



[157]

n = 2,3,4

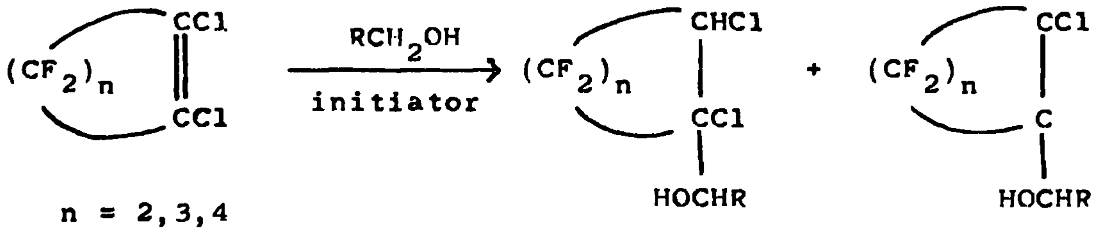


[158]

n = 2 or 4

The corresponding 1-chloro-,[159] 1-hydro-,[160] and 1,2-dichloro-F-cycloalkenes [161,162] undergo similar reactions. However, in some cases dehydrohalogenation occurs in situ and the resultant alkenes can often react further to give a 1:2 adduct.[162]

Other compounds such as silanes,[163,164] dialkyl phosphites [165] and toluene [166] have also been added to F-cycloalkenes by a free radical process.



[161]

The F-cycloalkenes readily add halogen,[5,45,87-90] hydrogen [88,167,168] and hydrogen halide [87,88,169] either thermally or photochemically. In some cases addition occurs in the absence of light [88] suggesting an electrophilic mechanism. Indeed, it has been suggested that thermal chlorination of F-cyclohexene is a bimolecular and not a radical process.[170] In the fluorination of F-cyclobutene a small amount of F-cyclobutylcyclobutene is formed,[171] presumably as a consequence of the low temperature and low fluorine concentration.

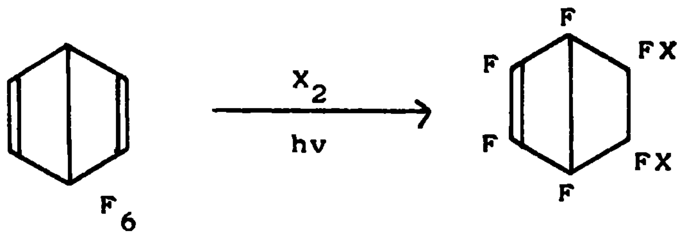
Additions also occur with many other compounds in which homolytic fission is a fairly easy process: with trifluoro-methyl iodide and interhalogens [172]; peroxides [173,174]; compounds containing nitrogen to fluorine [175,176] or oxygen to fluorine [177,178] bonds; dinitrogen tetroxide [179]; etc.. These reactions are all summarised in Table 4.

1.B.4b Polymerisations

In keeping with their acyclic analogues very drastic conditions are usually required to effect polymerisation of F-cycloalkenes. Thus F-cyclobutene (in the presence of a trace of F-acetone)[180] and F-cyclopentadiene require very high temperatures and pressures before they are

Table 4

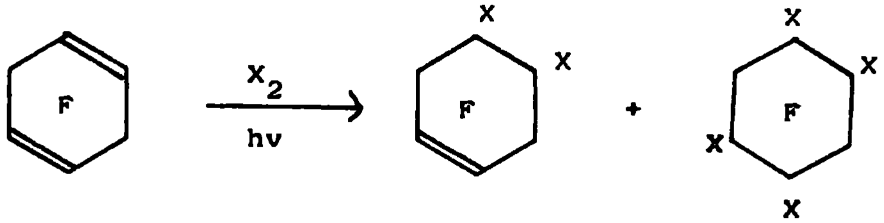
Addition Reactions of F-cycloalkenes



X = Cl, Br

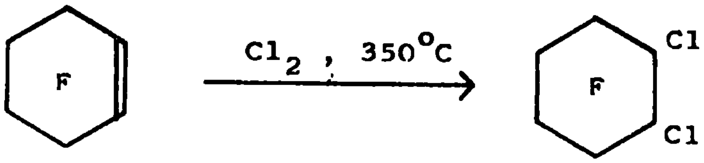
[87,88]

cis- & trans-isomers

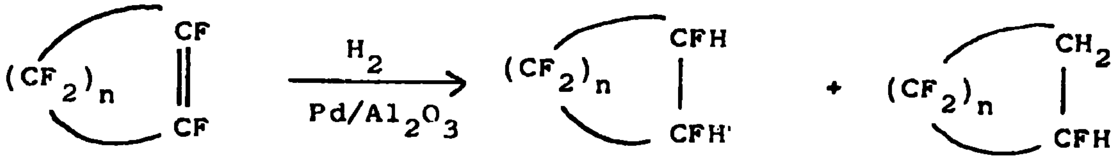


X = Cl, Br

[45]



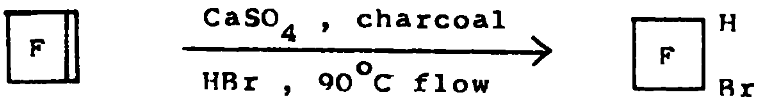
[170]



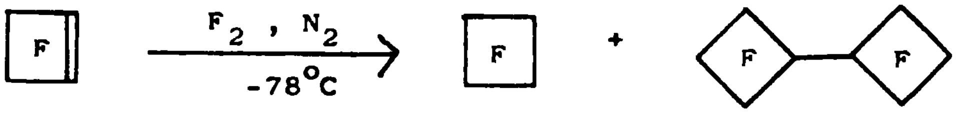
n = 2,3, 4

cis- & trans-isomers

[168]



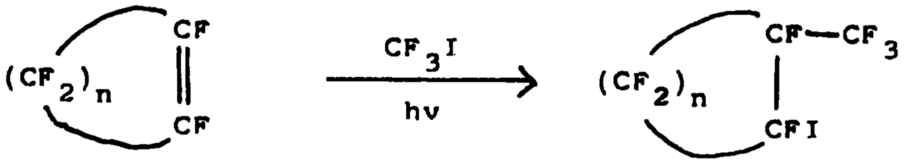
[172]



trace

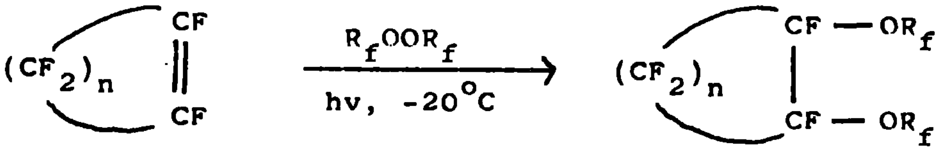
[171]

Table 4 - continued



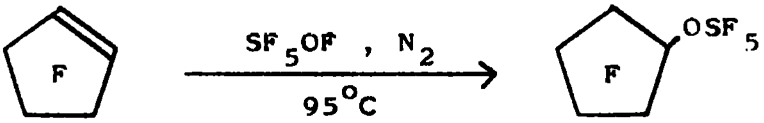
[172]

n = 2 or 4



[174]

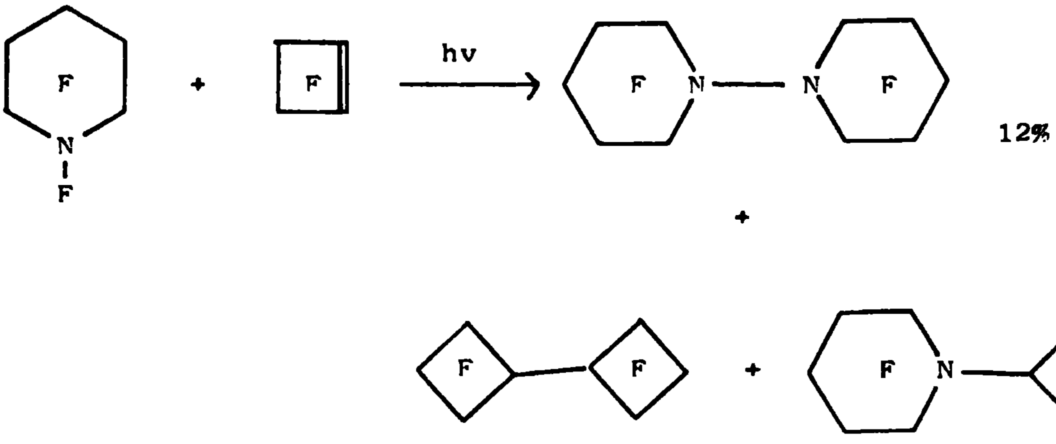
n = 2 or 3 R_f = F – ᵗbutyl or CF_3



[177]

[179]

at 130°C - no reaction
at 160°C - explosive



[175]

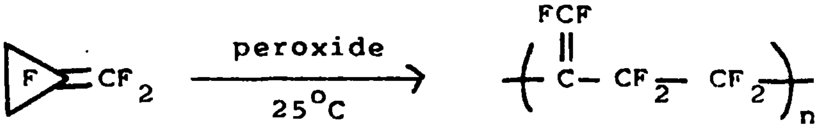
12%

18%

44%

homopolymerised.

An exception is F-methylenecyclopropane which readily polymerises in the presence of an initiator to give a ring opened polymer which retains vinylic difluoromethylene groups.[6]

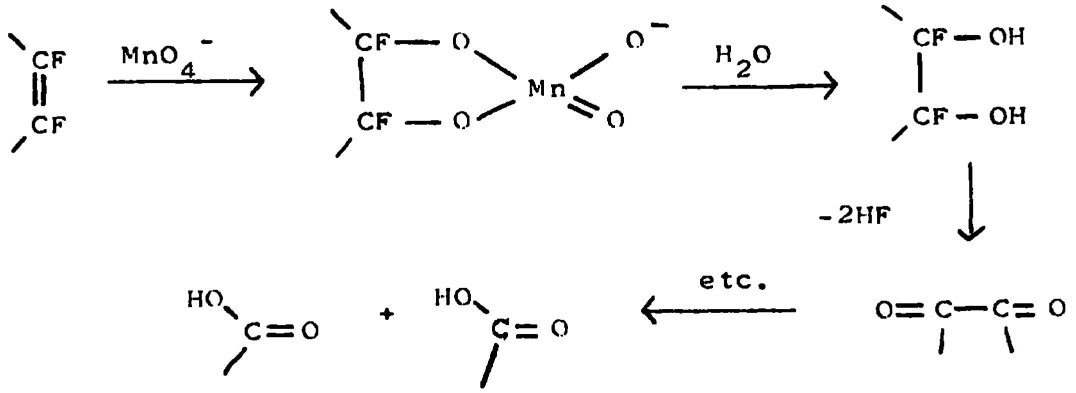


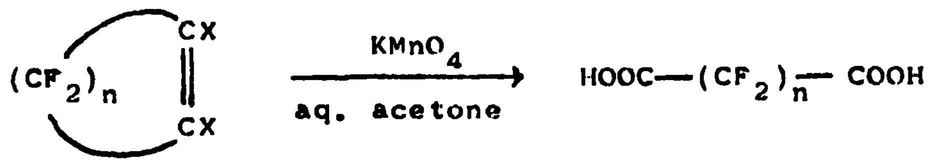
It is claimed that a surface film of poly-F-cyclobutene is readily formed on glass by exposure to ultraviolet radiation in the presence of monomer.[182]

Other F-cyclo-alkenes and -dienes have not been homo--polymerised. In contrast, co-polymerisation with a variety of substrates, e.g. styrene, vinyl chloride, acrylonitrile, 1,3-butadiene, etc., is often quite a facile reaction and co-polymers have been reported for F-cyclopropene (in which the propane ring remains intact below about 200°C),[2,3] F-cyclobutene,[180,184,185] F-cyclo-pentene and -hexene,[184] F-cyclopentadiene [187] and F-cyclohexadienes.[188]

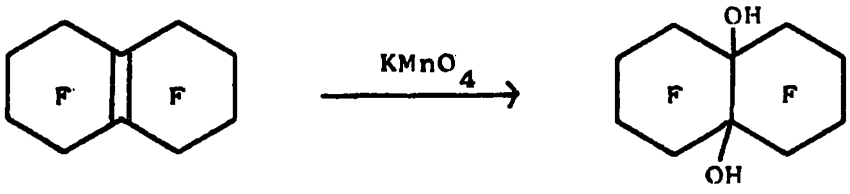
1.B.4c <u>Oxidations</u>

Oxidation of F-cycloalkenes occurs to give the corresponding acyclic dicarboxylic acid.[3,30,189,190] The mechanism probably involves initial formation of a cyclic manganese complex which is hydrolysed by water to give a diol. Loss of hydrogen fluoride then occurs and further oxidation follows.



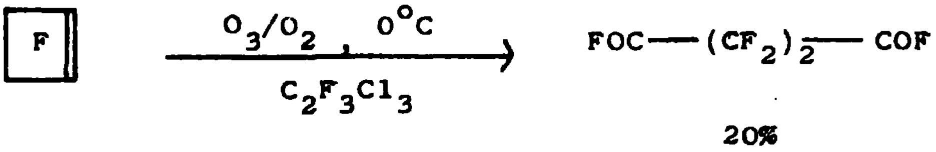


$n = 1\text{-}4 \qquad X = F, Cl$



($\underline{9}$)

[191]



[192]

In substituted cycloalkenes containing no vinylic halide, e.g. ($\underline{9}$), the reaction gives a diol.[191]

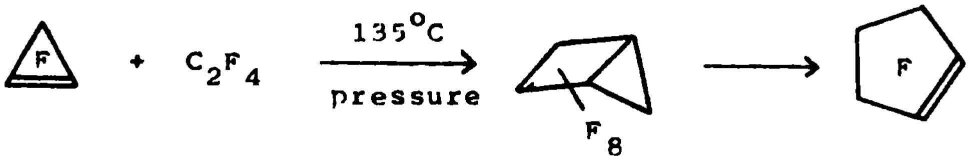
Oxidation with ozone gives the corresponding diacid-difluorides but reaction times are lengthy and the yields are low.[192]

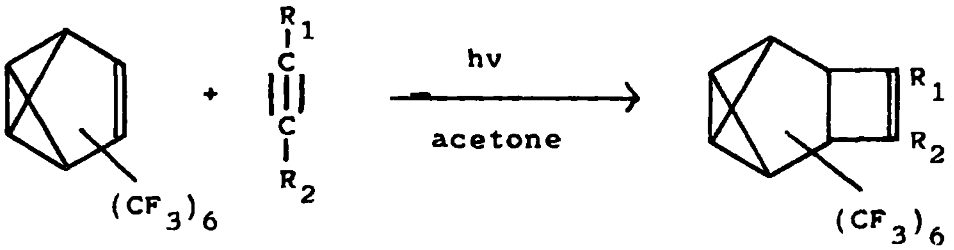
1.B.5 Cycloadditions

These can be divided into three areas: reactions involving (2+2) cycloadditions; reactions involving (4+2) cycloadditions i.e. Diels Alder reactions; and reactions involving dipolar species.

1.B.5a (2+2) Cycloadditions

Thermal (2+2) cycloadditions of F-cycloalkenes are rare; one noticeable example being the reaction of F-ethylene with F-cyclopropene.[2]





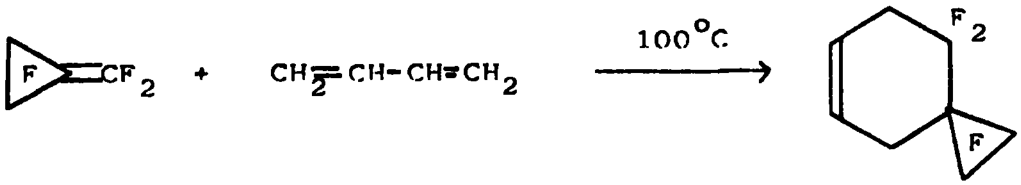
[193]

$R_1 = R_2 = CH_3$, C_2H_5 $R_1 = CH_3$, $R_2 = C_2H_5$

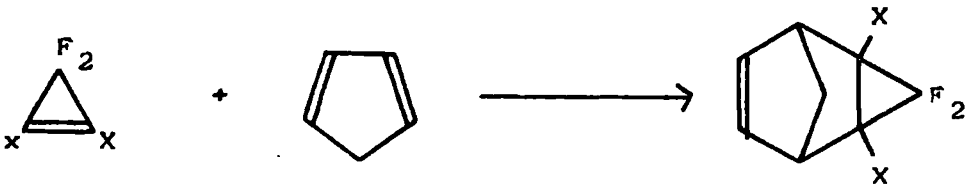
Photochemical (2+2) additions are more common. Thus F-hexamethyl benzvalene gives moderate yields of adducts with acetylenes.[193] Photochemical addition of 1,2-dichloro--F-cyclobutene and -pentene to indene is reported to give excellent yields of addition products [194] whilst the corresponding reaction with F-cyclobutene gives only poor yields.

1.B.5b (2+4) Cycloadditions

Only the most strained F-cyclo--alkenes react as dienophiles in the Diels Alder reaction. For example, F-cyclopropenes react with several dienes.[6,195]



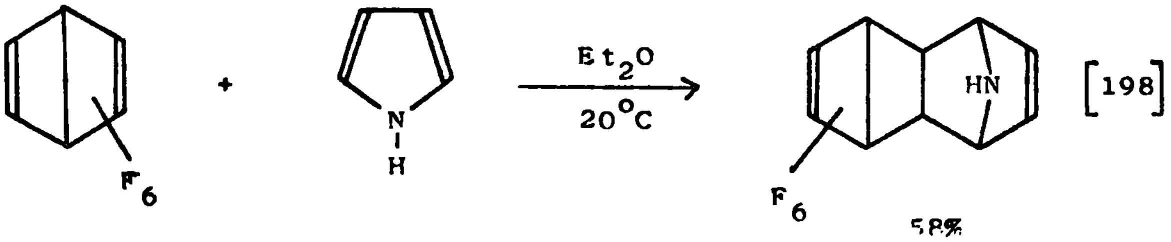
[196]

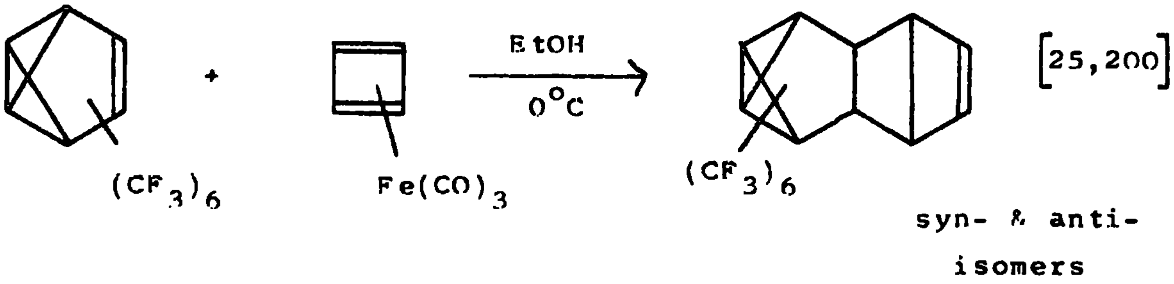


[195]

. X = F , CF_3

Other tetrahalocyclopropenes undergo similar reactions.[197] A particularly voracious dienophile is F-bicyclo(2.2.0.)-hexadiene which even gives an adduct with pyrrole,[198] although not with thiophen. F-Hexamethyl benzvalene also acts as a dienophile.[199,200]



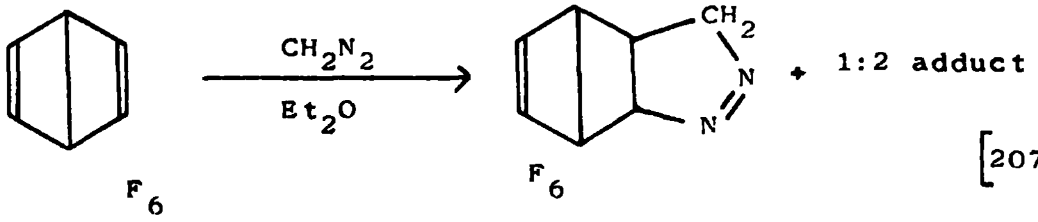


Not suprisingly, F-cyclopentadiene [201] and F-1,3-cyclohexadiene [202,203] act as dienes, and in some cases as dienophiles,[201,203] in Diels Alder reactions.

1.B.5c <u>1,3-Dipolar Additions</u>

It is claimed that "chlorinated and fluorinated alkenes are especially poor dipolarophiles' " and hence should not readily react with dipoles.[204] However, whilst this is true for compounds containing vinylic fluorine, it is not true for those with vinylic chlorine or perfluoro-alkyl substituents, where considerable activation is observed.[205] Some F-alkenes will react with 1,3-dipolar species under extremely forcing conditions, e.g. F-propene with phenyl azide, but in the main they are unreactive.

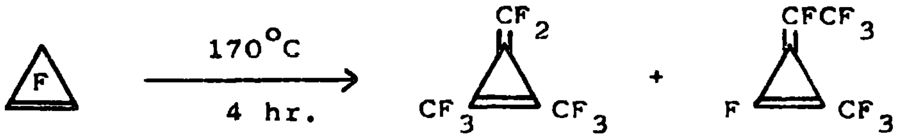
The exceptions are the valence isomers of F-benzenes which react readily with numerous dipolar species.[199,207] Presumably the driving force in these reactions is relief of ring strain, which suggests that F-cyclopropene should also react.



[207]

1.B.6 Thermal and Photochemical Reactions

Rearrangements of F-cyclohexene were mentioned earlier,[31-33] as was the rearrangement of F-1,3-cyclohexadiene.[51] F-Cyclopentene is very thermally stable[33] but F-cyclopropene oligomerises on heating:-[3]



[3]

+ 3 trimers + tetramer

The thermal behaviour of F-cyclobutene will be discussed later. Passage of F-cyclohexadienes through an old nickel tube at elevated temperatures gives an equilibrium mixture of the 1,3- and 1,4- dienes and, in some cases, the products of disproportionation.[208] In contrast, through a new tube defluorination occurred.[209] Similar defluorination reactions occur over iron.[210]

It is claimed that static, mercury-sensitized photolysis of F-cyclobutene gives mainly F-1,3-butadiene and that photolysis of the butadiene gives the cyclobutene - it seems obvious that something is amiss with these observations.[211]

Quantitative ring opening of F-cyclobutene can be achieved by infrared laser irradiation in the presence of helium.[212]

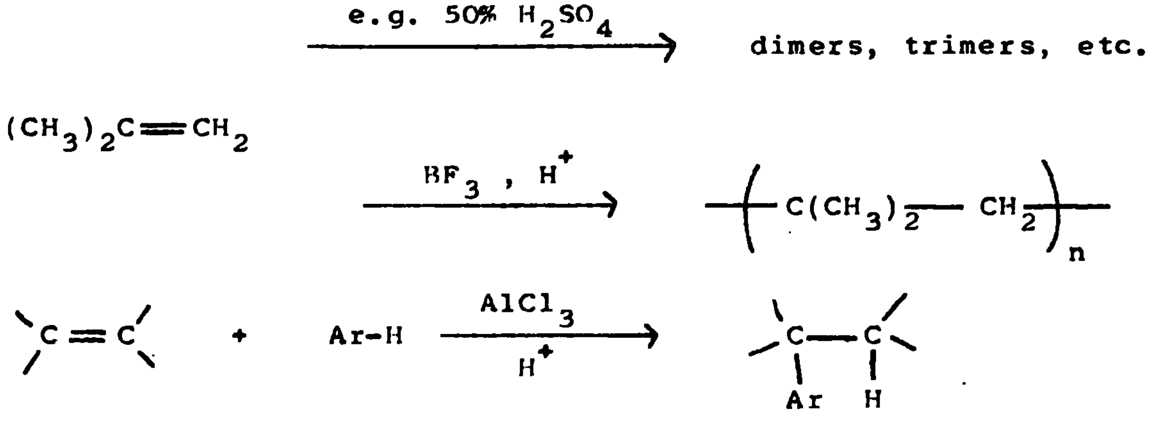
DISCUSSION

CHAPTER 2

OLIGOMERS FROM PERFLUOROCYCLOALKENES

Introduction

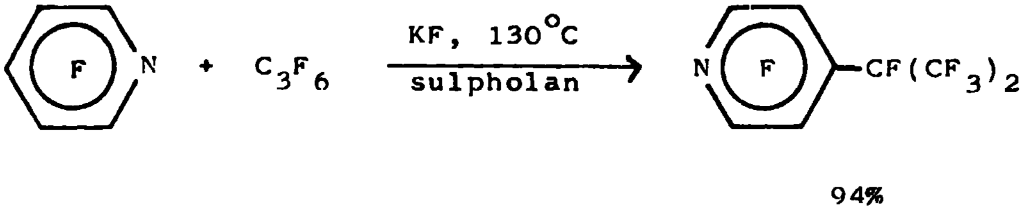
An important analogy can be drawn between the role of the proton in hydrocarbon chemistry and that of fluoride ion in fluorocarbon chemistry. For example, under acidic conditions, many alkenes undergo rearrangement, polymerisation, act as alkylating agents, etc..



In the presence of fluoride ion, F-alkenes: rearrange to give an isomer(s) containing the least possible number of vinylic fluorines;[58] undergo the anionic equivalent of the Friedel-Crafts reaction with activated polyfluoroaromatics; oligomerise to give, usually, dimers and trimers.

$$F_2C{=}CF{-}C_2F_5 \xrightarrow[\text{sulpholan}]{\text{KF, }60^\circ C} CF_3CF{=}CFCF_3$$

[58]



[213]

$$CF_3{-}CF{=}CF_2 \xrightarrow[\text{solvent}]{F^-} \text{dimers, trimers, tetramer}$$

[57]

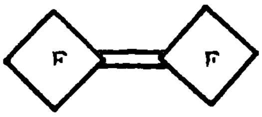
It is important to realise, however, that fluoride ion does not polymerise F-alkenes. This is because the growing F-alkyl chain can lose fluoride ion very readily, giving oligomers which are usually much less reactive towards F-alkyl anions than is the starting material.

The analogy between fluorocarbons and hydrocarbons can be taken one step further: thus, the advent of "super acids" has allowed the preparation of carbocations from alkenes and these can be observed by ^{1}H n.m.r.spectroscopy. As will be seen in chapter 3, this thesis reports the preparation of F-alkyl anions, from reaction of F-alkenes with fluoride ion, and these can be observed in solution by ^{19}F n.m.r. spectroscopy.

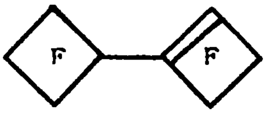
This chapter deals with the oligomerisation of F-cyclobutene and the reactions of F-cycloalkenes with other F-alkenes in the presence of fluoride ion or pyridine (for convenience called co-oligomerisation reactions).

2.A. Oligomers from F-Cyclobutene

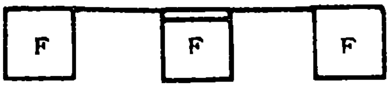
The fluoride ion initiated oligomerisation of F-cyclobutene has been studied previously[214] and was reported to give two dimers, (16) and (17), together with a mixture of three trimers, the major one of which was wrongly assigned structure (18).



(16)



(17)

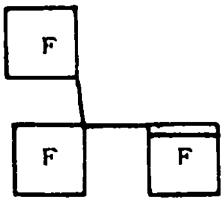


(18)

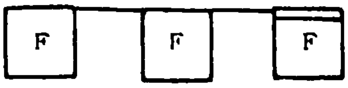
In dimethylformamide (DMF) as solvent, at room temperature with caesium fluoride as a source of fluoride ion, the yield of dimers was about 50%; with potassium fluoride only trimers were obtained.

In tetrahydrothiophen dioxide (sulpholan) as solvent, at 125°C, a single trimer was obtained[148] and shown to have structure (19),[148,215] i.e. the major trimeric product from fluoride ion induced oligomerisation of F-cyclobutene is (19) and not (18).

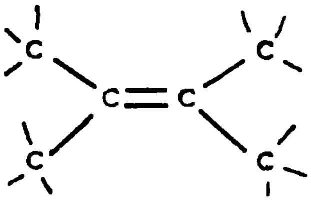
In a survey of the reactions of amines with F-cyclobutene, Pruett observed that oligomerisation occurred with pyridine, to give two dimers, (16) and (17), and a trimer assigned structure (20).[94] The product composition was found to be dependant on the ratio of pyridine to F-cyclobutene used.



(19)



(20)

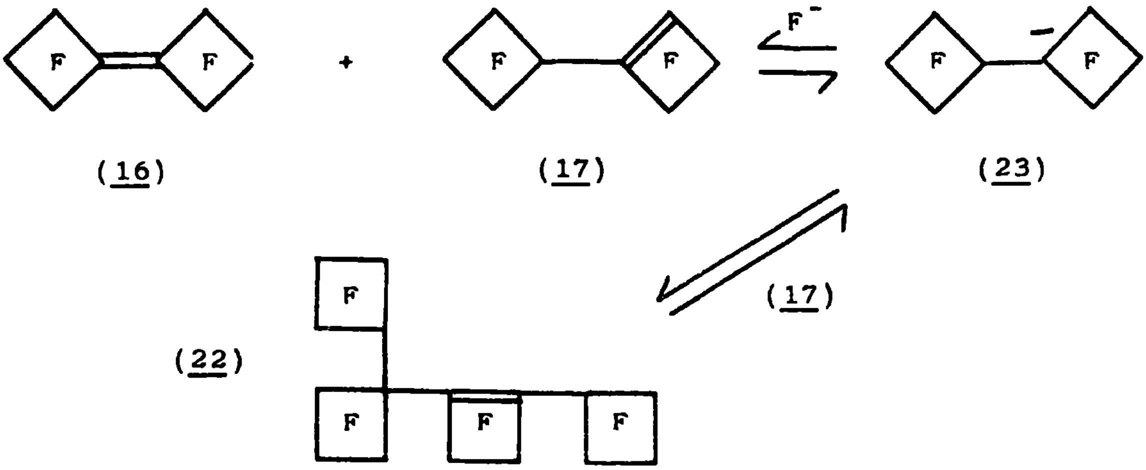


(21)

Workers at Durham have been investigating the reactions of F-alkenes of the type (21) i.e. where each of the substituents on the double bond is carbon. This general type of alkene is proving particularly interesting for a number of reasons, e.g. nucleophilic substitution must occur via an S_n2' mechanism (see reactions of compounds (9) and (10) in chapter 1). In this context dimer (16) is a very interesting molecule since not only is it of the type (21) but also it possesses considerable angle strain which could have a profound effect on its reactivity. In view of the potentially interesting chemistry of this dimer it was decided to re-investigate the oligomerisation of F-cyclobutene with a view to obtaining dimer (16) in high yield.

2.A.1 With Fluoride Ion

In the presence of caesium fluoride F-cyclobutene oligomerised rapidly at room temperature in either DMF or 2,5,8,11,14-pentaoxapentadecane (tetraglyme). The reaction could be carried out at atmospheric pressure using a variable gas reservoir or under autogenous pressure in, for example, a nickel tube. The major product from these reactions was always trimer (19) containing a small amount of another, as yet uncharacterised, trimer. The amount of dimers (16) and (17) was usually of the order of 20%. A new product, not reported before, was the tetramer (22) which could also be obtained by further reaction of (16) and (17) in the presence of a deficiency of fluoride ion. In the presence of excess fluoride ion, dimers (16) and (17) did not react further but gave the long-lived, observable carbanion (23) - see chapter 3. This anion was also obtained from the reaction of tetramer (22) with excess fluoride ion.



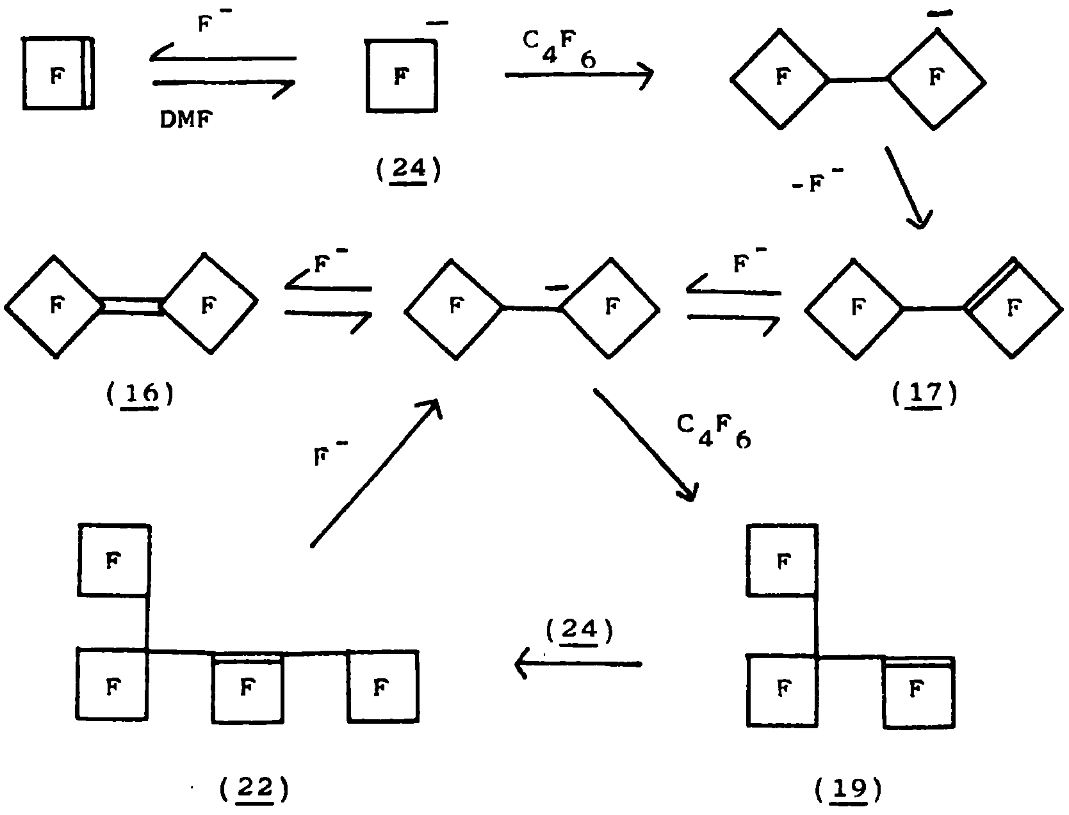
These results suggest that tetramer obtained in the oligomerisation of F-cyclobutene is formed by reaction of trimer (19) with anion (24). Production of the oligomers is rationalised by the mechanism outlined in scheme 4. Structural assignments will be discussed at the end of the chapter.

With sulpholan as solvent the oligomerisation was sluggish at 50°C and gave mainly trimer (19), whilst in acetonitrile, oligomerisation was either very slow or non-existant at room temperature. With potassium fluoride in DMF, with or without 18-crown-6-polyether, oligomerisation was slow at room temperature and gave mainly trimer (19). Several attempts were made to try to reverse the oligomerisation and obtain dimeric material from the trimer (19) (c.f. reaction of tetramer to give anion (23) and hence a mixture of the two dimers). However, in all cases, trimer (19) was recovered unchanged and no dimeric material could be detected.

Hence, under the conditions employed, fluoride ion induced oligomerisation of F-cyclobutene is of limited value in obtaining dimers (16) and (17).

Scheme 4

Fluoride Ion Induced Oligomerisation of F-Cyclobutene



2.A.2 With Pyridine

This reaction has provided a route to the dimers (16) and (17) in fairly good yield.

At room temperature, under autogenous pressure, pyridine and F-cyclobutene are immiscible. Initially the pyridine layer assumes a blood-red colouration but it rapidly turns black. Oligomerisation occurs to give two dimers, (16) and (17), and a trimer. It was assumed by earlier workers in these laboratories[148] that this trimer had structure (19) rather than (20) as proposed by Pruett. In fact the trimer obtained has structure (18) and this follows simply from its spectral data (see end of chapter). Also compound (18) is uncontaminated by any other trimeric material, i.e. no trimer (19) was detectable in the product mixture.

The product composition and particularly the rate of reaction is critically dependant on the initial ratio of F-cyclobutene to pyridine used (see table at bottom of scheme 5), and also on reaction conditions e.g. the effectiveness of the stirring at mixing the pyridine and F-cyclobutene. In fact the reactions are not exactly reproducible but, in general, increasing the amount of pyridine used has the following effects:-

1) the reaction proceeds more rapidly,
2) the recovery of fluorocarbon is decreased,
3) the amount of trimer in the product is increased.

Nevertheless, mixtures containing as much as 60% of dimers can be obtained by this route, the only limitation being the lengthy reaction times required in these cases; from five to fifteen, or more, days before complete reaction occurs.

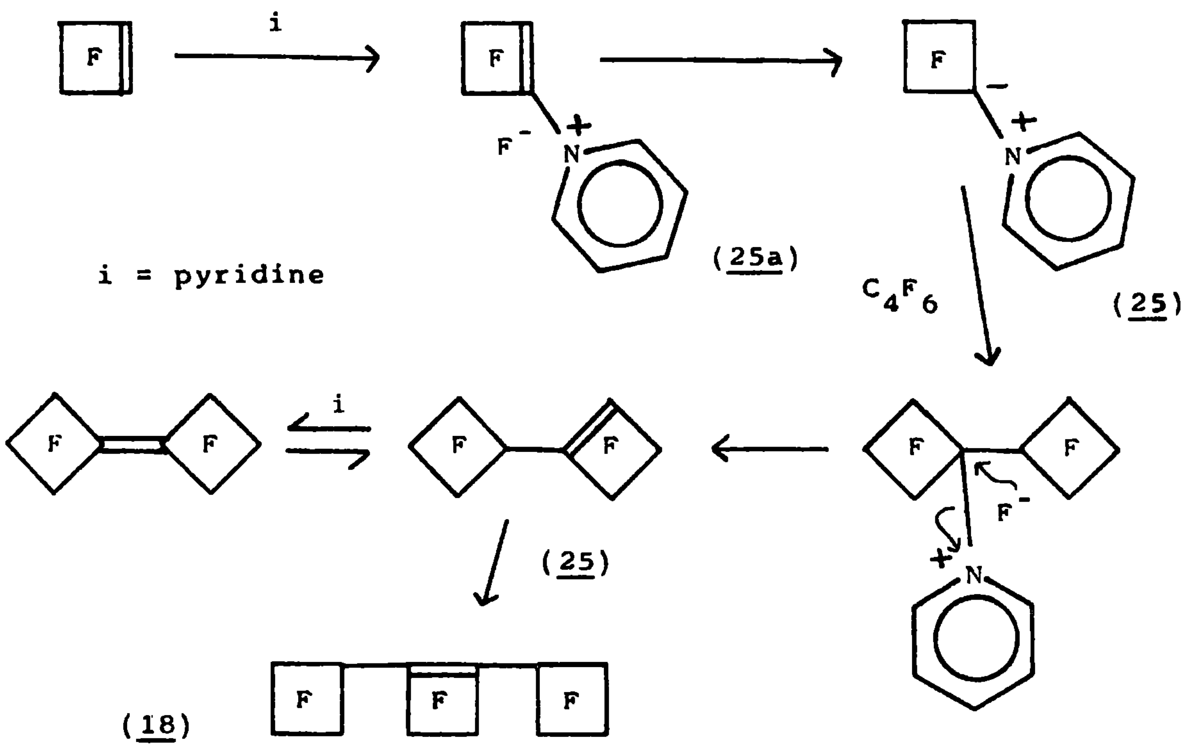
The suprising discovery that the trimer formed in this reaction is (18) rather than (19) means that different mechanisms must obtain in the fluoride ion and pyridine induced oligomerisations. It has long been suggested that F--cyclobutene and tertiary amines give ylides [91,92] and examples of these have recently been isolated by Burton.[93] It seems plausible therefore, to postulate the formation of an analagous ylide,(25), as a reactive intermediate in the reaction of pyridine with F-cyclobutene. The formation of trimer (22) is then understandable by the mechanism outlined in scheme 5.

Further evidence for this mechanism was obtained by carrying out the oligomerisation in the presence of dimers (16) and (17) when an amount of trimer (18) was obtained that was in excess of that which could have been obtained solely from F-cyclobutene. This demonstrates that ylide (25) can react with dimer (17) to produce trimer (18). The two seperate dimers, (16) and (17), are each rapidly isomerised by pyridine to give a typical equilibrium mixture, (16) : (17) = ca. 11 : 9, even though the fluorocarbon and pyridine are immiscible.

An interesting point which arises from the mechanism outlined in scheme 5 is the involvement of fluoride ion salts as intermediates e.g. (25a). This fluoride ion cannot be available to the dimers (16) and (17) since otherwise anion (23) would result and this would give trimer (19). It follows therefore, that processes in scheme 5 which involve loss of

Scheme 5

Pyridine Induced Oligomerisation of F-Cyclobutene



ratio used $C_4F_6:C_5H_5N$	% recovery	% product composition C_4F_6	dimers	trimer	reaction time hrs.
20 : 1	74	50	36	14	336
16 : 1	79	24	50	26	360
15 : 1	81	3	63	34	130
14 : 1	84	6	57	37	190
12 : 1	87	1	43	56	130
9 : 1	67	0	21	79	15

Effect of Varying Pyridine to F-Cyclobutene Ratio fluoride ion and subsequent reaction to give, for example, ylide (25) or dimer (17) must proceed via a tight ion pair. These ion pairs are unaffected by the use of a solvent e.g. DMF since the product identity is unchanged.

The non-repeatability of this preparation is presumably due to its heterogenous nature.

2.B Fluoride Ion Initiated Co-oligomerisation Reactions

2.B.1 F-Cyclobutene with F-Propene

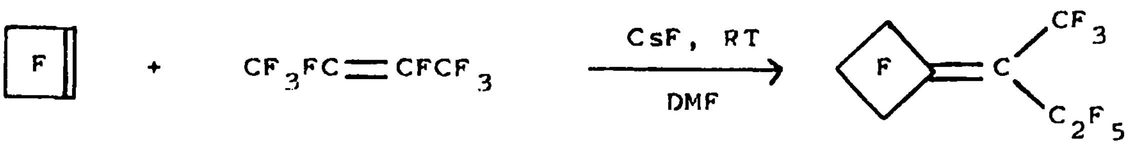
This reaction proceeded rapidly and exothermically to give a complex mixture of products from which compounds (26) - (29) were isolated and characterised. These compounds arise from several intermediate anions as indicated in scheme 6.

As will be seen shortly, compound (26) gives an observable carbanion with fluoride ion but none of the products isolated from this reaction was derived from this carbanion. This is presumably because F-cyclobutene and F-propene are better at competing for the available fluoride ion and the resultant anions (both with fluorine attached directly to the anionic site) are more reactive.

This reaction has been reported previously but the structures assigned to the three compounds (27) -(29) are all in error.[214]

2.B.2 F-Cyclobutene with F-2-Butene

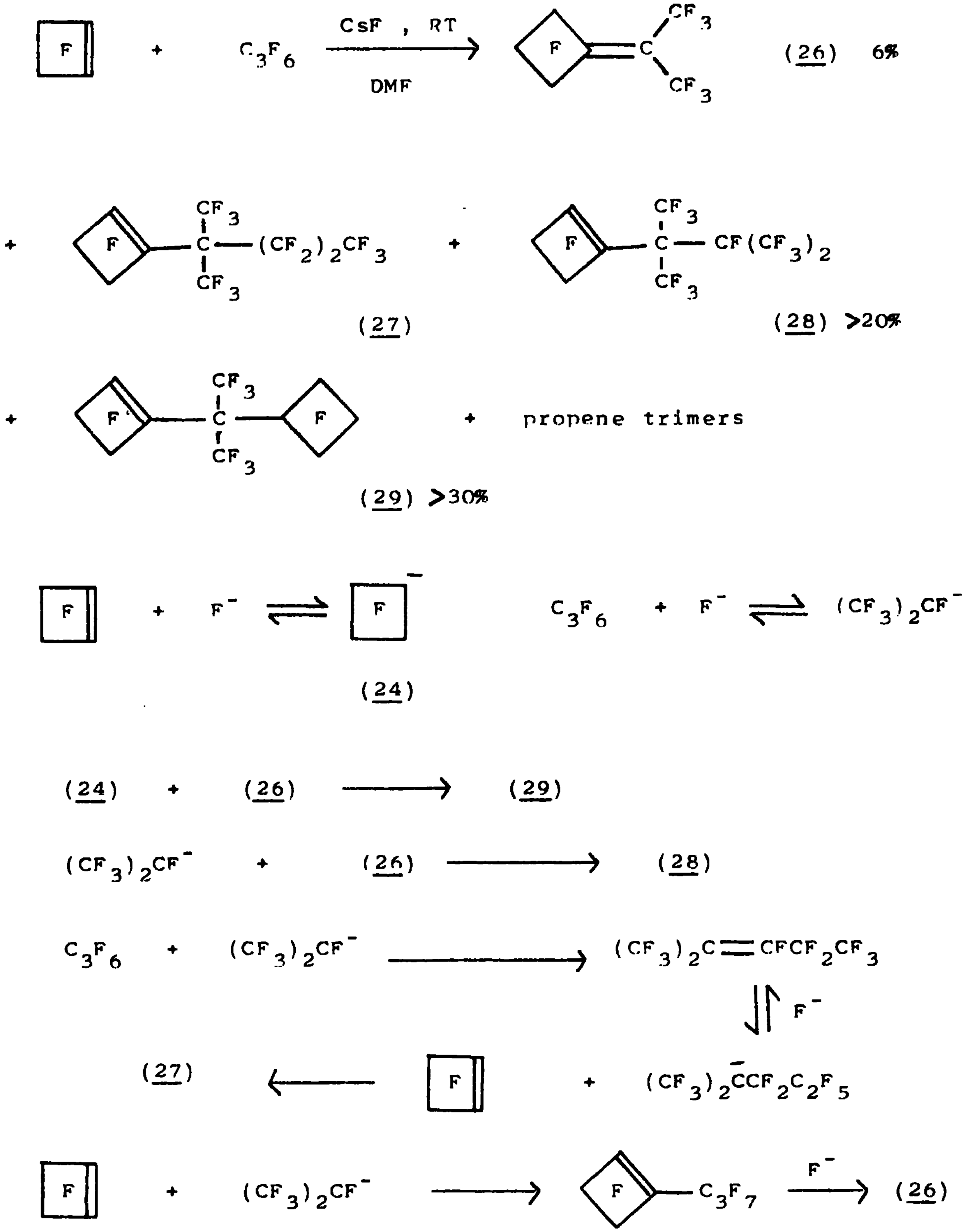
This reaction proceeded slowly to give a moderate yield of compound (30) along with oligomers of F-cyclobutene. Compound (30) is probably formed by attack of anion (24) on F-2-butene although, in principle, it could also be formed by attack of the anion $(C_2F_5)(CF_3)CF^-$ on F-cyclobutene. However, it is known that F-2-butene is much less reactive towards fluoride ion than F-cyclobutene.[216] This is most likely because of the strain energy of the latter compound.



(30) 30%

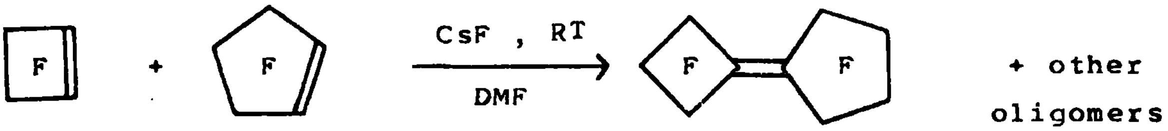
Scheme 6

Co-oligomerisation of F-Propene and F-Cyclobutene



2.B.3 F-Cyclobutene with F-Cyclopentene

This reaction proceeded slowly to give a complex mixture from which compound (31) was isolated. This compound formed about 95% of the C_9F_{14} fraction and the identity of the other component(s) was not established.

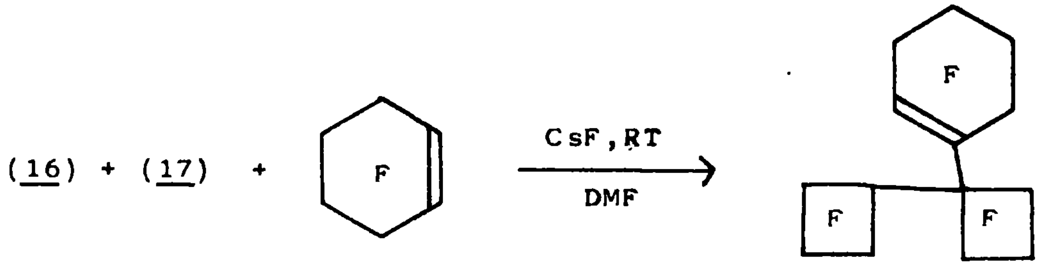


(31)

Compound (31) could of course arise by two processes, i.e. by attack of the F-cyclobutyl anion (24) on F-cyclopentene or of the F-cyclopentyl anion on F-cyclobutene. The former is the most probable route.

2.B.4 F-Cyclobutene with F-Cyclohexene

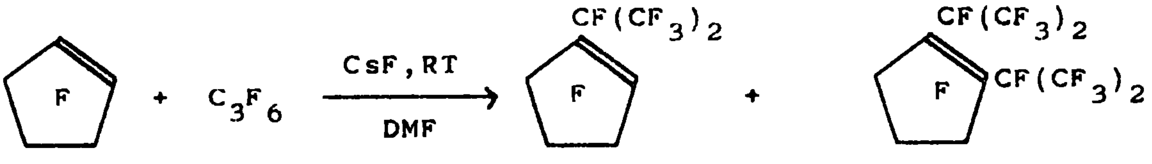
In contrast to the above, reaction of F-cyclobutene and F-cyclohexene gave mainly oligomers of F-cyclobutene, (16), (17), (19) and (22), together with a small fraction containing $C_{14}F_{22}$ isomers. The major isomer, (32), was prepared in a separate reaction between dimer mixture, (16) and (17), and F-cyclohexene. This shows that the $C_{14}F_{22}$ fraction is not derived entirely from dimer anion (23) but is due in part to trapping of an anion, or anions, derived from a 1:1 adduct of F-cyclo-butene and -hexene, even though this compound is not observed in the product mixture. Presumably the minor involvement of F-cyclohexene in the reaction is due to the far greater reactivity of F-cyclobutene towards nucleophiles.



(32) 29%

2.B.5 F-Cyclopentene with F-Propene

This reaction gave a simple product mixture containing F-1-isopropyl- and F-1,2-diisopropyl-cyclopentene, (33) and (34) respectively, together with oligomers of F-propene. Compounds (33) and (34) are formed by simple vinylic fluorine displacement by the F-isopropyl anion.



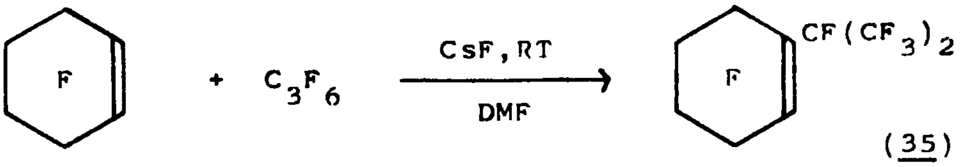
(33) 75%

(34) 10%

Under the conditions,employed compound (33) was the major product but the reaction conditions could presumably be changed, by using more F-propene, to favour compound (34). F-Dialkylcyclopentenes have been reported by other workers.[32]

2.B.6 F-Cyclohexene with F-Propene

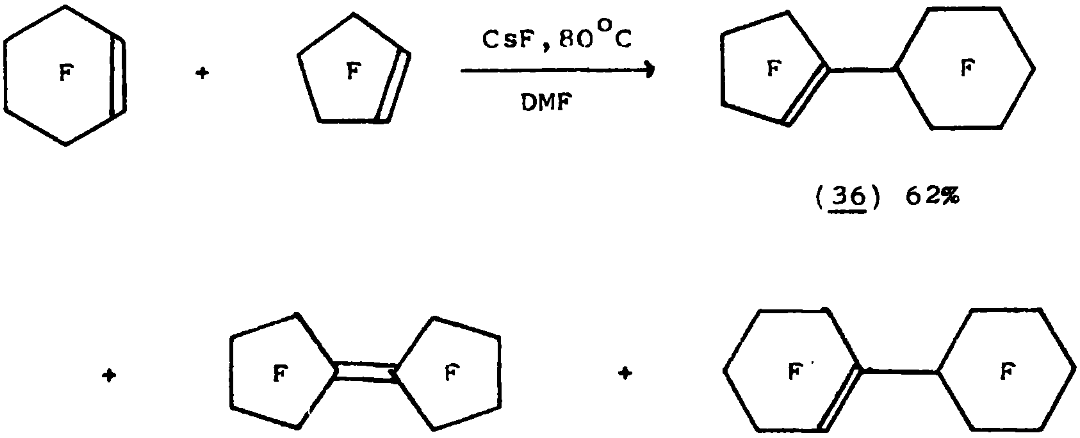
F-Cyclohexene is less reactive than F-cyclopentene towards nucleophiles and consequently with F-propene only monosubstitution occured, to give F-1-isopropyl-cyclohexene, (35), together with F-propene oligomers.



(35)

2.B.7 F-Cyclohexene with F-Cyclopentene

For co-oligomerisation to occur elevated temperatures were required, but at 80°C a good yield of F-1-cyclohexylcyclopentene, (36), was obtained together with dimers of F-cyclo-pentene and -hexene, (37) and (38) respectively. Compounds (37) and (38) have been obtained previously by fluoride ion induced reactions of the individual F-cycloalkenes.[148] Compound (36) can be formed both by attack of the F-cyclopentyl anion on F-cyclohexene and by attack of the F-cyclohexyl anion on F-cyclopentene.



(36) 62%

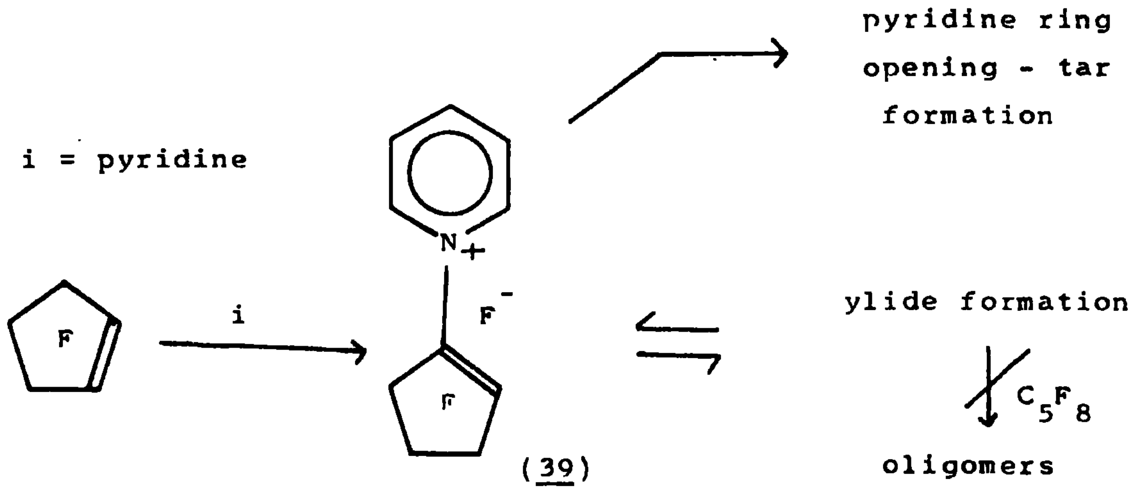
(37)

(38)

2.C Attempted Oligomerisations with Pyridine

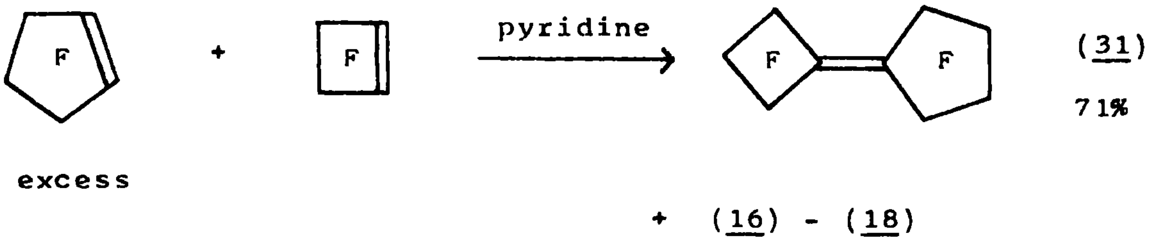
In view of the efficient F-cyclobutene oligomerisation induced by pyridine, the corresponding reactions with other F-alkenes were investigated in order to determine whether pyridine offered any advantages over fluoride ion as an initiator for oligom--erisation of these systems. Separate reactions were carried out between pyridine and F-cyclo-pentene, -hexene, F-2-butene, -propene, -ethylene and chlorotrifluoroethylene. In all but one case (C_2F_3Cl), however, some tar was produced and in all cases there was significant recovery of F-alkene, but no oligomers could be detected. Hence F-cyclobutene is unusual in its reaction with pyridine, but the reasons for this special behaviour are not clear.

Betaines, derived from hydrolysis of ylides, have been obtained from the reaction of pyridine with 1,2-dichloro-F--cyclo-pentene and -hexene in wet acetic acid.[95] It seems probable, therefore, that ylide formation occurs between pyridine and F-cycloalkenes and possibly acyclic F-alkenes as well. Dimers (16) and (17) are formed by reaction of the ylide (25) with F-cyclobutene and it is possible that with other F-alkenes, e.g. F-cyclopentene, the initial product (39) undergoes pyridine ring-opening with fluoride ion far more readily than further reaction occurs via the ylide.



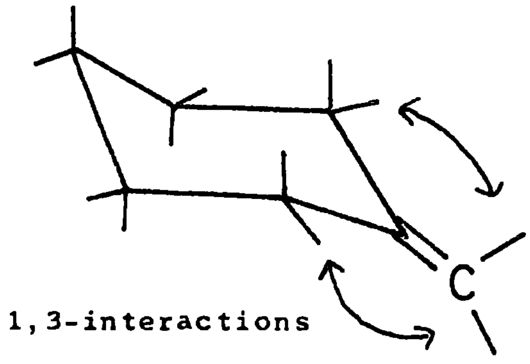
Thus, for example, an ylide analagous to (25) may be formed but if it is insufficiently nucleophilic to attack another molecule of F-cyclopentene then it could slowly be destroyed by reversion to (39) and subsequent pyridine ring opening.

Another puzzling feature is the failure, in all but one case, to trap ylide (25) with an F-alkene other than F-cyclo-butene. A mixture containing excess F-cyclopentene together with F-cyclobutene and pyridine gave a substantial amount of compound (31) together with the expected F-cyclobutene oligomers,(16) -(18). Of course, compound (31) could possibly be formed by reaction of F-cyclobutene with an F-cyclopentene ylide analagous to (25), even though this ylide does not react with F-cyclopentene itself. The lack of reactivity of other F-alkenes is difficult to explain; it cannot be rationalised in terms of their respective susceptibilities to nucleophilic attack since this would require that F-cyclo-butene and -pentene were more susceptible to carbon nucleophiles than F-propene - a result not borne out by, for example, their respective fluoride ion induced oligomerisation reactions.

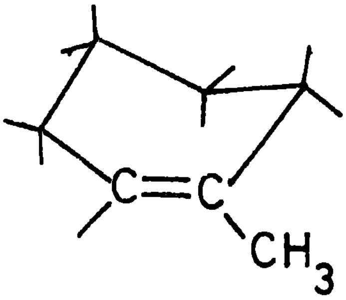


2.D Rationale of Structure in F-Cycloalkene Derivatives

The F-cycloalkene derivatives described above and elsewhere [148] exhibit an interesting variation in the position of the double bond between *exo-* and *endo-* positions under equilibrium control, i.e. in the presence of fluoride ion (see Table 5). This is best explained by reference to the factors affecting ring strain in methylenecycloalkanes and the corresponding 1-methylcycloalkenes. The chemical effects of conformational interactions in five- and six-membered rings have been discussed extensively [217,218] and for these systems angle strain is relatively unimportant. Two general points should be borne in mind: introduction of an unsaturated site into a five-membered ring will *decrease* eclipsing interactions; introduction of a single unsaturated carbon into a six-membered ring will move the interactions slightly towards an eclipsing conformation but also, more importantly, there will be considerable 1,3-interactions in, for example, methylenecyclohexane between the olefinic hydrogens and the equatorial ring hydrogens alpha to the double bond.



methylenecyclohexane



1-methylcyclohexene

This being the case then introduction of a second adjacent unsaturated carbon, e.g. as in 1-methylcyclohexene, should be more favourable than introduction of one since it eliminates these 1,3-interactions whilst still allowing the remainder of the ring considerable fluxional freedom.

For four-membered rings angle strain is an important feature, although Doering [219] has concluded that there is little difference in *total* strain energy between methylene-

-cyclobutane and 1-methylcyclobutene, i.e. that it is no more disadvantageous to have two unsaturated sites in a four-membered ring than one. Nevertheless, the reasons given for this conclusion were neither convincing nor clear.

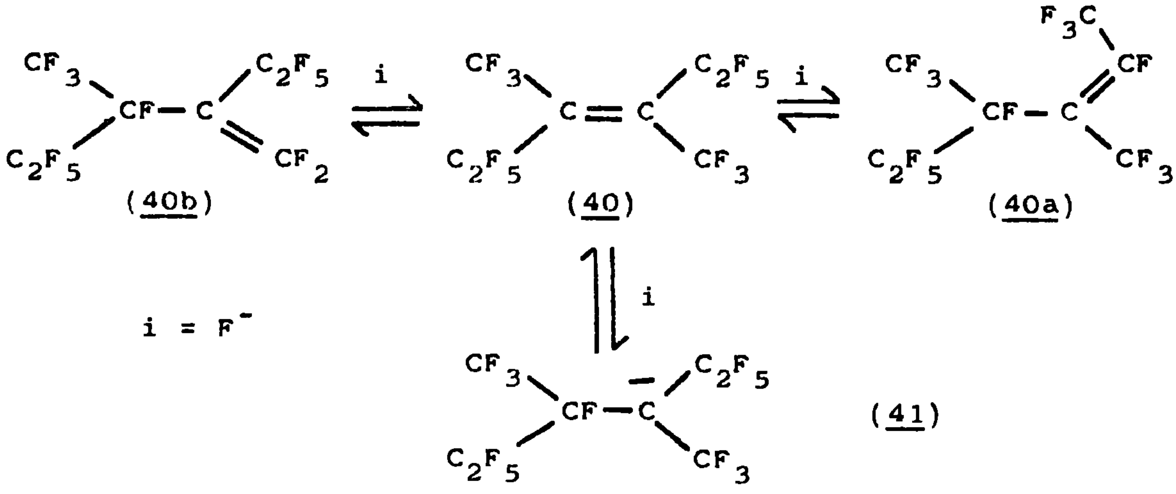
The above principles can be applied to the corresponding perfluorinated systems, provided the following points are kept in mind :-

1). angle strain will be much the same for both fluoro-carbon and hydrocarbon systems since it is a skeletal effect;

2). non-bonded interactions should be far more important for fluorinated systems because of the much larger size of fluorine, compared to hydrogen, and the presence of non-bonded electron pairs on fluorine;

3). the destabilising effect of vinylic fluorine will be significant.

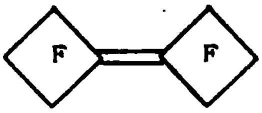
The importance of the last point is nicely illustrated, for acyclic systems, by reference to compound (40).



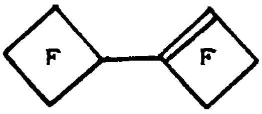
It is known 220 that in the presence of fluoride ion compound (40) is in equilibrium with its isomers (40a) and (40b). However, there is no evidence to suggest any significant concentration of anion (41) in solution (see chapter 3) nor is the ^{19}F n.m.r. spectrum of compound (40) changed by inter-action with fluoride ion. This illustrates the fact that, at least in acyclic systems, in the presence of fluoride ion, F - alkenes prefer to adopt structures having the least possible number of vinylic fluorine atoms.

Table 5

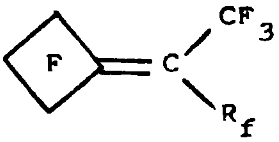
F-Cycloalkene Derivatives



(16)

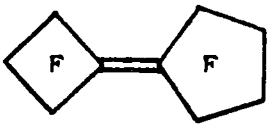


(17)

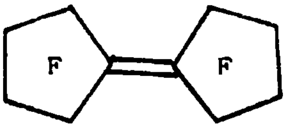


(26) $R_f = CF_3$

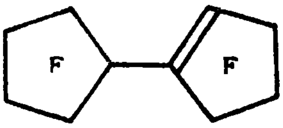
(30) $R_f = C_2F_5$



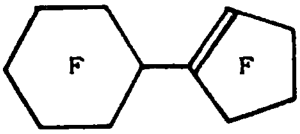
(31)



(37)



(37a)



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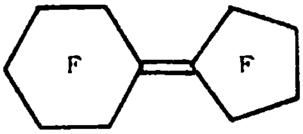
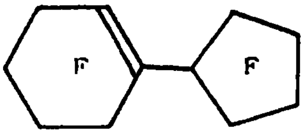
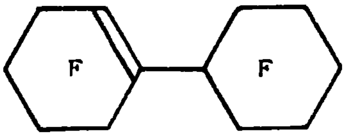


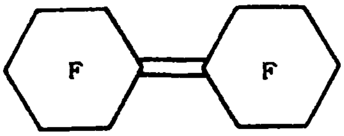
(36a)



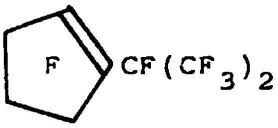
(36b)



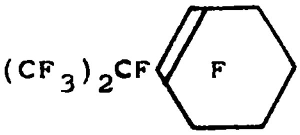
(38)



(38a)



(33)



(35)

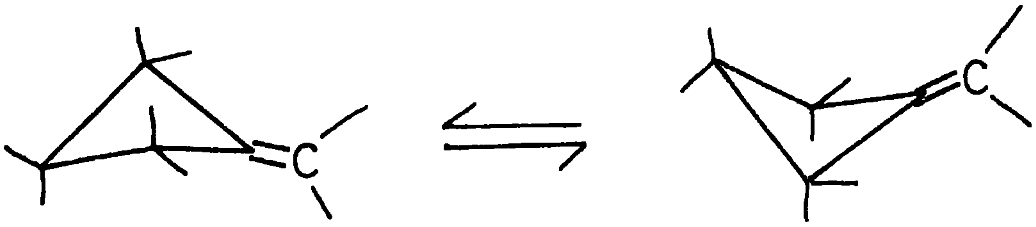
With reference to Table 5, compounds (31) and (37), containing no vinylic fluorine atoms, may be seen as those structures which also minimise conformational interactions. Thus, for example, compound (37) has eclipsing interactions removed from one position in each ring, i.e. the unsaturated carbon. The alternative structure (37a) has one ring with its maximum number of eclipsing interactions and although the second ring has eclipsing interactions reduced at two positions it is at the expense of a destabilising vinylic fluorine.

The systems (36) and (38) clearly demonstrate that it is more favourable to avoid unsaturated sites in a six-membered ring (i.e. 36) but that, where this is unavoidable then it is preferable to have both sites in the same ring (i.e. 38). Thus, for compound (38) the adopted structure contains a relatively unstrained cyclohexyl-ring together with a cyclo--hexenyl-ring which will have some eclipsing interactions and also contains a destabilising vinylic fluorine. However, the alternative (38a), containing no vinylic fluorine, will have considerable 1,3-interactions at the positions alpha to the double bond. Clearly, as (38) is the adopted structure, these interactions must lead to a higher energy system than the presence of a vinylic fluorine. Similarly, compound (36) contains a cyclohexyl-ring together with a cyclopentyl-ring in which there is a vinylic fluorine. The alternative (36b) contains a cyclopentyl-ring with its maximum number of eclipsing interactions and a cyclohexenyl-ring with a vinylic fluorine. This structure is clearly less favourable than (36), as is (36a) in which there would be considerable 1,3-interact--ions associated with the positions alpha to the double bond.

Similarly compound (33) may be seen as that structure which minimises eclipsing interactions in the five-membered ring, whilst structure (35) is preferred to its exo-isomer because of 1,3-interactions in the latter.

Formally, conformational effects should be very similar in compounds (16) and (37) but the fact that (16) and (17) occur in roughly the same proportions, i.e. that they are of comparable energy, can only be attributed to angle strain being a significant factor in raising the energy of (16) relative to (17). It follows from Doering's conclusions,[219] that having the carbon atoms of the double bond incorporated into seperate four-membered rings (i.e. 16) involves higher angle strain than the alternative (i.e. 17) - this is borne out by the much greater reactivity of (16) over analagous systems, e.g. (37) (see later).

Finally, compounds (26) and (30) have the exo- structure, presumably because of the fact that these isomers are able to flex more freely to relieve eclipsing interactions, whilst the corresponding endo- isomers would, of course, be fairly rigidly planar and eclipsing interactions would be at a maximum.



flipping in methylenecyclobutanes

In conclusion, it can be seen from the various structures described above that when exo- and endo- isomers are possible, interactions between non-bonded atoms are the features dominating the position of equilibrium rather than the presence, or otherwise, of a vinylic fluorine atom.

Hydrocarbon systems corresponding to the above have been synthesised[221-224] but, unfortunately, no reports have appeared on equilibrium studies of these compounds, and so a comparison between fluorocarbon and hydrocarbon systems is not possible as yet.

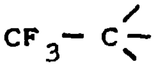
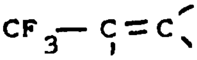
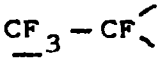
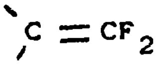
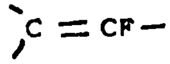
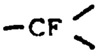
2.E Structural Assignments

All of the compounds described in this chapter gave satisfactory elemental analyses. Structures usually followed simply from ^{19}F n.m.r. spectra although, unfortunately, there is often a lack of model compounds with which to compare data. The position and intensity of the C=C stretch in the infrared or Raman spectrum was also a useful structural guide, although not as diagnostic as the ^{19}F n.m.r. data.

Structural assignments were made with reference to the data listed in Table 6 for ^{19}F n.m.r. spectra. These shifts are generally (but not exclusively) applicable to all compounds containing only carbon and fluorine.[225]

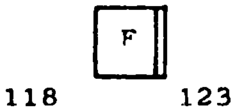
Table 6

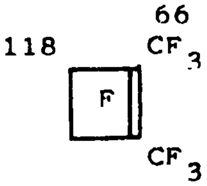
^{19}F n.m.r. Spectral Characteristics of Perfluorocarbons [225]

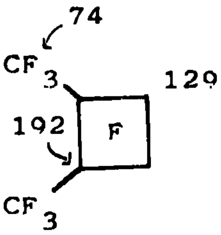
Structural Type	Approximate Shift Region P.P.M. (w.r.t. $CFCl_3$)
	60 - 70
	60 - 70
	70 - 80
$\underline{CF}_3-CF_2-$	80 - 90
	60 - 80
	90 - 120
$-CF_2-$	100 - 140
	>160

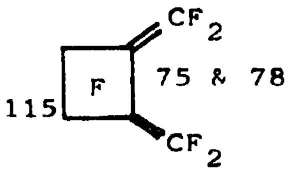
all unmarked substituents are carbon

Shifts for Some Model Compounds









$CF_3-CF_2-CF_2-CF_3$

83 129

$(CF_3)_3CF$

76 190

$(CF_3)_2C=CF_2$

61 66

shifts are in p.p.m. w.r.t. $CFCl_3$

It is known[226] that the intensity and frequency of the $C=C$ stretch in the infrared spectrum *decreases* with a decreasing number of vinylic fluorines. Also, double bonds attached only to carbon substituents are often very weak or absent in the infrared spectrum but they are Raman active.

Thus, for the compounds described in this chapter, (16), (18), (26) and (31) were easily identified in view of their symmetrical nature. Compounds containing vinylic fluorine, i.e. (17), (27), (28), (29), (32), (33) and (35) also have a tertiary fluorine. Compound (22) was identified by the observation of two non-equivalent tertiary fluorines and the method of preparation. (A tertiary fluorine is one attached to a saturated carbon on which all the other substituents are themselves carbon).

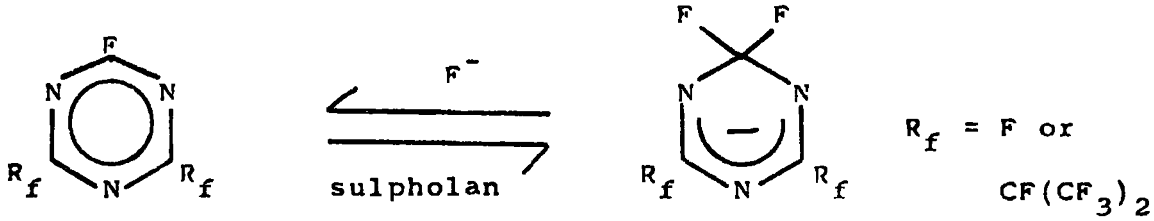
CHAPTER 3

OBSERVABLE F-CYCLOALKYL ANIONS

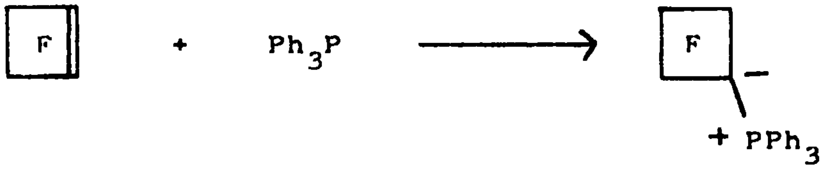
Introduction

One of the attractive objectives in the area of fluorocarbon chemistry is to generate long-lived, observable carbanions with fluoride ion.

This has been achieved in only a few cases. Thus, the addition of fluoride ion to triazines (42) resulted in formation of sigma complexes (43).[227]



(42) (43)



(44)

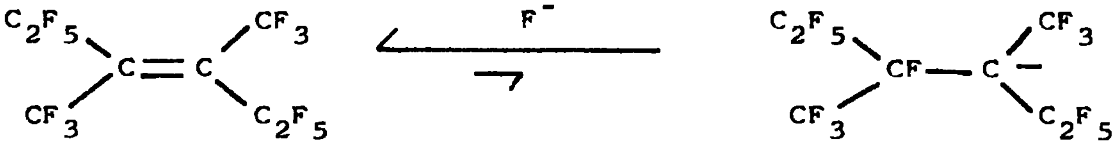
The formation of stable ylides from reaction of F-cyclo-butene with tertiary amines[93] or triphenyl phosphine[125,126] has already been mentioned and in the latter case the product has been shown to have structure (44) by X-ray crystal structure determination.[126] The data obtained showed that the carbon - phosphorus bond length (17.13 nm.) was one of the shortest reported for a stabilised ylide structure and this was taken to indicate considerable double bond character, arising from overlap of the phosphorus d-orbitals with the ylide carbon p-orbitals.

The generation of carbanions by addition of fluoride ion to a variety of F-alkenes and to F-2-butyne has been demonstrated in a now considerable literature on reactions of these species.[228,229] In one case there is evidence to suggest a long-lived anion.[230] However, as yet, no reports have appeared on the direct observation of F-alkyl anions even though considerable efforts have been made in this direction, e.g. with F-isobutene, where although fluoride ion and fluorocarbon are taken up into solution, only F-isobutene can be observed by ^{19}F n.m.r. spectroscopy due to rapid fluoride ion exchange.[231] Similar results were obtained for potassium fluoride and F-acetone in an attempt to observe the F-isopro-poxide ion.[231]

In complete contrast, many of the F-cycloalkyl derivatives described in chapter 2 give long-lived, observable anions, with fluoride ion, which are unchanged over a range of temperature or on prolonged standing - as indicated by their ^{19}F n.m.r. spectra. In each case formation of the anion can be rationalised in terms of relief of ring strain or removal of a destabilising vinylic fluorine.

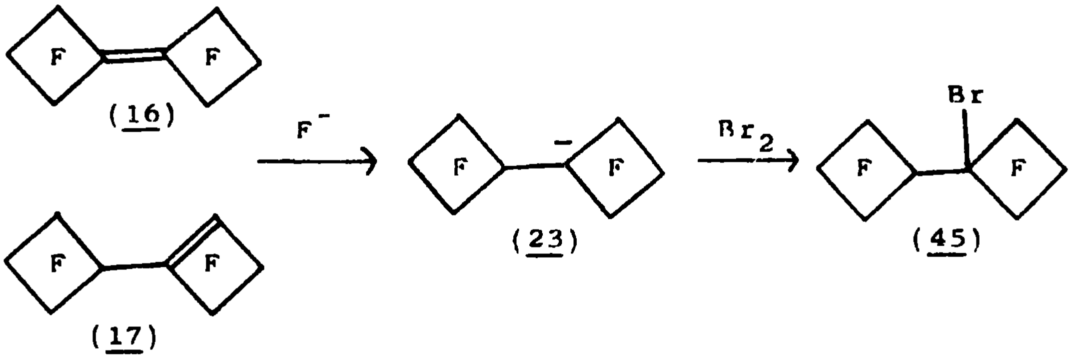
3.A Anion from F-Cyclobutene Dimers (16) and (17)

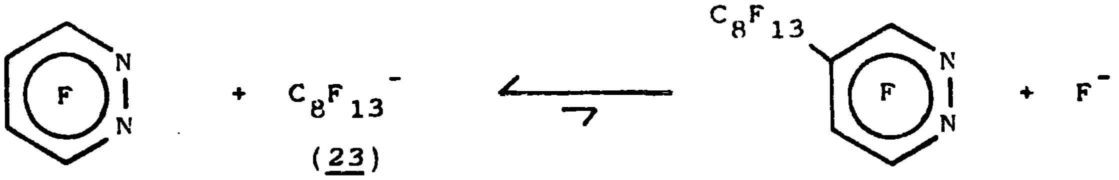
Formally, dimer (16) is related to alkene (40). However, as already mentioned, there is no evidence to suggest that, in the presence of fluoride ion, compound (40) gives any significant concentration of anion (41).[220]



(40) (41)

However, dimer (16) (and 17) readily dissolves caesium fluoride, in the presence of DMF, to give anion (23) whose formation can be explained in terms of relief of angle strain in the dimers. Anion (23) can be trapped with bromine to give the corresponding bromo-derivative (45) with no detectable reversion to starting material, (16) or (17). Unfortunately, however, attempts to trap (23) with iodine and activated F-diazines, i.e. F-pyrimidine and F-pyridazine, were unsuccesful. The inability to react with iodine can be explained in terms of steric crowding since some of the larger anions (see later) are unable to react even with bromine.



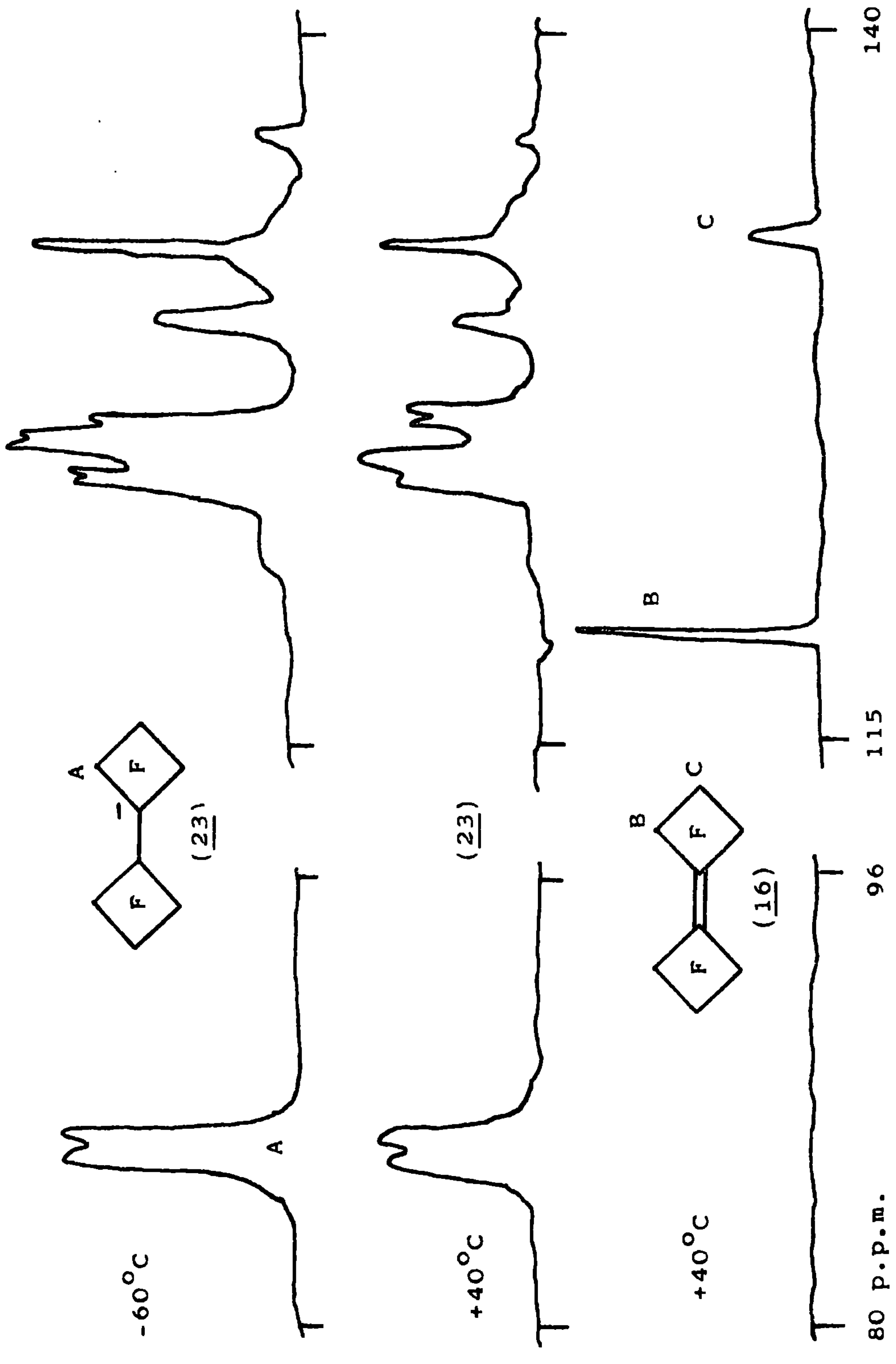


The lack of reactivity towards the F-diazines is puzzling but the system may be an equilibrium largely on the side of the anion.

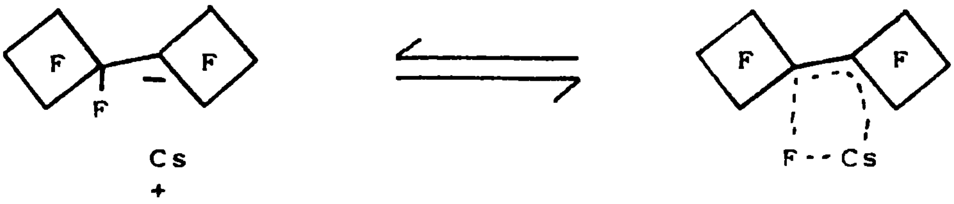
Significantly, anion (23) is directly observable by ^{19}F n.m.r. spectroscopy. Signals were observed for two non-equivalent ring systems (see fig. 1) and there was no evidence for the presence of the dimers (16), (17). The induced asymmetry of the system rules out the possibility of rapid intermolecular exchange of fluoride ion and this is supported by the observation that essentially only one molecular proportion of caesium fluoride dissolves for each molecular proportion of (16), (17). This fact was determined by filtration of a solution of (23), followed by removal of volatile material by heating under vacuum, leaving only caesium fluoride. Furthermore, the ^{19}F n.m.r. spectrum of (23) remains relatively unchanged over a very significant range of temperature i.e. -80 to +100°C and it can therefore be concluded that, within the limits of detection, the system is wholly in the form of the anion (23).

There are, however, two puzzling features of the spectrum of (23) and other anions described later that cannot be explained (by the author). Firstly, a resonance corresponding to the tertiary fluorine is not observed. Intermolecular fluoride ion exchange has been ruled out but there is the

Figure 1



^{19}F n.m.r. spectra of anion (23) and dimer (16) possibility that a degree of dissociation of anion (23) occurs but with rapid internal return to the same carbon atom.



This would maintain the asymmetry of the system but could lead to extensive broadening of the resonance associated with the tertiary fluorine. The second puzzling feature, of the spectrum of (23), is the fact that the resonance due to the difluoro--methylene groups adjacent to the charge centre occurs significantly downfield of the corresponding resonance in a saturated four-membered ring, e.g. as in compound (17) or F-cyclobutylcyclobutane, (46). In the ^{13}C n.m.r. spectrum of (23) the signal for two of the carbons adjacent to the charge centre, i.e. those bearing two fluorine atoms ('D' in Table 7), is also moved downfield of the corresponding resonance in compound (46). However, the third adjacent carbon, that bearing the tertiary fluorine ('B' in Table 7), appears to be little affected by the charge. Not suprisingly, the carbon atom formally bearing the negative charge is moved upfield and this is consistent with other carbanions that have been studied.[232]

Other anions descibed shortly all show a downfield shift for difluoromethylene groups adjacent to the charge centre as do ylides derived from F-cyclobutene.[93,126]

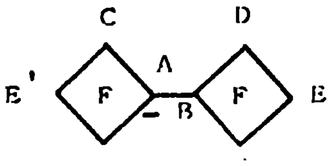
The possibility that the tertiary fluorine resonance was moved downfield and hidden under $-CF_2-$ resonances was ruled out by the following observations:-

1). anions described later contain only one or two $-CF_2-$ groups (other than those alpha to the charge centre) and no other signals could be observed in the $-CF_2-$ region of the ^{19}F n.m.r. spectrum of these anions.

2). Integration indicated that the ratio of low-field

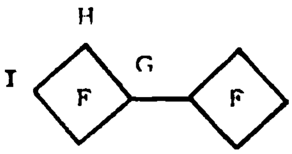
Table 7

C-13 n.m.r. data for compounds (23) and (46)



(23)

(46)

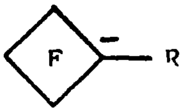


T.M.S. as external reference, 20°C, broad band decoupled
(downfield shifts are positive)

carbon atom	shift (p.p.m.)	carbon atom	shift
A	52·2	G	92·0
B	96·3		
C	112·9	H	111·6
D	128·9		
E, E'	113·8, 116·7	I	112·1

Table 8

F-19 n.m.r. data for anion (23) and related species



R		shift (p.p.m.)	
$\overset{+}{N}Et_3$		85·5	[93]
$\overset{+}{N}{}^nBu_3$		84·1	[93]
$\overset{+}{P}Ph_3$		86·9	[93, 126]
F-cyclobutyl	(23)	86·6	
F-isopropyl	(47)	88·6	
F-2-butyl	(48)	88·6	

shifts are relative to $CFCl_3$

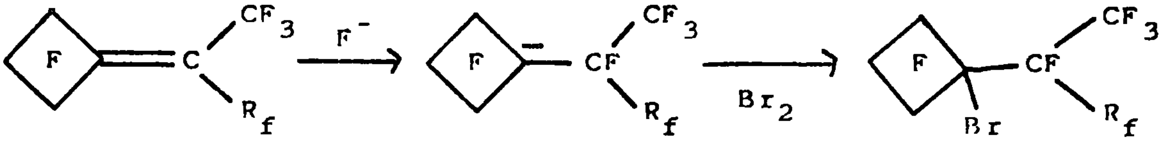
signals to signals in the $-CF_2-$ region was 1:2, i.e. 4:8 rather than 4:9 as it would have been had the tertiary fluorine resonance occurred in the $-CF_2-$ region.

3). In view of the ^{13}C n.m.r. data it seems unlikely that the resonance due to the tertiary fluorine would be shifted so far downfield, since the downfield shift of the difluoromethylenes adjacent to the charge centre is reflected in both the ^{19}F and ^{13}C n.m.r. spectra, and, as already stated, the resonance due to the carbon bearing the tertiary fluorine is relatively unaffected by the charge.

The ^{19}F n.m.r. spectrum of (23) was unaffected by a change from the use of caesium fluoride to potassium fluoride, with or without 18-crown-6-polyether. However, the potassium salt of anion (23) was less thermally stable; broadening occurred rapidly as the temperature was raised above about 40°C and was accompanied by precipitation of potassium fluoride and dimer mixture, (16) and (17). This is, of course, consistent with the well known fact that caesium fluoride is a better fluoride ion donor than potassium fluoride. A closely similar spectrum of (23) was obtained when the anion was generated in tetraglyme as solvent.

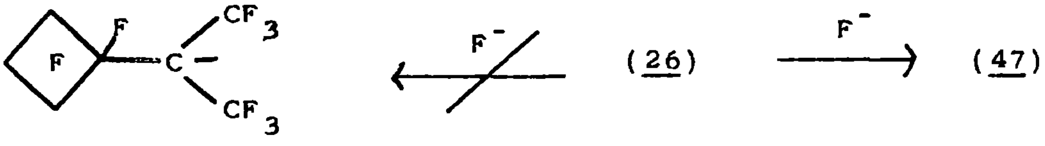
3.B Anions from Compounds (26) and (30)

Compounds (26) and (30) gave, respectively, anions (47) and (48) with fluoride ion. Quenching of these anions with bromine gave the corres-ponding bromo-derivatives, (49) and (50).



$R_f = CF_3$	(26)	(47)	(49)
$R_f = C_2F_5$	(30)	(48)	(50)

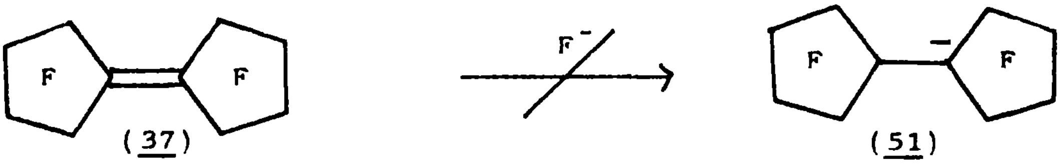
The anions were assigned structures (47) and (48), rather than the alternative structures (47a) and (48a), by identification of their bromo-adducts and by the similarity of the shifts, in their ^{19}F n.m.r. spectra, of difluoromethylene groups adjacent to the charge centre with the corresponding signal for anion (23). The fact that the charge sits exclusively on the four-membered ring is consistent with the electronegativity of a carbon atom in such a ring. Once again the formation of anions (47) and (48) is explained by release of angle strain in the starting alkenes, (26) and (30).



(47a)

3.C Attempted Anion Formation from Compound (37)

The much less strained compound (37) does not dissolve in the CsF/DMF system and thus behaves like alkene (40). Clearly the ring strain in (37) is an insufficient driving force to overcome the extra eclipsing interactions that would be introduced by forming anion (51).



(37) (51)

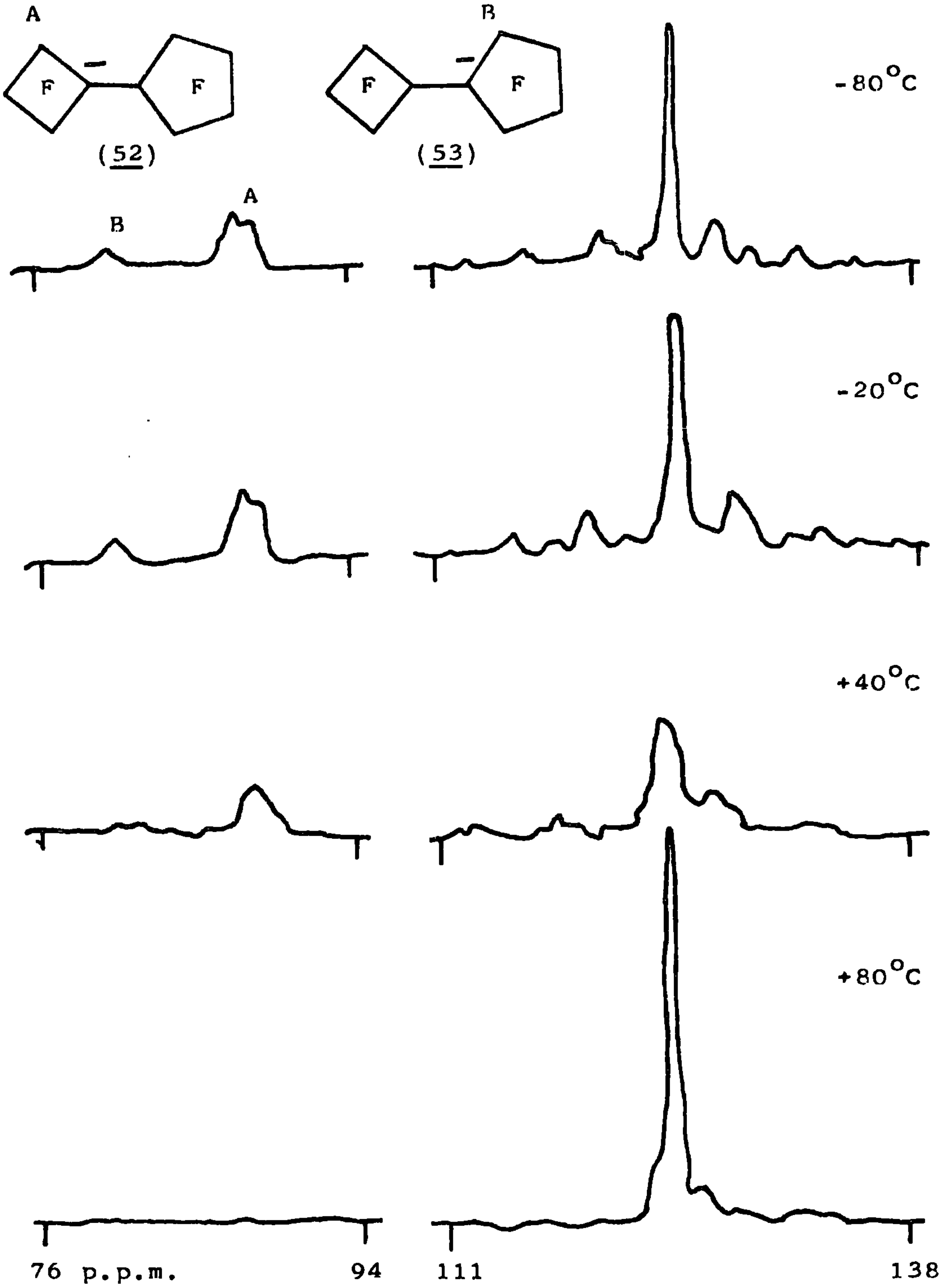
3.D Anions from Compound (31)

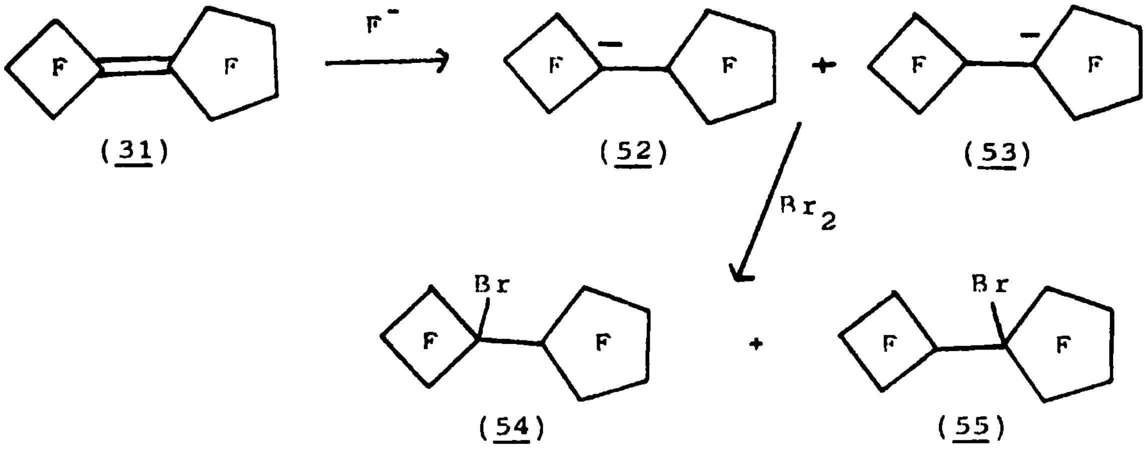
In contrast to the behaviour of compound (37), compound (31) readily dissolved CsF in the presence of DMF to give a mixture of two anions, (52) and (53), which were trapped with bromine to give two bromo-derivatives, (54) and (55), together with some unchanged (31) and minor amounts of chlorine containing products, the formation of which will be explained later.

Anion (52) was identified, from the ^{19}F n.m.r. spectrum,

Figure 2

Effect of Temperature on the ^{19}F n.m.r. of Anions (52) and (53)



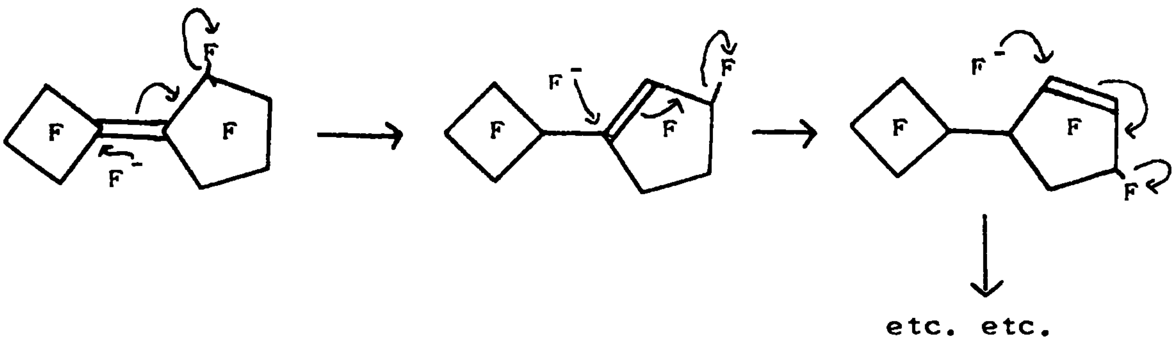


as the major ion present since the signal for the difluoro--methylenes adjacent to the charge centre occurred in the same region as those for anions (23), (47) and (48), whilst that for anion (53) occurred about 8 p.p.m. to lower field of that for (52). The ratio of (52):(53) was about 6:1 by integration. Compound (54)was identified as the major bromo-derivative by identification of the difluoromethylene signals, in the ^{19}F n.m.r. spectrum, adjacent to the bromine substituted carbon (see under structural assignments). The ratio of (54):(55) was about 3:1 by integration.

The formation of anions from compound (31) is interesting since two opposing effects will operate. Both anions will have the angle strain associated with an exocyclic double bond in a four-membered ring removed but eclipsing interactions will be raised. The additional eclipsing interactions associated with adding fluoride ion to the four- or five-membered ring of compound (31) would be reasonably similar and this accounts for the formation of *two* anions.

This idea of unavoidable extra eclipsing interactions in anions (52) and (53), accounts for the fact that they are much less thermally stable than, for example, anion (23). Thus as the temperature is raised, the signals for (52) and (53) in the ^{19}F n.m.r. spectrum rapidly broaden until, at 80°C, a single, sharp resonance is observed (see fig. 2). This rapid averaging of the fluorine atoms indicates a remarkably rapid series of S_n2' processes, some of which are illustrated on the next page.

The identification (by g.l.c.-m.s.) of small amounts of

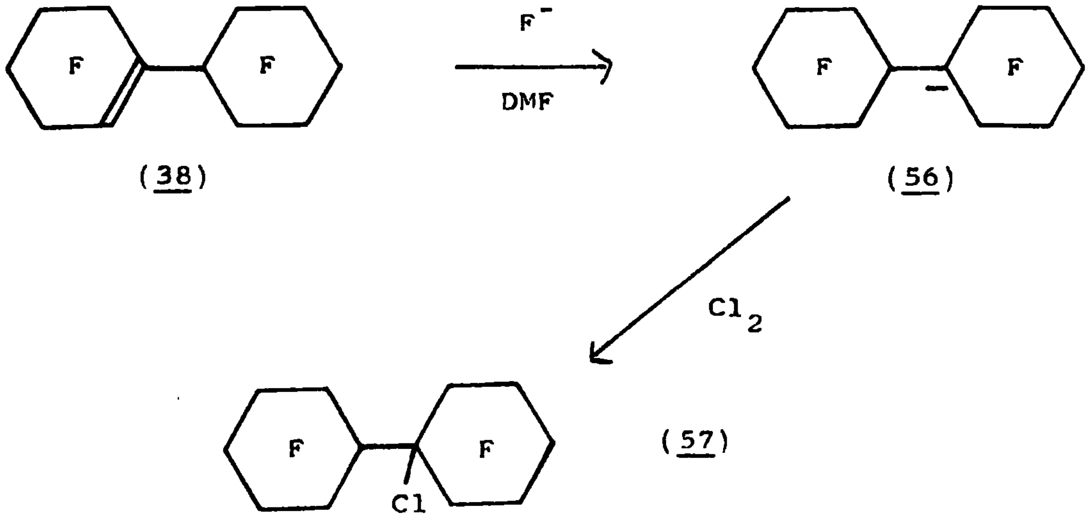


chlorine containing products from the trapping experiment was, to say the least, puzzling. However, analysis showed that caesium fluoride contains about 1-2% of caesium chloride as impurity. Thus the chloro- compounds could be formed from chlorine generated by interaction of caesium chloride with bromine. Since no chloro- derivatives are observed for trapping of anions (23), (47) or (48), it is tempting to suggest that trapping proceeds more slowly for anions (52) and (53) than, for example, anion (23) and that trapping with chlorine is much more favourable than with bromine. This, of course, is readily explainable in terms of the smaller size of chlorine which would lead to lower eclipsing interactions than in the bromo- derivatives (54) and (55), and a more favourable approach to the anionic centre. As will be seen, as the ring size increases, trapping by bromine becomes even more unfavourable.

3.E Anion from Compound (38)

Compound (38) gave anion (56), whose formation can be attributed to removal of destabilising vinylic fluorine from (38). The ^{19}F n.m.r. spectrum of anion (56) had the same characteristics as those of anions discussed above, i.e. a resonance due to tertiary fluorine could not be observed and the difluoromethylenes adjacent to the charge centre were again moved downfield. In fact this resonance was about 11 p.p.m. further downfield than the corresponding resonance in, for example, the spectrum of anion (23).

Anion (56) was readily trapped by chlorine to give (57). However, with bromine no trapping was observed and only starting material with a small amount of (57) was recovered. Moreover, anion (56) could be observed by ^{19}F n.m.r. spectros-copy even in the presence of bromine. This lack of reactivity

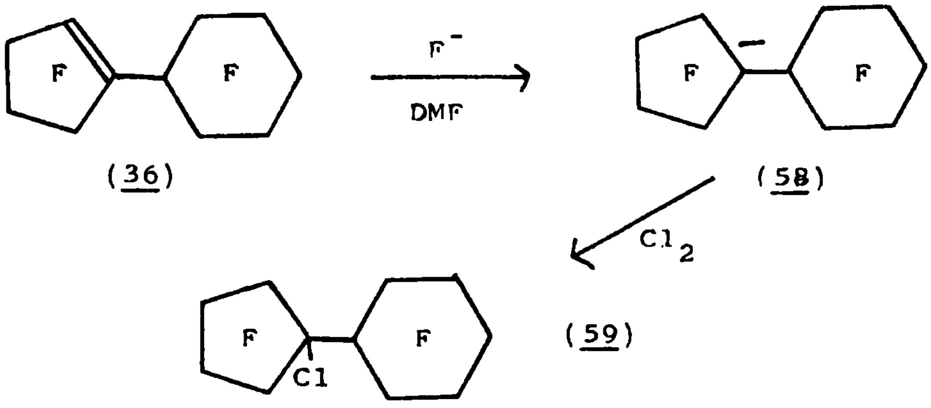


(38) (56) (57)

towards bromine is probably due to the anionic centre being too sterically crowded to allow approach of a bromine atom.

3.F Anion from Compound (36)

Compound (36) also gave an anion which was assigned structure (58) in view of the position, in the ^{19}F n.m.r. spectrum, of the resonance corresponding to the difluoromethylenes adjacent to the charge centre. This anion was readily trapped by chlorine to give (59) but again no trapping with bromine was acheived.



(36) (58) (59)

Although addition of fluoride ion to compound (36), to give anion (58), raises the eclipsing interactions it does remove a destabilising vinylic fluorine and this is presumably the driving force for the reaction.

3.G Structural Assignments

For the anions it seems probable that the position of the resonance, in the ^{19}F n.m.r. spectrum, of the difluoromethylenes adjacent to the charge centre is characteristic of ring size. Thus, for those anions with charge in a four-membered ring, i.e. (23),(47),(48) and (52), this resonance occurs at about 88 p.p.m.; with the charge in a five-membered ring, i.e. anions (53) and (58), it occurs at about 80 p.p.m.; and for anion (56) (charge in a six-membered ring) it occurs at 76 p.p.m..

All the bromo- derivatives showed a resonance due to a single tertiary fluorine, in the ^{19}F n.m.r. spectrum, and a useful criterion of structure was provided by the fact that signals arising from difluoromethylene groups adjacent to the carbon attached to bromine were significantly affected. These signals appear as AB's and one half of the signal (presumably corresponding to the fluorine atoms that are cis- to the bromine atom) is moved to lower field than, for example, corresponding signals in compound (17). The coupling constants for these AB's are characteristic of ring size; for the cyclobutyl- derivatives described above and later the coupling constants are about 225 Hz., whilst for compound (55) (bromine attached to a five-membered ring) and other F-cyclo--pentyl- derivatives [233] the coupling constants are about 250 Hz.. This fact was used to distinguish between compounds (54) and (55).

The chloro- derivatives (57) and (59) showed a single tertiary fluorine resonance in their respective ^{19}F n.m.r. spectra.

All the bromo- and chloro- derivatives gave satisfactory elemental analyses.

CHAPTER 4

NUCLEOPHILIC SUBSTITUTION REACTIONS OF F-CYCLOBUTENE OLIGOMERS

Introduction

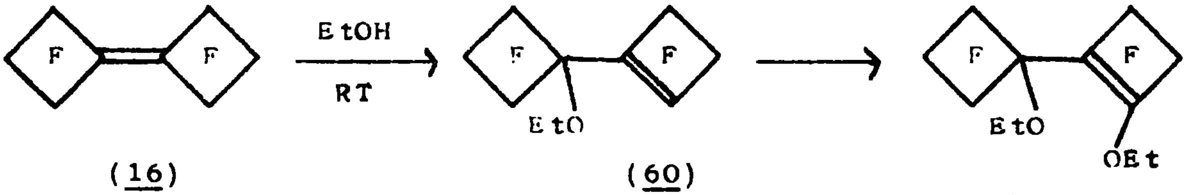
This chapter deals with the reactions of the dimers and trimers of F-cyclobutene with some simple nucleophiles. In general, the products are readily explainable in terms of vinylic substitution of fluorine or S_n2' displacement, and are those expected for F-cyclobutenes (see chapter 1). However, as will be seen, one of the very obvious differences is the much greater reactivity of these alkenes when compared with F-cyclo-butene or F-alkenes with formally similar structures, e.g. F-3,4-dimethylhex-3-ene (40).

Structural assignments will be discussed at the end of the chapter.

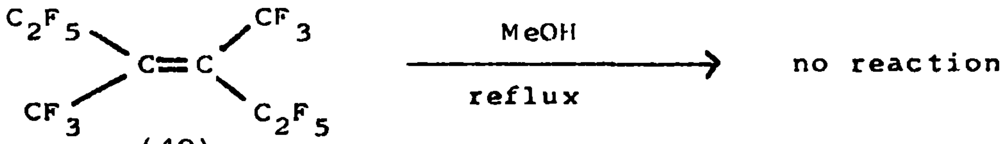
4.A Reactions with Alcohols

4.A.1 Dimer (16) with Neutral Ethanol

Addition of dimer (16) to excess neutral ethanol results in a very rapid exothermic reaction to give, initially, the monoethoxy compound (60), which can be isolated. However, compound (60) also reacts further to give a fairly complex mixture in which the diethoxy compound (61) is the major product.



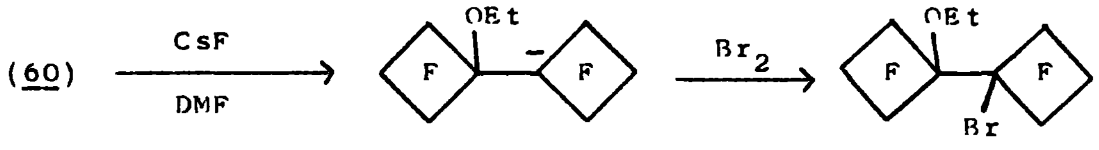
(16) (60) (61)



(40)

This rapid reaction of dimer (16) with ethanol can be contrasted with the failure of alkene (40) to react even with refluxing neutral methanol.[235] The mechanism of the reaction involves very rapid S_n2' displacement of fluorine followed by a slower vinylic substitution step.

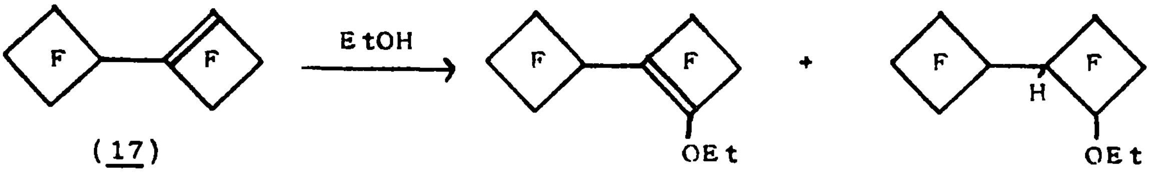
Interestingly, compound (60) gives an observable anion (62) in the presence of caesium fluoride and DMF. This anion shows the characteristic low field shifts of difluoromethylenes adjacent to the charge centre, in its ^{19}F n.m.r. spectrum. Although the bulk of the spectrum is unchanged by temperature, extra, small peaks do appear below about +10°C. In this anion, of course, there is no tertiary fluorine; however, integration of the ^{19}F n.m.r. spectrum indicates that the ratio of low field fluorines to other signals is 3:8, i.e. the added fluorine appears to be missing. Anion (62) can be trapped with bromine to give compound (63)



(62) (63)

4.A.2 Dimer (17) with Neutral Ethanol

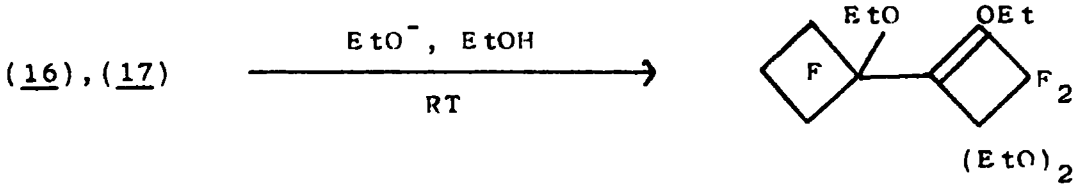
Again, reaction proceeded rapidly to give a mixture of mono- and di-substituted compounds from which (64) was isolated. Also isolated was a minor product having the formula $C_{10}F_{12}OH_6$ i.e. an addition product, assigned structure (65). Compound (64) is formed by vinylic substitution.



(17) (64) 60% (65) <10%

4.A.3 Dimers (16) and (17) with Ethoxide Ion

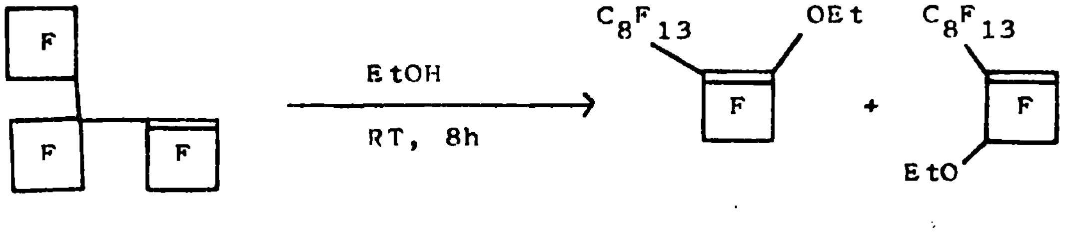
A mixture of dimers (16) and (17) gave a single tetrasubstituted compound, (66), when reacted with an excess of sodium ethoxide in ethanol.



(66) 67%

4.A.4 Trimer (19) with Neutral Ethanol

Reaction was slower than for the two dimers, (16),(17), but, nevertheless, proceeded fairly rapidly to give compounds (67) and (68) by vinylic substitution and S_n2' displacement respectively.

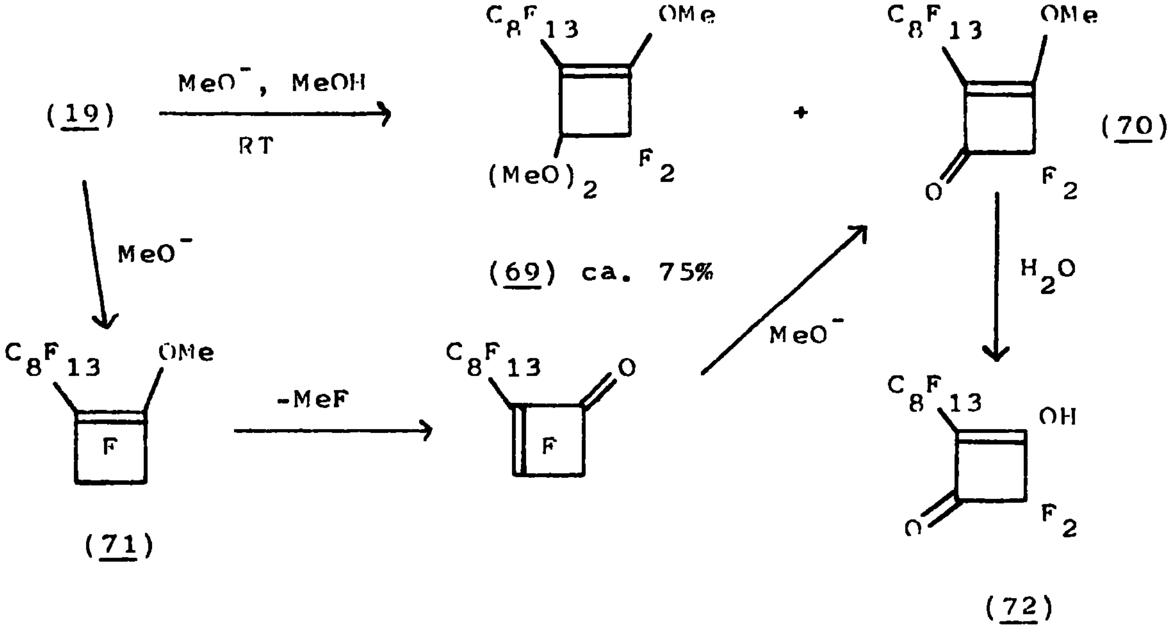


(19) (67) 80% (68) 10%

4.A.5 Trimer (19) with Methoxide Ion

Two products, (69) and (70), were obtained from this reaction. The major product, the tri-methoxy compound (69), is formed by a mixture of vinylic substitution and S_n2' displacement of fluorine. Compound (70) is possibly formed by loss of methyl fluoride from (71) followed by vinylic displacement by methoxide ion. Similar 1,4-eliminations have been observed previously in the presence of methoxide, e.g. with F-cyclopentene.[70]

On standing in air compound (70) was hydrolysed to the corresponding hydroxy compound (72), which is also obtained by direct hydrolysis of trimer (19).

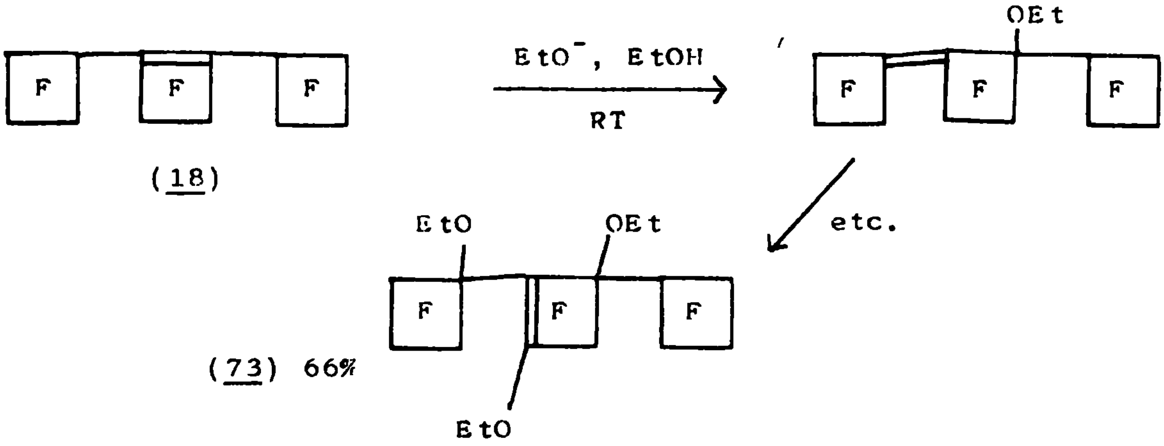


4.A.6 Trimer (18) with Neutral Ethanol

Trimer (18) is the least reactive of the F-cyclobutene oligomers and this is shown by the fact that there was no reaction with neutral ethanol, even on prolonged contact.

4.A.7 Trimer (18) with Ethoxide Ion

Despite its lack of reactivity with neutral ethanol, trimer (18) readily reacts with sodium ethoxide in ethanol to give a single, triethoxy derivative, (73), presumably via the sequence indicated.



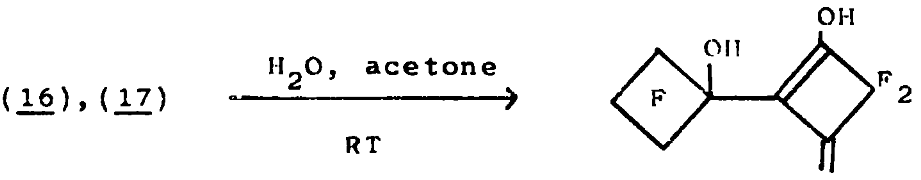
Pruett has obtained compound (73) previously [94] but, not suprisingly, he failed to assign the correct structure. This was because he had not assigned trimer (18) its correct structure in the first place.

4.B Hydrolysis Reactions

All of these reactions were carried out in aqueous acetone at room temperature, without added base, the exception being the hydrolysis of trimer (18).

4.B.1a Dimers (16) and (17) with Excess Water

Dimers (16) and (17), seperately or in a mixture are readily hydrolysed to a single, heat sensitive compound, (74).

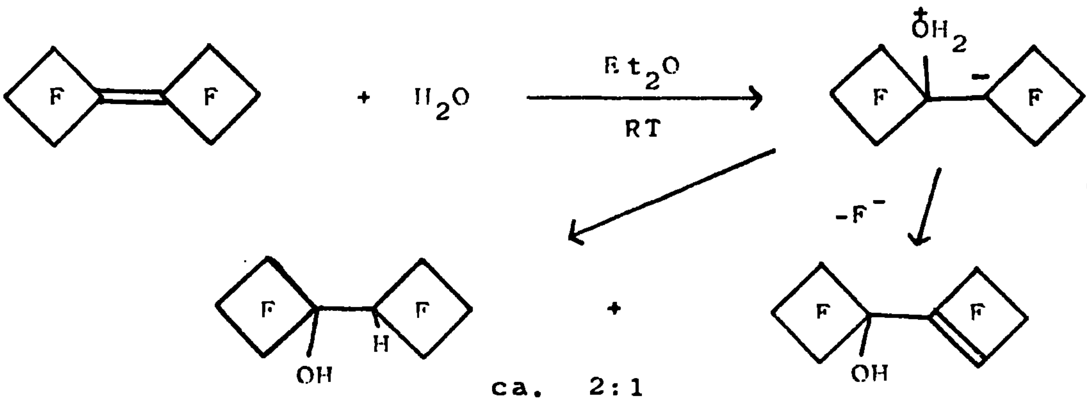


(74) 70%

The mechanism may be similar to that for formation of, for example, compound (66), followed by loss of water from the resultant gem-diol, or it may involve 1,4-elimination of hydrogen fluoride from an intermediate product.

4.B.1b Dimer (16) with an Equivalent of Water

Two products, (75) and (76), were obtained in the approximate ratio 2:1.



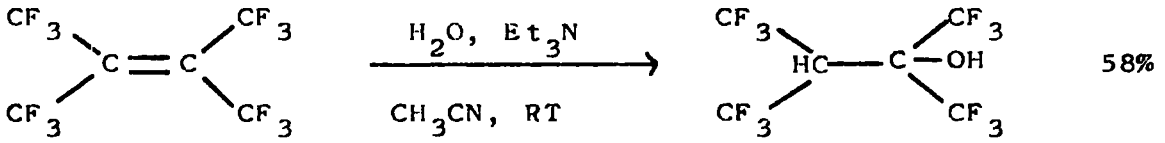
(77)

(75)

(76)

Compound (76) is the product expected from S_n2' displacement of fluorine, c.f., for example, formation of compound (60), whereas (75) is presumably formed via proton transfer from the intermediate carbanion (77). Both compound (75) and (76) reacted further, in aqueous acetone, to give (74).

Addition of water has also been reported for the structurally similar F-2,3,-dimethylbut-2-ene.[234]

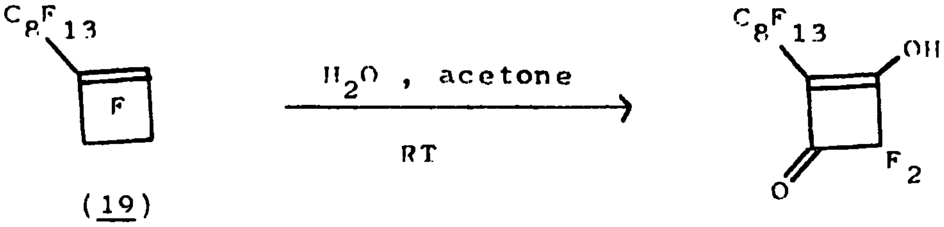


4.B.1c Dimer (17) with an Equivalent of Water

This reaction gave a mixture containing dimer (17), a small amount of dimer (16) (presumably formed by fluoride ion induced isomerisation), and compound (74) as the major product. This indicates that the initially formed product is more reactive than dimer (17) towards water.

4.B.2 Trimer (19)

The expected product, (72), was obtained.



(19)

(72) 90%

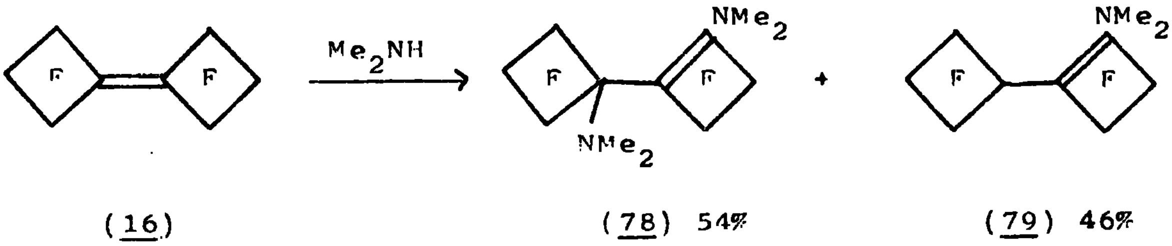
4.B.3 Trimer (18)

In the absence of added base, trimer (18) reacted very slowly or not at all with aqueous acetone. In the presence of sodium carbonate, however, a quite rapid and exoth--ermic rection occurred to give a yellow, heat sensitive liquid which was shown by ^{19}F n.m.r. spectroscopy to be a mixture. Various attempts to separate this mixture were unsuccessful.

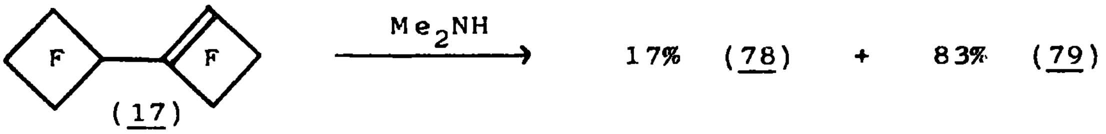
4.C Reactions with Amines

4.C.1 Dimers (16) and (17) with Dialkylamines

Reaction of the separate dimers, (16) and (17), with dimethylamine under autogenous pressure using excess amine gave two products, (78) and (79), in each case. Presumably the reaction proceeds slowly enough to allow fluoride ion to cause some isomerisation of the dimers.



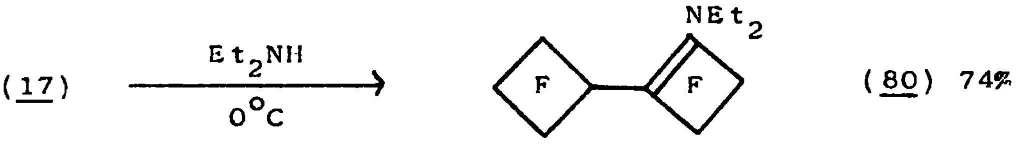
(16) (78) 54% (79) 46%



(17) 17% (78) + 83% (79)

Not suprisingly, both (78) and (79) are very susceptible to hydrolysis.

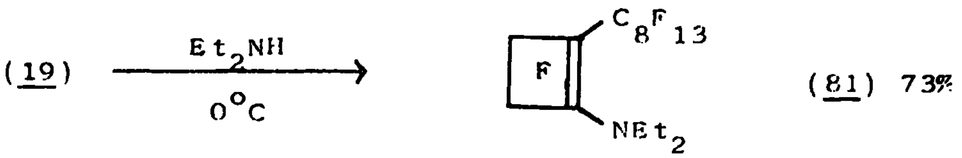
In contrast to the above reactions, when dimer (17) was added slowly to an excess of diethylamine a vigorous reaction ensued to give a single product, (80).



(17) (80) 74%

4.C.2 Trimer (19) with Diethylamine

This reaction gave the expected monosubstituted product, (81).



(19) (81) 73%

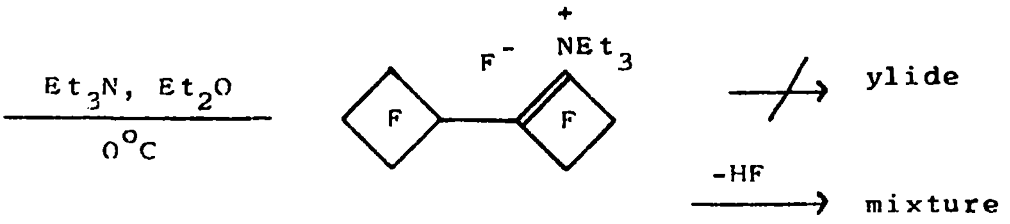
4.C.3 Trimer (18) with Diethylamine

A vigorous reaction occurred to give a complex mixture. Attempts to isolate components of this mixture were unsuccessful.

4.C.4 Dimer (17) with Triethylamine

This reaction was carried out in order to see if an ylide could be isolated analagous to those obtained from F-cyclobutene and tertiary amines. Unfortunately, however, the reaction gave a large quantity of triethylammonium fluoride and a heat sensitive, fluorocarbon oil shown by ^{19}F n.m.r. to be a complex mixture. The difference in reaction compared to F-cyclobutene [93] is puzzling, but it could be due to the inability of the fluoride ion, for steric reasons, to add to the other end of the double bond from which it came; however, in view of other reactions described later this is doubtful.

(17)



4.C.5 Trimer (19) with Tertiary Amines

Interaction of trimer (19) with trimethylamine at room temperature gave only a very small amount of a white solid which was not identified.

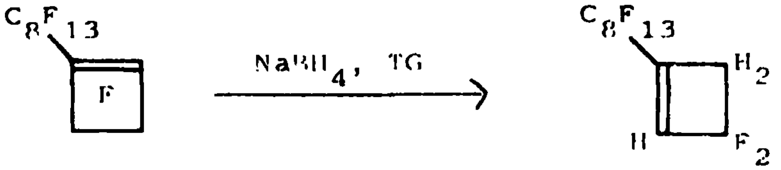
4.C.6 Trimer (18) with Tertiary Amines

With pyridine, trimer (18) gives an homogeneous black oil which slowly tars. A similar reaction is obtained with triethylamine. As will be seen later, trimer (18) undergoes a fascinating rearrangement with fluoride ion and it is possible that tertiary amines initiate the same rearrangement but that tarring occurs due to the many possible side reactions.

4.D Reactions with Sodium Borohydride

4.D.1 With Trimer (19)

Reaction occurred in tetraglyme to give a trisubstituted product, (82).



(82) 80%

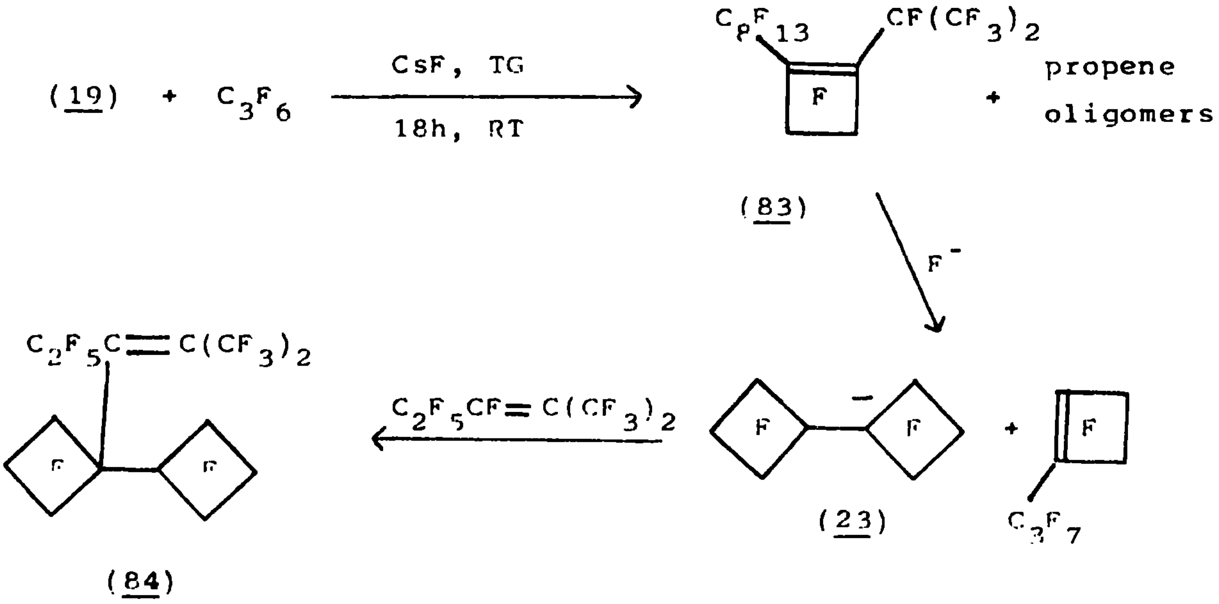
4.D.2 With Trimer (18)

Although a vigorous reaction occurred the fluorocarbon recovery was so small and the product mixture so complex that the experiment was not pursued further.

4.E Carbon Nucleophiles

4.E.1 Trimer (19) with the F-isopropyl Anion

An interesting reaction occurred when F-propene was oligomerised in the presence of trimer (19) and the reaction mixture allowed to stir overnight. Apart from F-propene oligomers, two other products, (83) and (84), were obtained, and the mechanism of formation is probably as indicated below:-

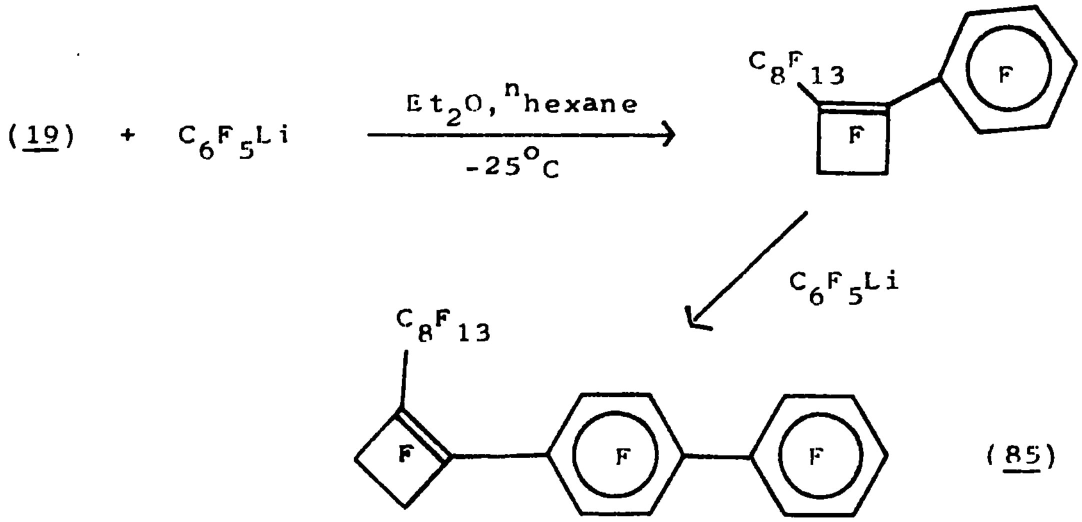


This mechanism, to give compound (84), is analogous to that assumed for the breakdown of the F-cyclobutene tetramer (22) to give dimers (16) and (17) (see chapter 2) and has as its driving force production of the stable anion (23).

Compound (84) was also obtained from reaction of F-propene with fluoride ion in the presence of dimers (16) and (17).

4.E.2 Trimer (19) with Excess F-Phenyl Lithium

The F-phenyl lithium was made in situ by addition of ^{n}butyl lithium to pentafluorobromobenzene. With a large excess of the aryl lithium a single product, (85), was obtained

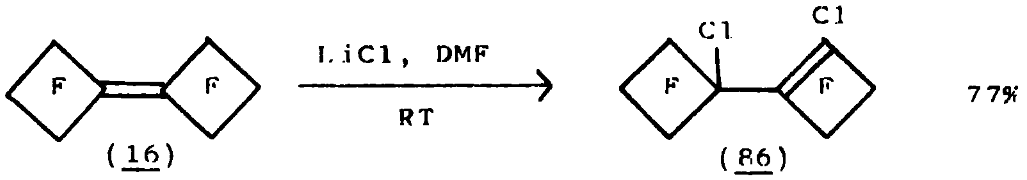


(85)

The product is assigned structure (85) rather than an alternative since it is known that F-alkylbenzenes are most susceptible to nucleophilic attack para to the alkyl substituent.[108] Also, in view of the known chemistry of F-cycloalkenes towards carbon nucleophiles (see chapter 1) and the presence of only a single tertiary fluorine resonance in the ^{19}F n.m.r. spectrum of (85) it is unlikely that further substitution has occurred in the cyclobutene ring.

4.F Reaction of Dimer (16) with Lithium Chloride

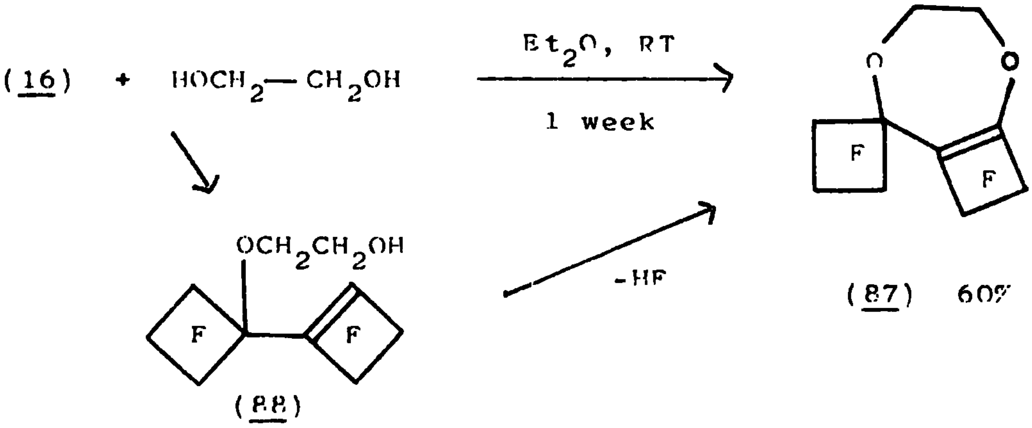
This is another example of the enhanced reactivity of compound (16) over its acyclic analogue, compound (40). Under the conditions employed (16) gives the disubstituted product (86) whilst compound (40) is unreactive.[235]



4.G Reaction of Dimer (16) with Ethylene Glycol

Workers in these laboratories have obtained good yields of products from reactions between F-alkenes and difunctional nucleophiles by carrying out the experiments in high dilution.

In keeping with this observation, in the presence of a large amount of ether as solvent, compound (16) and ethylene glycol gave a good yield of (87). Because of the high dilution of the reaction, the initially formed product, (88), undergoes intra rather than inter molecular substitution.



4.H Other Nucleophiles

The side reaction of dimer (16) with sodium chloride in an attempted carbene addition will be discussed in chapter 5.

The highly novel rearrangement of trimer (18) with fluoride ion will be discussed in chapter 6.

4.J Summary of Reactions with Nucleophiles

In general the reactions of F-cyclobutene oligomers with nucleophiles proceed readily at room temperature, or below, to give good yields of products. The enhanced reactivity of dimer (16) over its analogues, e.g. compounds (37) and (40), can be rationalised in terms of the angle strain present in (16). The least reactive oligomer is trimer (18) and this often gives complex, inseparable mixtures with nucleophiles.

The extent of substitution is dependant on the attacking nucleophile, and the products obtained are readily rationalised in terms of vinylic and/or S_n2' substitution of fluorine. The identity of the products can usually be predicted by reference to the known chemistry of F-cyclobutenes with nucleophiles (see chapter 1).

4.K Structural Assignments

All the compounds described in this chapter gave satisfactory elemental analyses. In all cases the structure followed simply from the spectral data.

Thus, compound (60) gave a signal, in its ^{19}F n.m.r. spectrum, at 98.9 p.p.m. characteristic of -CF= ; the position of the C=C absorption in the infrared spectrum, 1712 cm.$^{-1}$, is very similar to those in compounds (27)-(29).

Compound (61) gave signals for two non-equivalent ethyl groups in its ^{1}H n.m.r. spectrum and a strong C=C absorption at 1687 cm.$^{-1}$ in it's infrared spectrum. The ^{19}F n.m.r. spectrum showed only signals due to $-CF_2-$ groups. Anion (62) was identified by comparison of its ^{19}F n.m.r. spectrum with those of anions (23),(47) and (48). Compound (63) gave only signals arising from $-CF_2-$ groups in its ^{19}F n.m.r. spectrum and these included a low field AB typical of a compound containing bromine at a tertiary position on a four-membered ring, c.f. compounds (45),(49) and (50).

Other compounds described in this chapter were identified by similar means to those mentioned above; for more information see the relevant experimental section and spectra.

CHAPTER 5

ADDITION REACTIONS OF F-CYCLOBUTENE OLIGOMERS

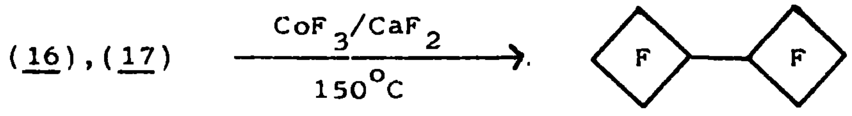
This chapter deals with a preliminary investigation into the addition reactions of the F-cyclobutene oligomers and includes halogen additions, Diels Alder reactions, polymerisations, etc.. As will be seen, the special reactivity of dimer (16) becomes apparent in some of these reactions.

5.A Fluorinations

These were carried out by passing the material to be fluorinated, in a stream of dry nitrogen, over a bed of cobalt trifluoride on calcium fluoride.

5.A.1 Dimers (16) and (17)

Fluorination of a mixture of dimers (16) and (17) occurred readily to give the expected bicyclobutyl, (46). The conditions were not optimised but presumably the percentage of fluorination could be increased by raising the temperature. Compound (46) has been obtained before in various reactions.[171,175]

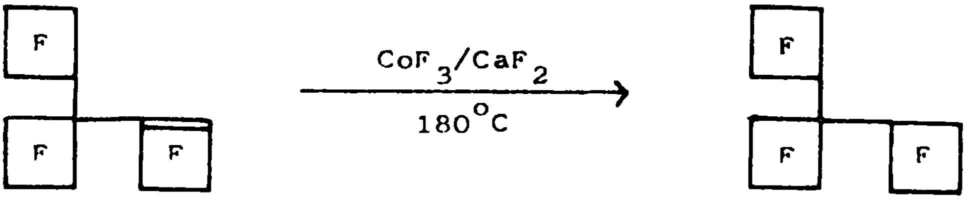


(46)

ca. 70% conversion

5.A.2 Trimer (19)

Fluorination gave F-1,1-dicyclobutylcyclobutane (89) as a low melting solid.



(19)

(89) ca. 80% conversion

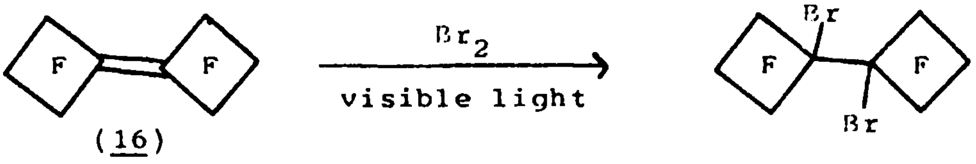
Compound (89) is very thermally stable, being recovered unchanged after prolonged heating with iron filings at ca. 320°C or passage over platinum at ca. 600°C. Its volatility (b.p. 161°C) is such that it could be of use as a blood substitute.

5.B Addition of Bromine

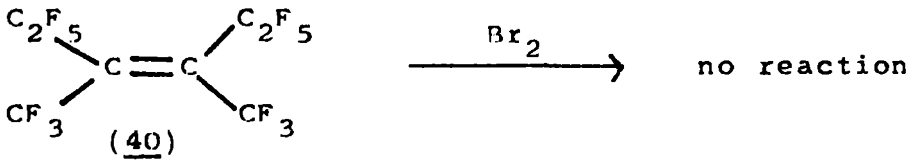
Although bromine addition is often readily accomplished upon ultraviolet irradiation, there are only a few examples where this is accomplished by visible light.[88]

5.B.1 Addition to Dimer (16)

Addition occurred slowly in visible light to give the expected dibromo- product (90) as a low melting solid. Compound (90) boiled without decomposition but partially decomposed at higher temperatures, e.g. on a g.l.c. column at 200°C. The ease of addition is explainable in terms of relief of angle strain and can be contrasted with the failure of compound (40) (or, indeed, the other F-cyclobutene oligomers) to react under the same conditions.



(16) (90)



(40)

5.C Polymerisations

These were all carried out using gamma ray irradiation (from ^{60}Co) as a means of initiating the reactions.

5.C.1 Dimer (16) with 1,3-butadiene

Dimer (16) and 1,3-butadiene gave an homogeneous mixture which when irradiated gave a co-polymer containing ca. 50% fluorine. The speed of the reaction is astounding; thus, a reference reaction using 1,3-butadiene only, gave less than 1% of polymerisation in the same amount of time. Once again the reaction can be rationalised in terms of relief of angle strain in dimer (16).

Dimer (17) and alkene (40) did not give co-polymers under the same conditions with 1,3-butadiene; indeed, they appeared to inhibit the polymerisation of the butadiene.

Dimer (16) was recovered unchanged after prolonged irradiation on its own.[239]

5.C.2 Other Attempted Co-Polymerisations with Dimer (16)

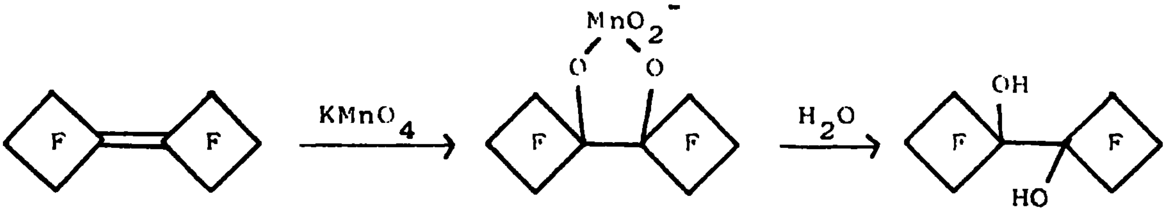
Dimer (16) did not give a co-polymer with F-2-butyne nor with F-ethene. In the latter case, increasing the amount of dimer present decreased the rate of polymerisation of the F-ethene.

The failure of these two systems to give co-polymers is, perhaps, not suprising since, in both cases, the reactants are highly electrophilic and will both give highly electro--philic radicals.

5.D Oxidation Reactions

5.D.1 Dimer(16)

Addition of dimer (16) to a solution of potassium permanganate in dry acetone gave a high yield of diol (91), presumably via a cyclic manganese complex. The diol (91) could not be separated from the solvent acetone except by preparative scale g.l.c.. An attempt to remove the elements of water from (91) with phosphorus pentoxide was unsuccesful.

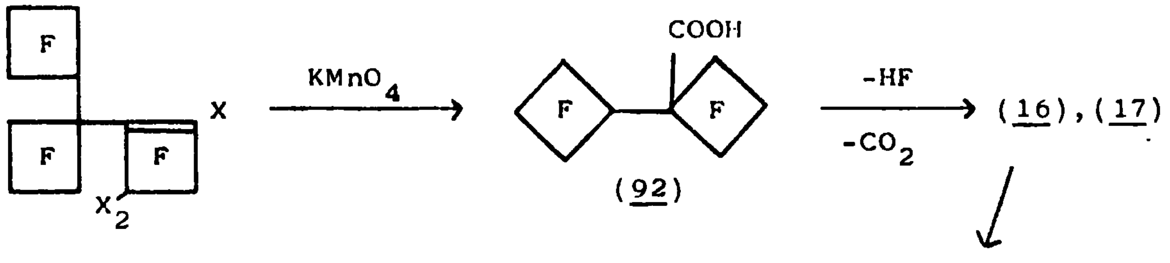


(91) 90%

The corresponding reaction with F-cyclopentene dimer (37) also gives a diol.[236]

5.D.2 Trimer (19)

Oxidation occurs to give diol (91) in moderate yield, presumably via acid (92) as intermediate:-



(92)

(16), (17)

(19) X = F, (82) X = H

(72) X = OH, no reaction

(91) 60%

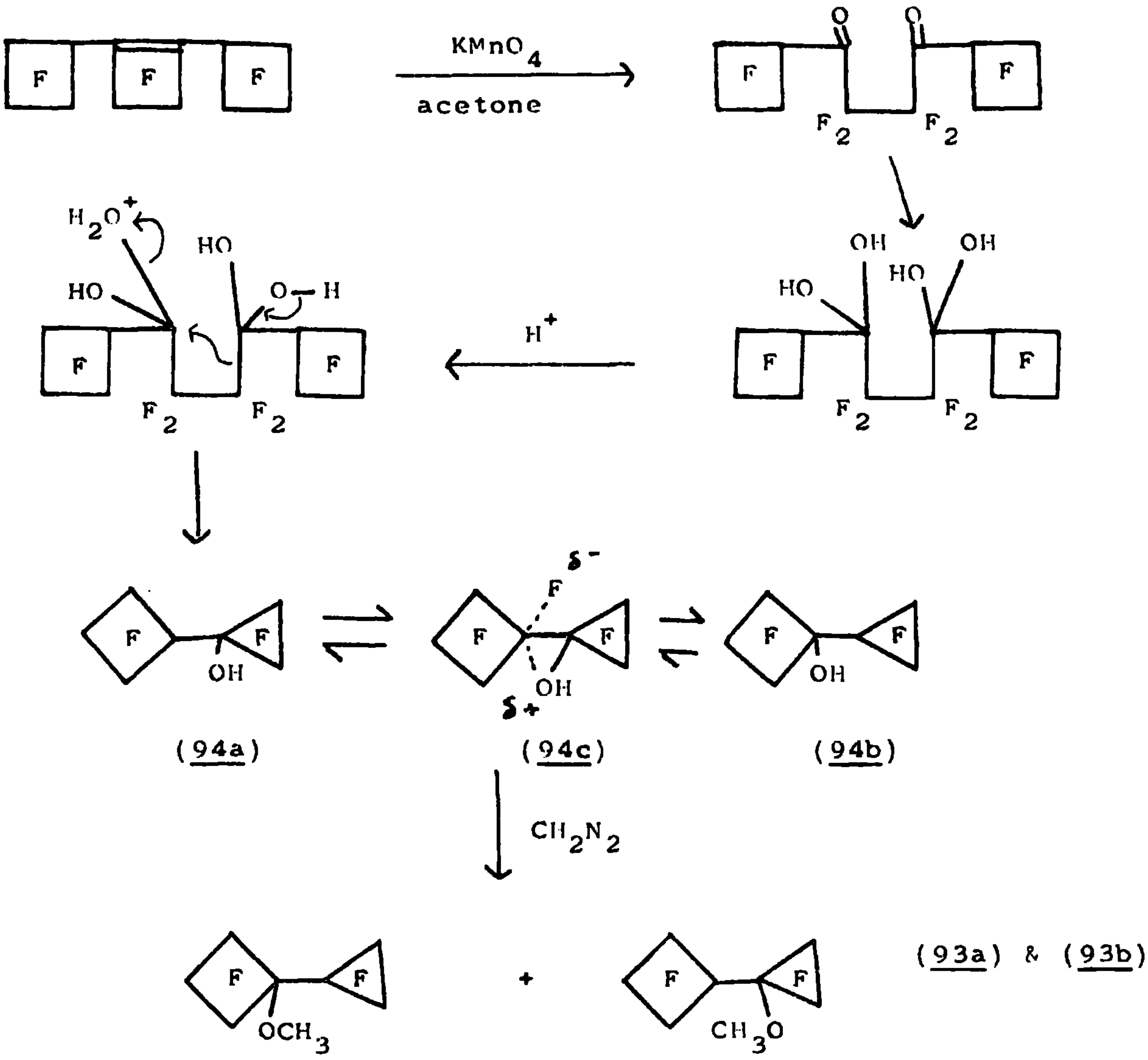
Oxidation of trimer derivative (82) also gives the diol (91), but compound (72) is unaffected under the same conditions.

5.D.3 Trimer (18)

A highly intriguing reaction occurred between trimer (18) and potassium permanganate to give a mixture of compounds which could not be isolated. Subsequent methylation with diazomethane gave two major products which were separated by preparative scale g.l.c. and shown to be $C_7F_{11}OCH_3$ isomers. The ^{19}F n.m.r. spectrum of the products before and after methylation was virtually identical. This shows that the diazo-methane had methylated an hydroxy function rather than under-going some other reaction with the oxidation products.

The ^{19}F n.m.r. spectrumof both isomers shows a single resonance due to a tertiary fluorine and unassigned signals, in the $-CF_2-$ region of the spectrum, corresponding to ten fluorines. The proton spectra gave single resonances typical of hydrogens in a methoxy group. The infrared spectra did not contain absorptions due to hydrogen bonding, C=C or carbonyl functions. Satisfactory elemental analyses were obtained and both compounds gave a parent peak at M/e 324 in their mass spectra.

The data is consistent only with structures (93a) and (93b) and a mechanism for their formation is given on the next page. Note that this mechanism involves decomposition of an



(94a) (94c) (94b)

(93a) & (93b)

intermediate dicarbonyl compound in the presence of water. Since the oxidation is carried out under anhydrous conditions, this might seem to imply that breakdown of the dicarbonyl occurs on work-up. Although this is possible, it is equally plausible that breakdown occurs under the oxidation conditions and is initiated by permanganate (or similar species) rather than by water. Also, in order to account for the formation of two isomeric products , it is necessary to invoke the isomerisation of (94a) to (94b). This isomerisation cannot be rapid since both isomers are observed by ^{19}F n.m.r. spectroscopy. It seems plausible that compound (94a) should want to eliminate hydrogen fluoride . However, the resulting epoxide would be very highly strained and this may be the reason why isomerisation to (94b), perhaps via (94c), is observed rather than epoxide formation.

5.E Cycloadditions

This section includes attempted carbene additions, (2+2) and (4+2) cycloadditions and reactions with diazomethane.

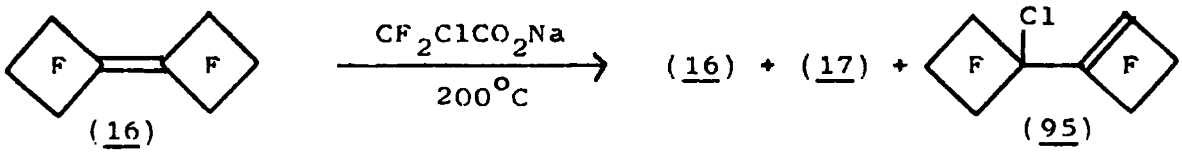
5.E.1 Attempted Carbene Additions

The area of carbene additions to F-cycloalkenes and their derivatives has received very little attention. Earlier workers at Durham were unsuccessful in attempts to add difluorocarbene across the double bond of F-cyclopentene dimer, (37).[233]

5.E.1a Attempted Addition of Difluorocarbene to Dimer (16)

Dimer (16) was heated with sodium chlorodifluoroacetate in a sealed tube to give a mixture of dimers (16) and (17) and compound (95). No carbene addition products could be detected. Compound (95) presumably arises from nucleophilic attack by sodium chloride on dimer (16) and the sodium fluoride thus formed causes isomerisation to occur.

A similar reaction with trimer (19) was also unsuccesful.



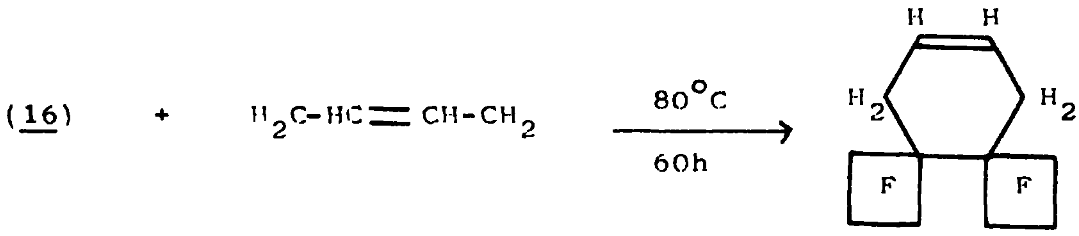
5.E.2 Attempted (2+2) Cycloadditions

As mentioned in chapter 1, thermal (2+2) cycloadditions of F-cycloalkenes are rare. In keeping with this, dimer (16) did not undergo addition with either F-ethylene or F-2-butyne.

5.E.3 (4+2) Cycloaddition of Dimer (16) with 1,3-Butadiene

Dimer (16) undergoes Diels Alder reaction with 1,3-butadiene under mild conditions to give compound (96) almost quantitatively. The reaction can be attributed to release of angle strain in dimer (16) since, under more forcing conditions, dimer (17), trimer (18), F-cyclopentene dimer, (37), and alkene (40) are all unreactive.

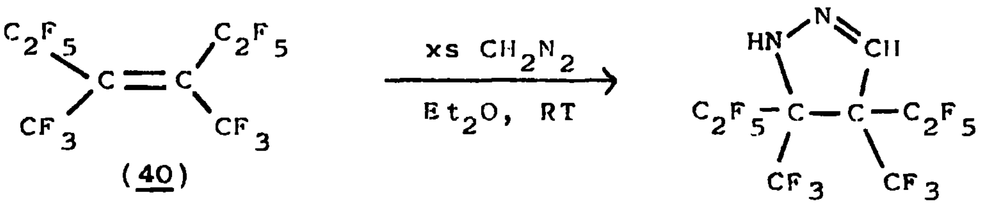
The angle strain in dimer (16) was not sufficient to allow it to undergo Diels Alder reaction with the more electrophilic F-1,3-cyclohexadiene at ca. 260°C.



(95) 99%

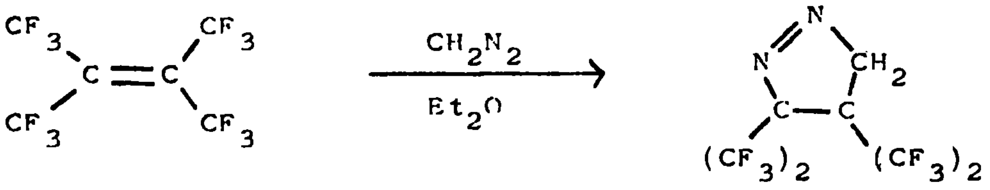
5.E.4 Reactions Involving Diazomethane

Workers at Durham are finding that diazomethane readily adds across the double bond of F-alkenes with no vinylic fluorines, e.g. compound (40)[237] which gives the 2-pyrazoline (97). In contrast, addition to the structurally similar F-2,3-dimethylbut-2-ene was claimed to give 1-pyrazoline (98a).[238]



(40)

(97)

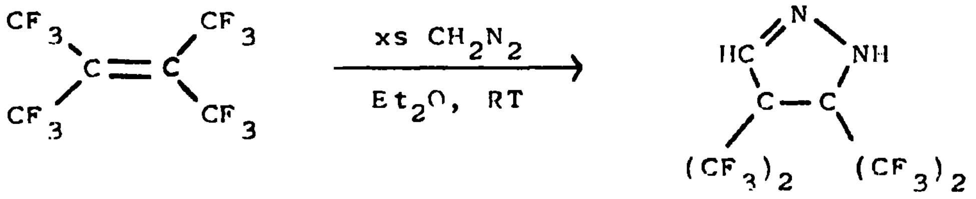


(98a)

5.E.4a With F-2,3-Dimethylbut-2-ene

This reaction gave a crystalline solid identified as the 2-pyrazoline (98) rather than the isomeric 1-pyrazoline (98a). The infrared spectrum of

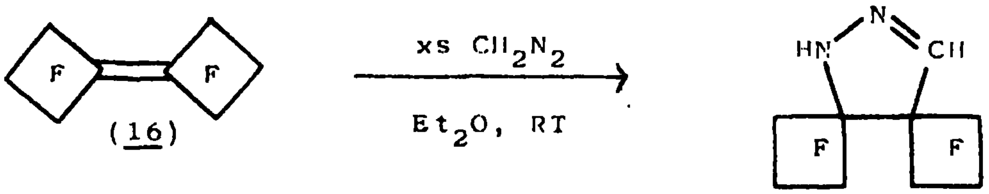
(98) showed an absorption at ca. 3350 cm.$^{-1}$ due to an -NH- group, and the ^{1}H n.m.r. spectrum contained two resonances of equal intensity arising from an -NH- and an olefinic hydrogen.



(98)

5.E.4b With Dimer (16)

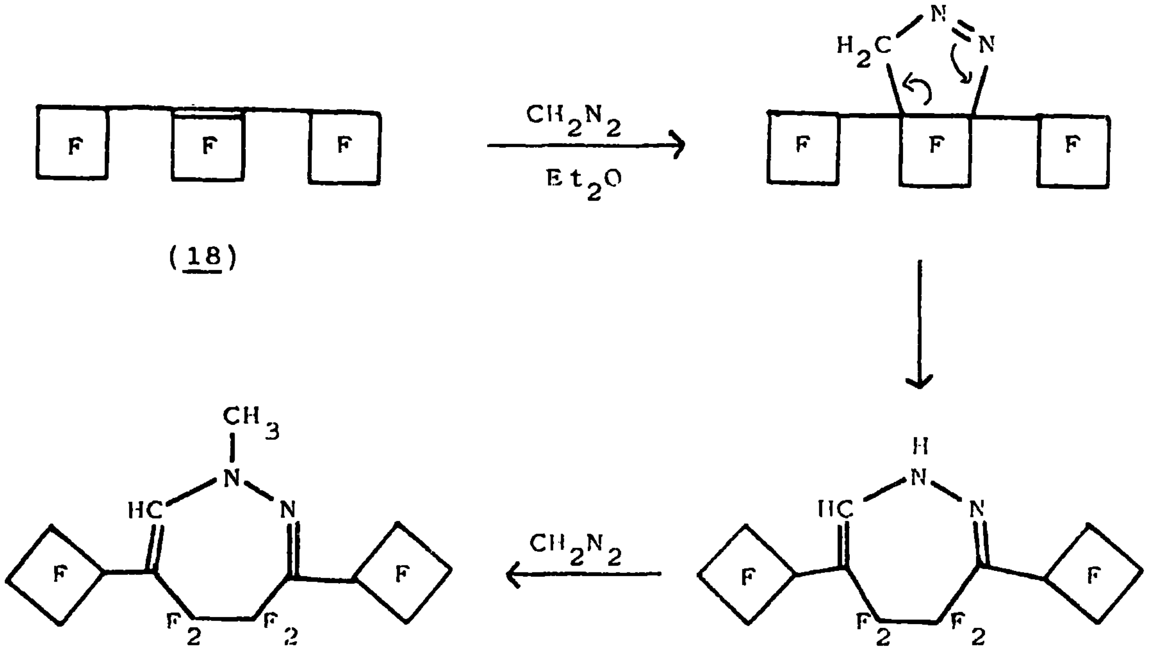
Reaction occurred rapidly at room temperature to give one major product identified as the 2-pyrazoline (99) from its n.m.r. spectra. Thus, the ^{1}H n.m.r. showed signals for an olefinic hydrogen and one other hydrogen assigned as an -NH-. The ^{19}F n.m.r. showed signals for two non-equivalent F-cyclobutene rings. The observation of an -NH- stretch in the infrared spectrum helped to confirm the assignment.



(99)

5.E.4c With Trimer (18)

A single, crystalline product was obtained and identified by elemental analysis and mass spectroscopy as being $C_{14}F_{18}N_2H_4$, (100). The infrared spectrum did not contain absorptions due to hydrogen bonding but it did contain two medium absorptions at 1642 and 1592 cm.$^{-1}$, suggesting the presence of two double bonds. The ^{1}H n.m.r. spectrum showed two resonances in the ratio 3:1, assigned as a methyl group attached to nitrogen and an olefinic hydrogen respectively. The ^{19}F n.m.r. spectrum showed signals for two non-equivalent tertiary fluorines and signals in the -CF$_2$- region resulting from sixteen fluorines. In view of this data (100) was assigned the structure shown and a mechanism for its formation is given below:-

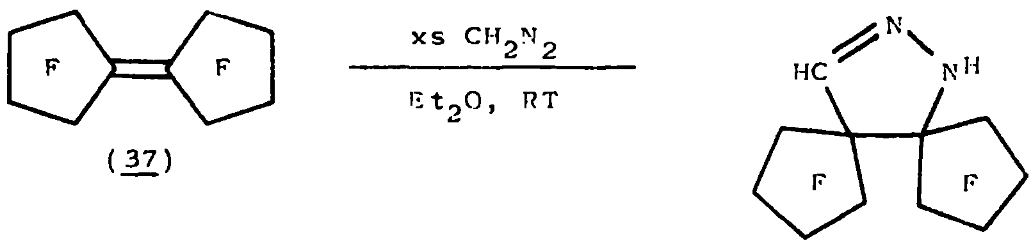


(18) (100) (101)

Presumably the proton on the nitrogen in compound (101) is made sufficiently acidic by its allylic nature to be methylated by more diazomethane.

5.E.4d With F-Cyclopentene Dimer (37)

Compound (37) reacted with diazomethane to give the expected product, (102). The product was identified by reference to its infrared and ^1H n.m.r. spectra. The ^{19}F n.m.r. spectrum was highly complex and no signals could be assigned; however, they all occurred in the $-CF_2-$ region.



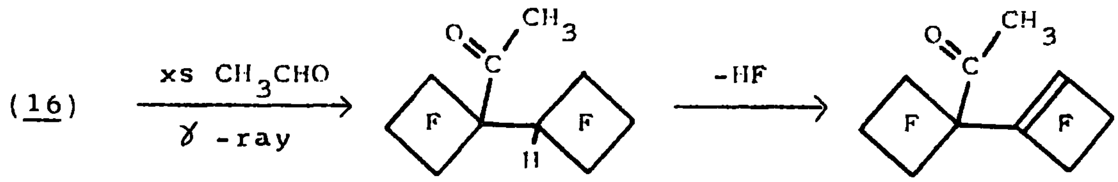
(37) (102) 80%

5.F Structural Assignments

All the compounds described in this chapter gave satisfactory elemental analyses. Compounds (89)-(91) were easily identified from their ^{19}F n.m.r. spectra since they are symmetrical. Compound (95) showed a vinylic fluorine in its ^{19}F n.m.r. spectrum and a $C{=}C$ absorption at 1721 $cm.^{-1}$ in its infrared spectrum, c.f. compounds (27)- (29). Structural assignments for other compounds have already been discussed.

5.G Free Radical Addition of Acetaldehyde to Dimer (16)

Another worker at Durham has added acetaldehyde to dimer (16) by gamma ray induced free radical reaction, to give compound (103) which slowly loses hydrogen fluoride on standing.[230]



(103)

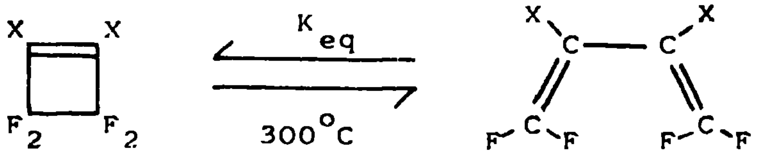
CHAPTER 6

REARRANGEMENTS OF F-CYCLOBUTENES

Introduction

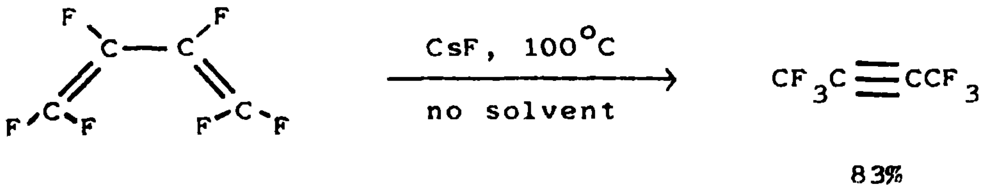
One of the special features of the cyclobutene ring is its thermal isomerisation to give a 1,3-butadiene. At high temperatures both compounds often exist in an equilibrium mixture although the position of the equilibrium is dramatically changed on going from a hydrocarbon to a fluorocarbon system. Thus, cyclobutene itself undergoes thermal ring opening virtually irreversibly to give 1,3-butadiene.[240] In complete contrast, F-1,3-butadiene undergoes ring closure to give F-cyclobutene.[241]

It has been shown[242] that for cyclobutene (104), the rate of ring opening, to give butadiene (105), is only slightly affected by the identity of X; however, the position of equilibrium is strikingly altered, existing largely on the side of (104) for X = F (K_{eq} = ca. 7×10^{-3}); on the side of (105) for X = H (K_{eq} = 200); and intermediate between the two for X = CF_3 (K_{eq} = 8). The authors[242] interpreted these results as indicating that the greater stability of F-cyclobutenes over F-1,3-butadienes was due to the destabilising effect of vinylic fluorines in the latter. Clearly, however, in view of the difference between the systems for X = H and X = CF_3 some other factor must also be involved, possibly electronic in nature.

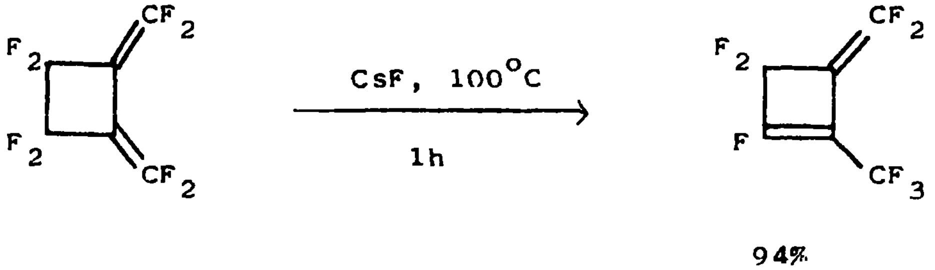


(104) (105) X = F, H, CF_3

It is well established that terminal difluoromethylene groups are particularly susceptible to attack by fluoride ion, leading to formation of a trifluoromethyl group. In particular, where it is possible, compounds containing terminal difluoromethylene groups are rapidly isomerised with elimination of allylic fluorine.



[243]



[244]

As will be seen in this chapter, the ring opening of cyclo-butenes, coupled with fluoride ion induced isomerisation of terminal difluoromethylene groups, provides a wealth of highly novel chemistry when applied to F-cyclobutene and its oligomers.

6.A Thermal Behaviour of F-Cyclobutene

6.A.1 In Flow Systems

All the flow pyrolyses described in this chapter were carried out by passing the material to be pyrolysed through a tube packed with the desired material (e.g. iron filings, platinum foil, fluoride ion), maintained at the required temperature.

6.A.1a Over Platinum

F-Cyclobutene was recovered virtually unchanged at temperatures of up to 670°C; several trace components were observed in the product gases but not invest-igated.

6.A.1b Over Fluoride Ion

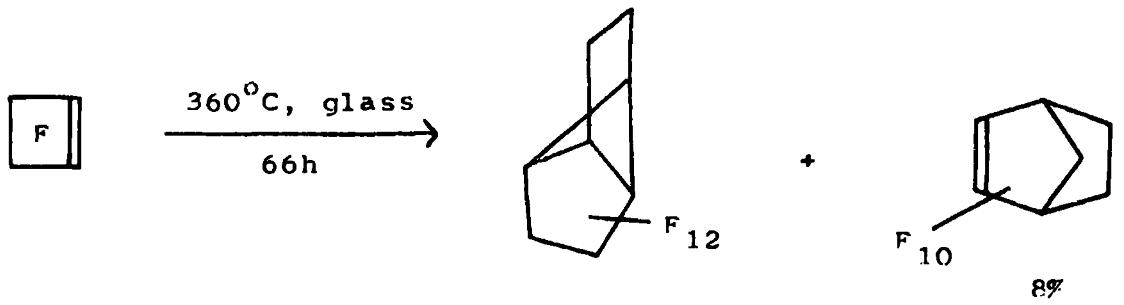
In contrast to the above, over caesium or potassium fluoride rearrangement occurred to give high yields of F-2-butyne. Conversions as high as 90% could be obtained at temperatures of about 600°C. However, at higher temperatures the F-2-butyne undergoes side reactions to give amounts of liquid products.[245] Formation of the butyne is explainable by initial ring opening of F-cyclobutene followed by fluoride ion induced isomeristion.

This is a very clean, simple preparation of F-2-butyne and, for laboratory scale work is preferable to the route involving dechlorination of 2,3-dichloro-F-but-2-ene.

6.A.2 In Static Systems

A complex gaseous mixture, together with a small amount of liquid, was obtained by heating F-cyclobutene with caesium fluoride in a nickel tube at 300°C. A ^{19}F n.m.r. spectrum of the mixture indicated, amongst other things, the presence of F-cyclobutene and small amounts of F-2-butyne.

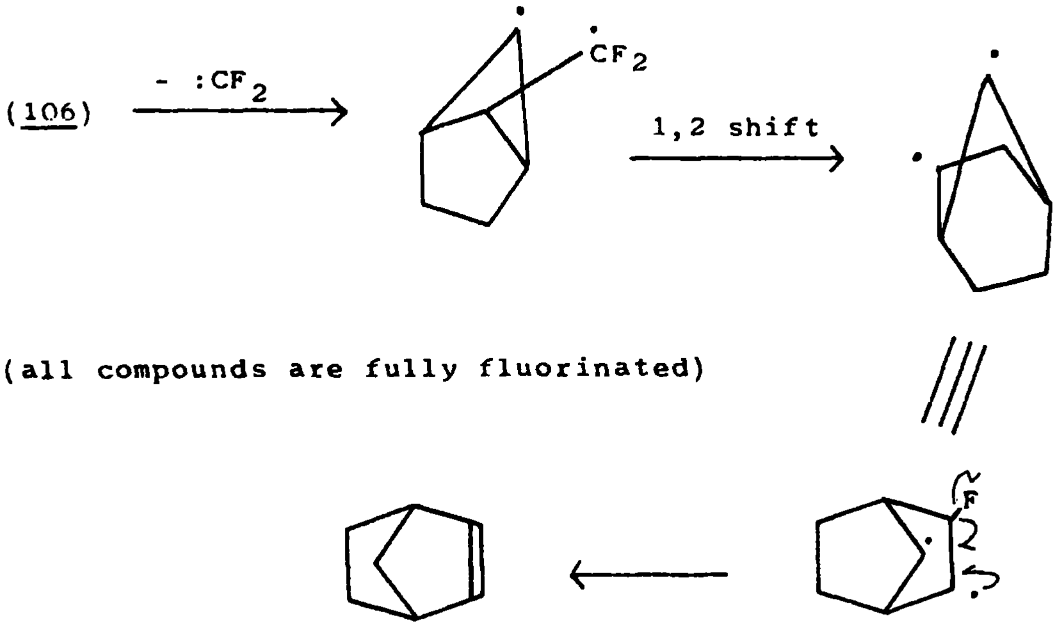
At 360°C, in a glass carius tube, with or without potassium fluoride, F-cyclobutene gives a complex mixture from which the unusual dimer (106) and F-norbornene can be isolated.



(106) 49%

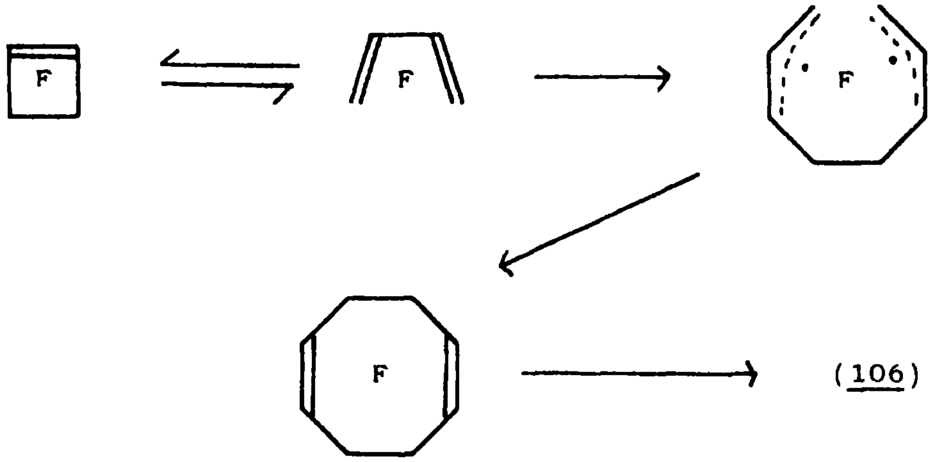
Compound (106) has been obtained previously by thermal dimerisation of F-1,3-butadiene at 150°C, followed by prolonged heating of the dimer fraction at 200°C,[246] and identified by X-ray crystallography;[247] however, its spectral data has not been published. F-Norbornene was identified by comparison of infrared and ^{19}F n.m.r. data with that of an authentic sample.[56]

A mechanism for production of F-norbornene from compound (106) is given below:-



(all compounds are fully fluorinated)

Production of compound (106) presumably results from ring opening of F-cyclobutene, to give 1,3-butadiene, dimerisation to give F-1,4-cyclooctadiene and subsequent (2+2) addition.



A similar reaction, in a nickel tube, gave a very low recovery of material from which compound (106) could be isolated. Presumably intermediate products are undergoing reaction on the nickel surface, e.g. defluorination, with the result that tarring occurs.

6.B Thermal Behaviour of F-cyclobutene Dimers

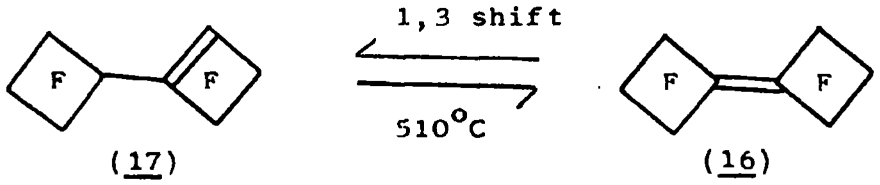
6.B.1 In Flow Systems

6.B.1a Over Platinum

Passage of either of the two seperate dimers, (16) or (17), over platinum at 510°C gave a mixture containing mainly dimers (16) and (17) together with minor amounts of other compounds which were identified by g.l.c.-m.s. as C_8F_{12} isomers. At higher temperatures the percentage of these unidentified compounds increased but the major product was always a mixture of dimers (16) and (17).

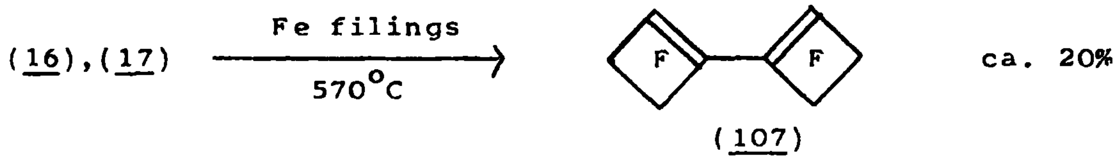
At these high temperatures the equilibrium is on the side of dimer (17), although the exact position of this equilibrium at a given temperature was not determined.

The isomerisation of the dimers presumably results from 1,3-migration of fluorine, although it is conceivable, but unlikely, that it could result from fluoride ion on the surface of the platinum. A similar isomerisation was observed for F-cyclopentene dimer, (37).[233]



6.B.1b Over Iron Filings

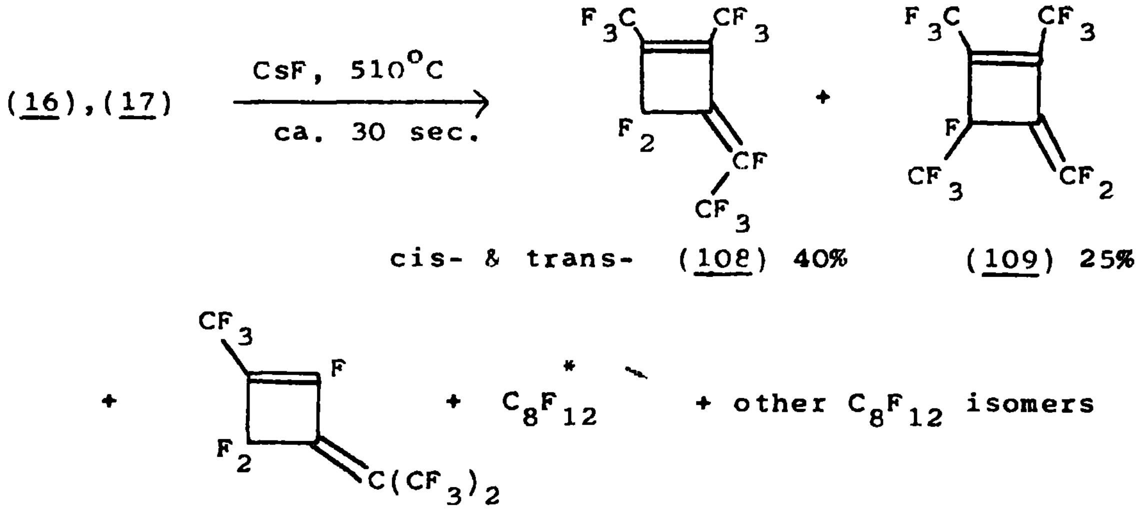
A very similar reaction occurred over iron filings. However, in this case small amounts of two defluorinated products were also observed. The amount of defluorination varied from reaction to reaction but was never more than about 20%. The major defluorinated product was separated and identified as F-bicyclobutyl, (107), from its ^{19}F n.m.r. spectrum (symmetrical) and it's mass spectrum.



As will be seen in this chapter, defluorination of F-cyclo-butene derivatives is not a very facile reaction, possibly due to the angle strain which would be present in the products.

6.B.1c Over Fluoride Ion

Passage of either dimer over caesium fluoride at 420°C gave a mixture of (16) and (17) and unidentified C_8F_{12} isomers. In a similar reaction at 510°C a complex mixture was obtained (>10 components). However, 90% of the mixture consisted of four components, three of which (108)-(110) were separated by a mixture of fractional distillation and preparative scale g.l.c.. The fourth component could not be isolated from the pyrolysis mixture by preparative g.l.c. and disappeared (presumably isomerised to one of the other components) on distillation.



cis- & trans- (108) 40%

(109) 25%

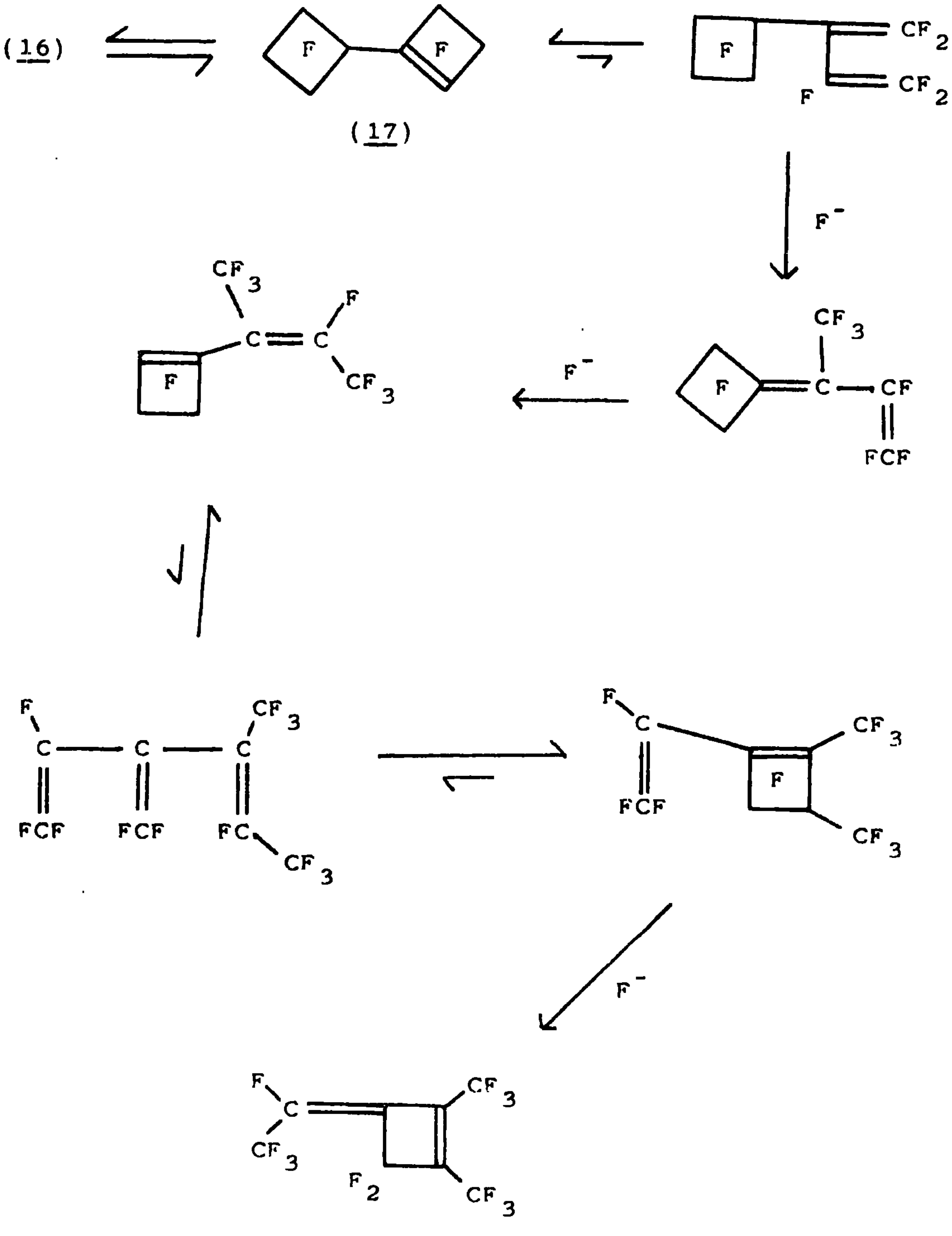
(110) 10%

* (111) 15%

At the same temperature over potassium fluoride, compound (108) forms ca. 70% of the product mixture. Recirculation at a higher temperature (570) gave larger amounts of (109)-(111). This suggests that the initially formed product is (108) and that this undergoes further isomerisation to the other compounds. A mechanism for formation of (108) is outlined in scheme 7. Formation of (109) and (110) from (108) is rather more puzzling although a possible reaction route is outlined in scheme 8. This mechanism is given some credibility by the observation that rearrangement occurs more readily with caesium fluoride which is the better fluoride ion donor.

Scheme 7

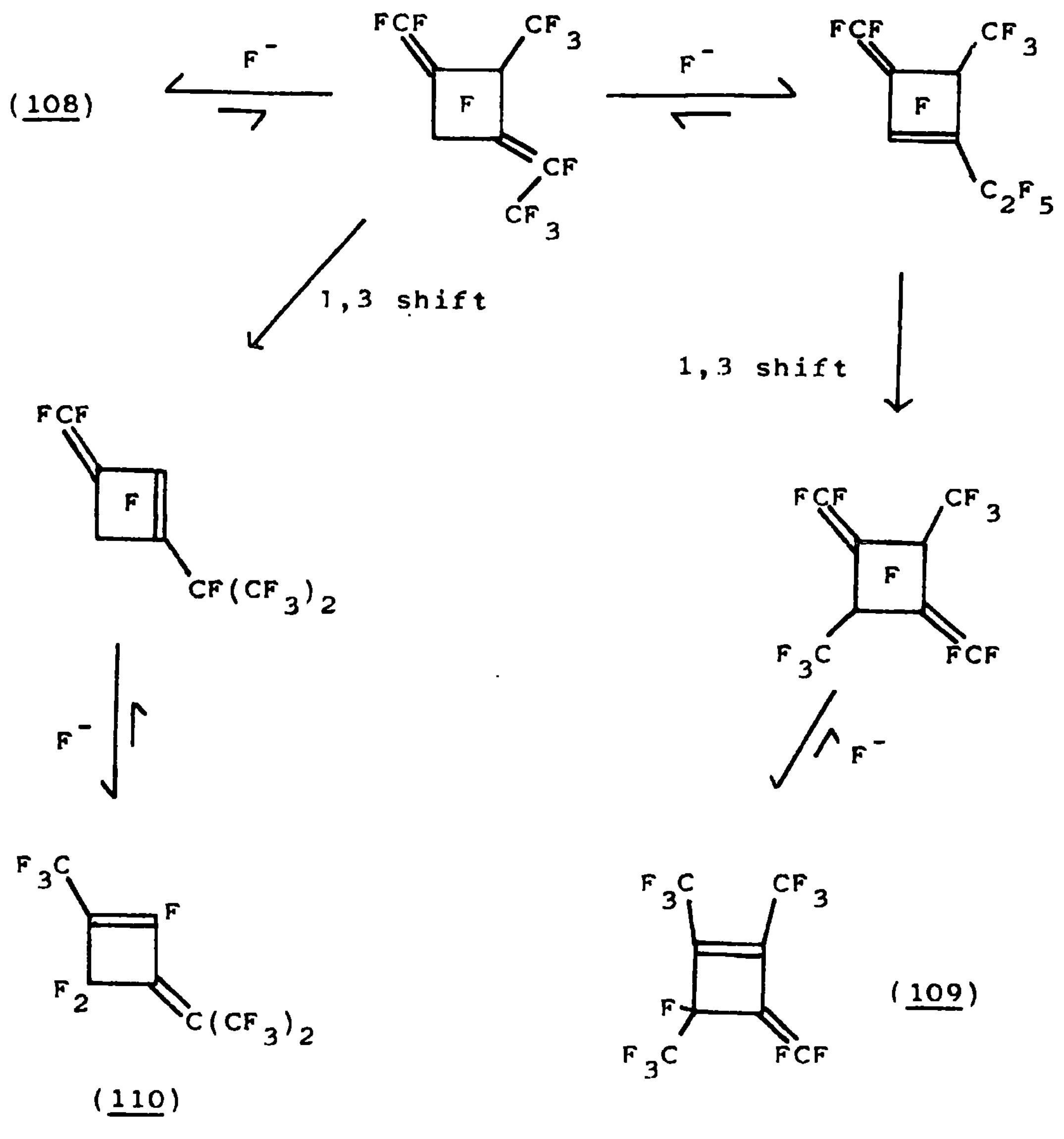
Rearrangement of F-Cyclobutene Dimers



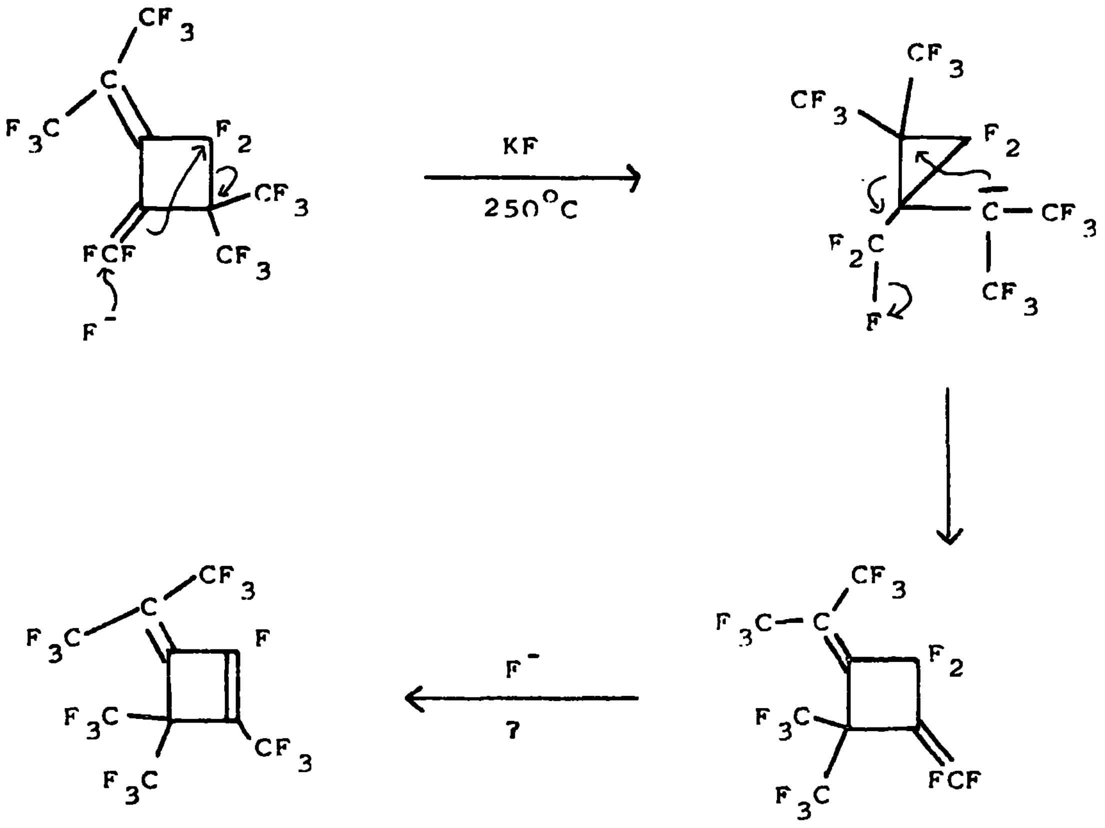
(108)

Scheme 8

Isomerisation of (108)



Fluoride ion induced rearrangements of some F-methylene-cyclobutanes have appeared in the literature. Thus, it is claimed that the dimer of F-2-methyl-2,3-butadiene is rearranged by potassium fluoride to give (112).[248] However, in view of the structures of the products described above, it seems likely that the product is (112a) rather than (112).



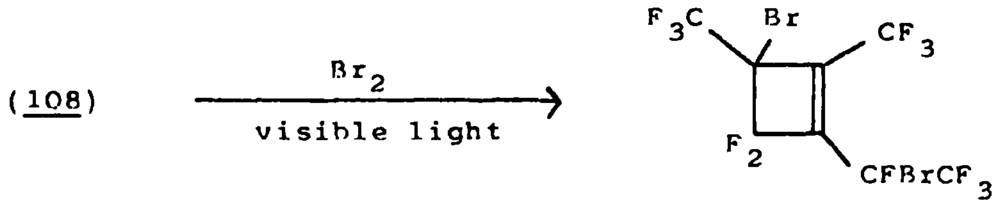
(112a)

(112)

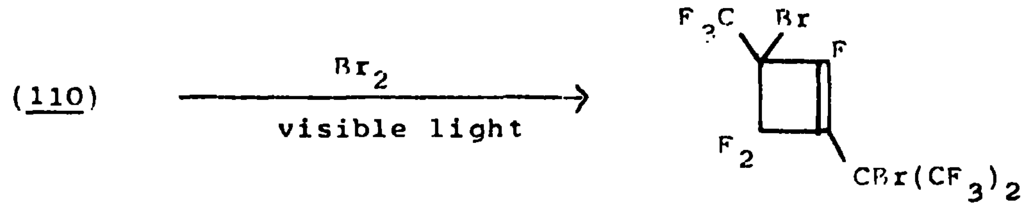
6.B.1d Structural Assignments

Compound (109) has been obtained previously in the generation of F-tetramethylcyclobutadiene.[26] Compounds (108) and (110) could not be identified conclusively solely on spectral data, although the ^{19}F n.m.r. spectrum of (108) indicated it to be a mixture of cis- and trans- isomers (ca. 1:5).

The structures of compounds (108) and (110) were finally assigned by identification of their bromine addition products, since it is known that F-methylenecyclobutenes and related compounds undergo 1,4-addition of bromine.[248] Thus, the ^{19}F n.m.r. spectrum of compound (108) shows 3 vinylic $-CF_3$ groups, a vinylic fluorine, and a $-CF_2-$ (for both isomers). The spectrum of its bromine addition product (a single compound (113)) shows a vinylic $-CF_3$ group, a $-CBr(CF_3)-$ group, a $-CFBr(CF_3)$ group, and a $-CF_2-$. Similarly the spectrum of (110) shows 3 vinylic $-CF_3$ groups, a vinylic fluorine, and a $-CF_2-$. The spectrum of



(113)



(114)

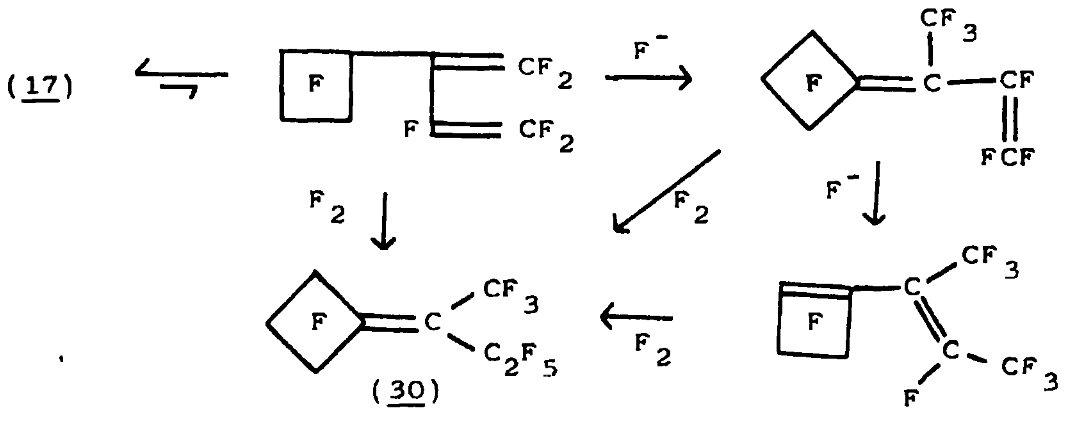
its bromine addition product, (114), shows a -CBr(CF_3)- group, a $(CF_3)_2$CBr- group, a vinylic fluorine, and a $-CF_2-$.

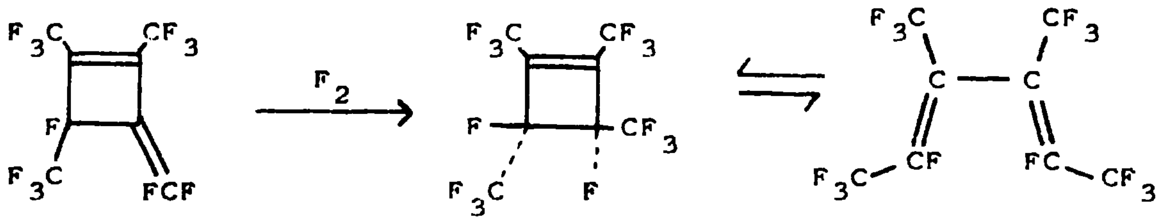
6.B.2 With Caesium Fluoride in a Static System

Heating dimer mixture, (16),(17), with caesium fluoride in a nickel tube gave a similar rearrangement, but with low recovery. However, in this case, the major products were C_8F_{14} isomers, i.e. fluorination had occurred during the reaction. Presumably the nickel surface of the tube causes defluorination and then some fluorine is available, from the nickel surface, for addition to products, or intermediates, of the rearrangement; this would also account for the low recovery since defluorination could well lead to tarring.

The major product was identified as compound (30), also obtained from the co-oligomerisation of F-cyclobutene and F-2-butene (see chapter 2), which could be formed by fluorination of any of the intermediates (scheme 7) after a single ring opening reaction of dimer (17).

The second C_8F_{14} fraction could not be separated on the available g.l.c. columns, but was identified as being mainly compound (115), together with its ring opened analogue, by comparison of its ^{19}F n.m.r. and infrared spectra with those of authentic samples.[26] Compound (115) could be formed by





(109) (115)

fluorination of compound (109). The two other major components of the product mixture were identified as compounds (108) and (110)- no compound (109) could be detected.

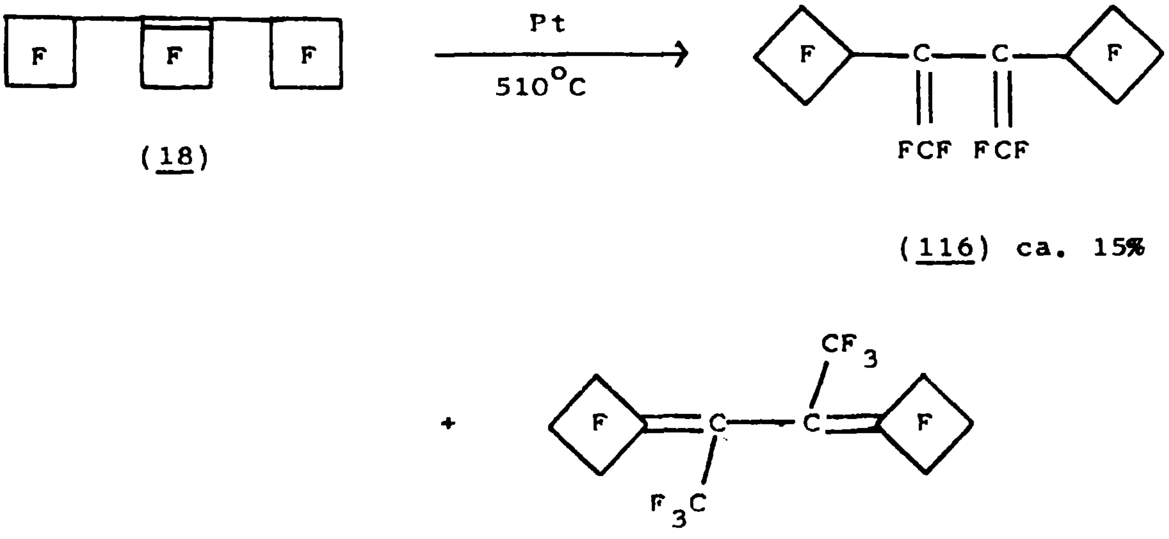
6.C Thermal Behaviour of F-Cyclobutene Trimers

6.C.1 Flow Pyrolyses of Trimer (18)

6.C.1a Over Platinum

Passage of trimer (18) over platinum, at 510°C, gave a mixture containing compound (18), two ring opened products, (116) and (117), and several minor components which were not identified.

Identification of compounds (116) and (117) followed simply from their ^{19}F n.m.r. spectra, since they are symmetrical. Compound (116) is formed by ring opening of the cyclobutene ring in trimer (18), and compound (117) by fluoride ion induced rearrangement of (116)



(18)

(116) ca. 15%

(117) ca. 40%

6.C.1b Over Iron Filings

Over iron filings, at 480°C, trimer (18) was largely unreactive, but it did give small amounts of compounds (116) and (117) together with a defluorinated product, $C_{12}F_{16}$ ca. 5%, identified by g.l.c.-m.s. but not separated.

6.C.1c Over Caesium Fluoride

Over caesium fluoride, trimer (18) gave mainly compound (117) together with some (116) and small amounts of other, unidentified components.

6.C.2 In Static Systems

6.C.2a Ring Opening of Trimer (18)

Heating trimer (18) in a Carius tube at ca. 300°C gives an equilibrium mixture of trimer (18) and its ring opened butadiene, (116)

$$\underset{\text{ca. }80\%}{(18)} \quad \underset{\text{Carius tube}}{\overset{300^{\circ}\text{C}}{\rightleftharpoons}} \quad \underset{\text{ca. }20\%}{(116)}$$

6.C.2b Ring Opening of Trimer (18) in the Presence of Fluoride Ion

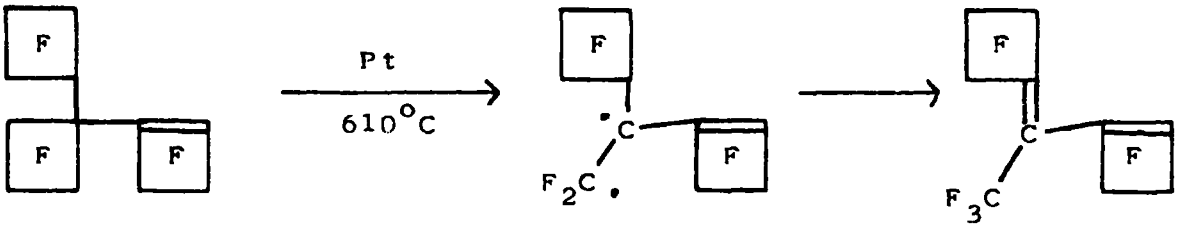
Heating trimer (18) in a nickel tube in the presence of caesium or potassium fluoride gives compound (117) almost quantitatively.

$$(\underline{18}) \xrightleftharpoons{300^\circ C} (\underline{116}) \xrightarrow{F^-} (\underline{117})$$

6. C.3 Flow Pyrolyses of Trimer (19)

6.C.3a Over Platinum

Over platinum at 610°C, trimer (19) gave a complex mixture of $C_{10}F_{14}$ isomers from which compound (118), the major product, was isolated. At lower temperatures compound (118) was still the major pyrolysis product but significant amounts of trimer (19) were also obtained.



(19)

(118)
ca. 30%

6.C.3b Over Iron Filings

No defluorination could be detected up to 525°C and at this temperature pyrolysis started to occur. Similarly, no defluorination was detected on prolonged heating with iron filings at 300°C.

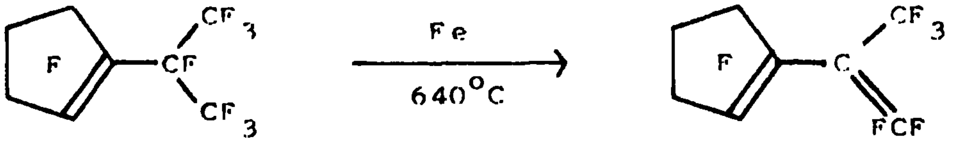
6.C.3c Over Caesium Fluoride

Pyrolysis over caesium fluoride gave a highly complex mixture which was not investigated.

6.D Miscellaneous Pyrolysis Reactions

6.D.1 Defluorination of Compound (33)

An attempt to obtain a fulvene derivative by defluorination of F-1-isopropylcyclopentene, (33), was unsuccessful. At 640°C, over iron filings, a diene, (119), was obtained but at higher temperatures complex mixtures were formed.

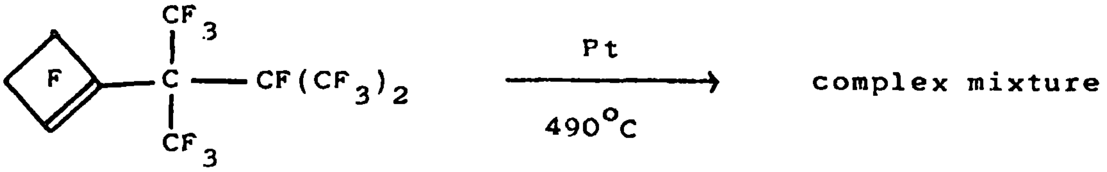


(33) (119) 35%

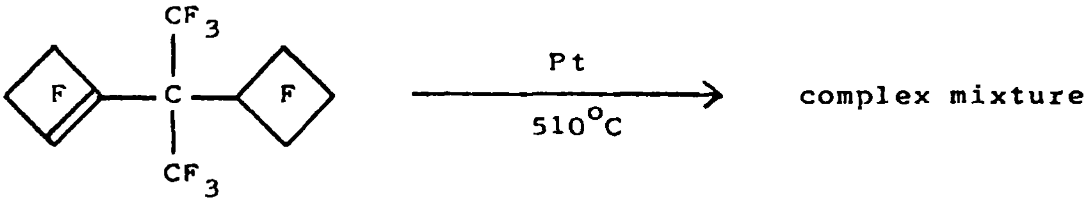
6.D.2 Other Pyrolysis Reactions

Passage of F-1-isopropylcyclohexene, (35), over iron filings did not give the expected benzene, but rather, a complex mixture. A similar reaction is reported for the attempted defluorination of F-isopropylcyclohexane.[249]

It was expected that compounds (28) and (29) would easily lose CF_4 upon pyrolysis, but although thermolysis did occur over platinum the product, in each case, was a complex mixture.



(28)



(29)

6.E Reaction of Trimer (18) with Fluoride Ion

Reaction of trimer (18) with caesium fluoride in DMF at room temperature gave a compound, (120), which was isomeric with (18).

6.E.1 Structural Proof

The ^{19}F n.m.r. spectrum of compound (120) was fairly complex and showed signals only in the $-CF_2-$ region, i.e. there were no resonances due to tertiary fluorines. The infrared spectrum contained a weak C=C absorption at 1678 $cm.^{-1}$ which was also Raman active. The position and intensity of the C=C absorption in the infrared spectrum of (120) rules out the possibility of vinylic fluorines.[226] Also, the fact that no tertiary fluorines are observed in the ^{19}F n.m.r. spectrum indicates that ring enlargement has occurred. A second helpful point from the n.m.r. spectrum is the observation of two AB's in the ratio 2:1, with coupling constants of 231 and 223 Hz. respectively, which suggest the presence of a cyclobutane ring in compound (120)

The structure of (120) could not be assigned on the available information and so various attempts were made to identify it chemically. Compound (120) gave a complex mixture of dicarboxylic acids upon permanganate oxidation, did not defluorinate, was only very slowly photolysed at 253.7 nm., and gave a complex mixture upon fluorination. However, pyrolysis over platinum resulted in loss of F-ethylene to give three isomeric $C_{10}F_{14}$ products, (121)-(123), along with a small amount of a C_9F_{10} compound, (124), which was not obtained pure.

The two major products, (121) and (122), were recirculated over platinum to give a mixture of compounds (121)-(124) in which the major product was compound (124). These experiments show that compounds (121) and (122) are interchangable and that compound (124) is formed by overall loss of CF_4 from a $C_{10}F_{14}$ isomer rather than by loss of C_3F_8 from compound (120).

Compound (121) was shown by n.m.r. spectroscopy to contain a vinylic $-CF_3$ group, a vinylic fluorine and five $-CF_2-$ groups, two of which were almost equivalent. The compound also gave an ultra violet absorption at 245 nm. (log. ε = 4.13). The formula $C_{10}F_{14}$ requires four double bond equivalents and the presence of an ultra violet spectrum requires two, or more, double bonds <u>within a ring</u>, since acyclic F-dienes are unconjugated. Hence compound (<u>121</u>) must contain two rings and two, conjugated, double bonds. As can readily be demonstrated, however, this data is consistent with several structures.

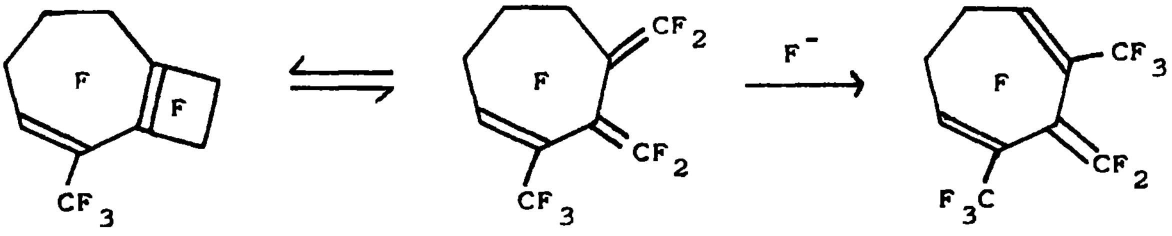
The ^{19}F n.m.r. spectrum of compound (<u>122</u>) shows resonances due to a vinylic -CF_3 group, a vinylic fluorine, two non-equivalent terminal difluoromethylene groups, and three -CF_2- 's. This compound also shows an ultra violet absorption, at 228 nm. log. ε = 3.57. Now it is known that compounds (<u>121</u>) and (<u>122</u>) are interchangable and the presence of two terminal difluoromethylene groups in compound (<u>122</u>) suggests a ring opened cyclobutene. If it is assumed that this is the case then (<u>121</u>) could contain a cyclobutene ring, in which case there are only two possible structures, shown below:-

possible structures of (<u>121</u>)

This would mean that there were only two possible structures for compound (<u>122</u>):-

possible structures of (<u>122</u>)

The final piece of evidence required for structural assignment is provided by the fact that the ^{19}F n.m.r. spectrum of compound (<u>123</u>) is symmetrical, showing resonances due to two vinylic -CF_3 groups, a terminal difluoromethylene, two vinylic fluorines, and two -CF_2- groups. In view of the possible structures of compounds (<u>121</u>) and (<u>122</u>) these facts are consistent with only one structure, shown below, together with its probable mode of formation.

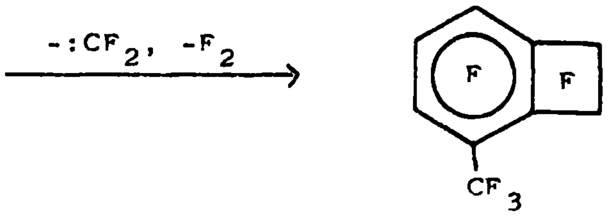


(<u>121</u>) (<u>122</u>) (<u>123</u>)

Although not obtained pure, the fourth component of the pyrolysis mixture, (<u>124</u>), is tentatively assigned the structure shown below, in view of its spectral data. The infrared spectrum shows several absorptions between 1450 and 1600 cm.$^{-1}$; these are characteristic of aromaticity.^{236} The ^{19}F n.m.r. spectrum shows resonances arising from 3 non-equivalent benzylic fluorines, a vinylic (benzylic) $-CF_3$ group, and two $-CF_2-$ groups. A mass spectrum shows a large peak at M/e 298 (and much smaller peaks above this, e.g. at 336, assumed to be due to impurity). Obviously more work needs to be done to characterise this product conclusively.

Compound (<u>124</u>) could be formed by loss of $:CF_2$ and fluorine from compound (<u>121</u>).

(<u>121</u>)

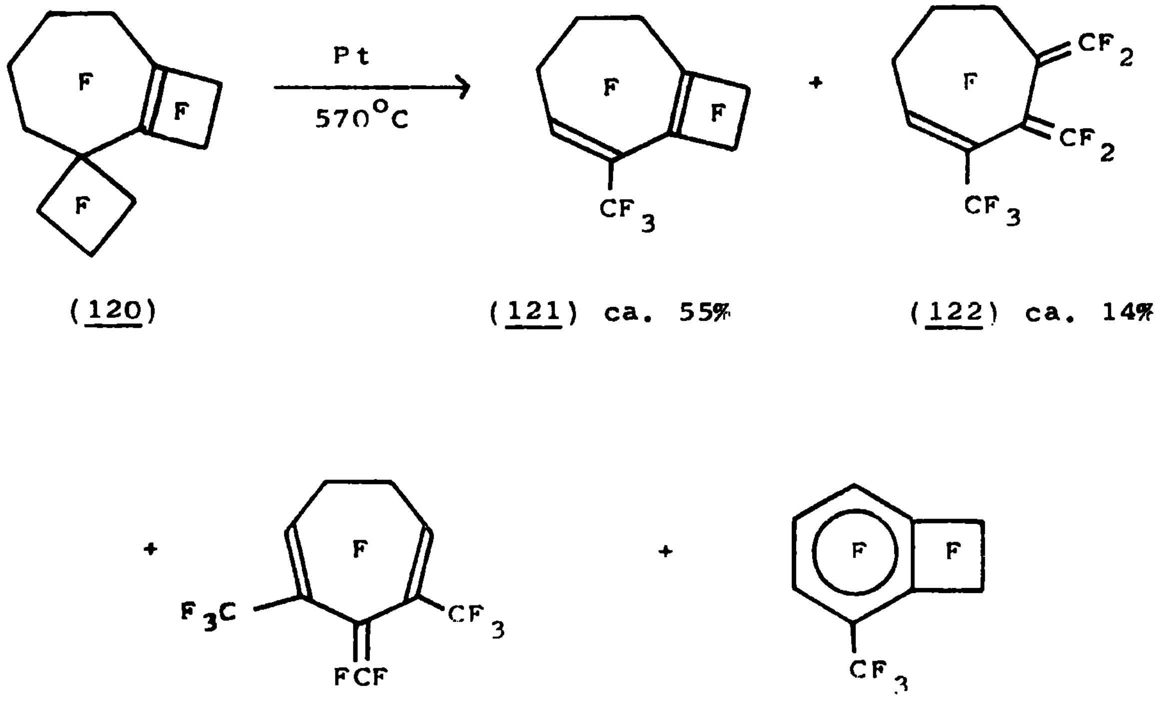


(<u>124</u>)

Now if we work backwards from compound (<u>121</u>) then loss of F-ethylene from compound (<u>120</u>) presumably occurred to give the $-CF_3$ group in (<u>121</u>), (c.f. pyrolysis of trimer (<u>19</u>) to give (<u>118</u>)). This means that compound (<u>120</u>) contains a spiro cyclo-butene ring and has the structure shown in Table 9, which summarises its pyrolysis reaction.

Table 9

Pyrolysis of Compound (120)



(120) (121) ca. 55% (122) ca. 14%

(123) ca. 10% (124) ca. 20%

$$(\underline{121}) \xrightarrow[600^{\circ}C]{Pt} (\underline{121}) + (\underline{122}) + (\underline{123}) + (\underline{124})$$

ca. 70%

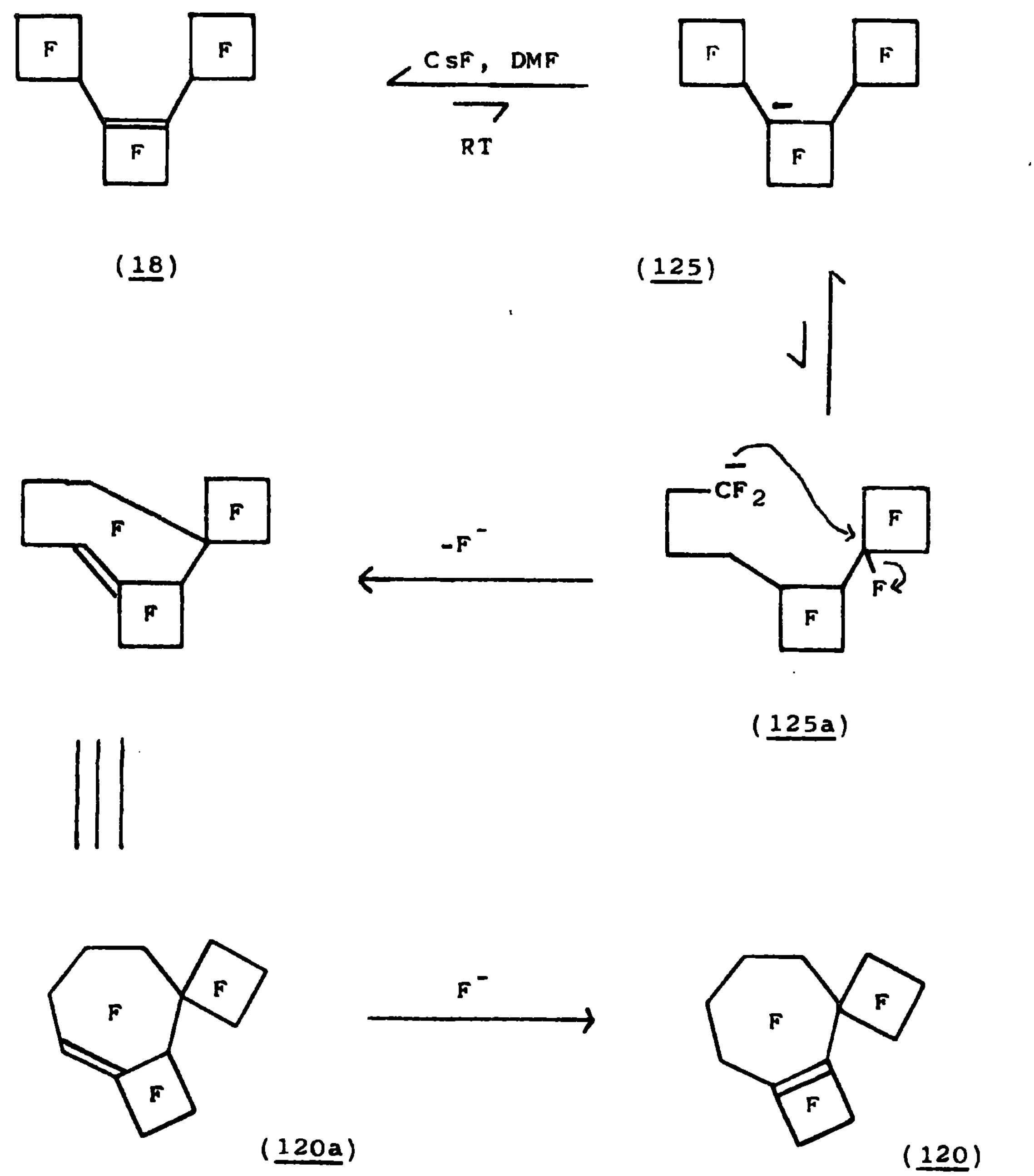
$$(\underline{122}) \xrightarrow[600^{\circ}C]{Pt} (\underline{121}) + (\underline{122}) + (\underline{123}) + (\underline{124})$$

6.E.2 Mechanism for Formation of Compound (120)

The most likely mechanism is outlined in scheme 9. The reaction of, for example, cyclobutylmethyl chloride with sodium metal is well known to result in ring opening of the cyclobutane ring,[250,251] due to rearrangement of the intermediate cyclobutylmethyl anion.

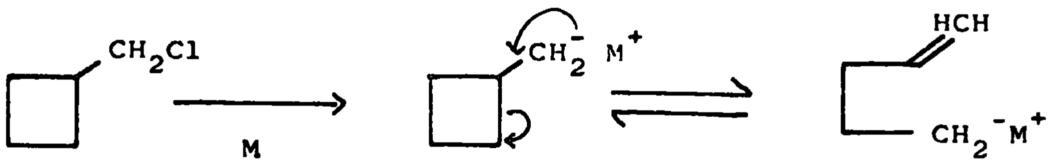
Scheme 9

Fluoride Ion Induced Rearrangement of Trimer (18)



(18) (125) (125a) (120a) (120)

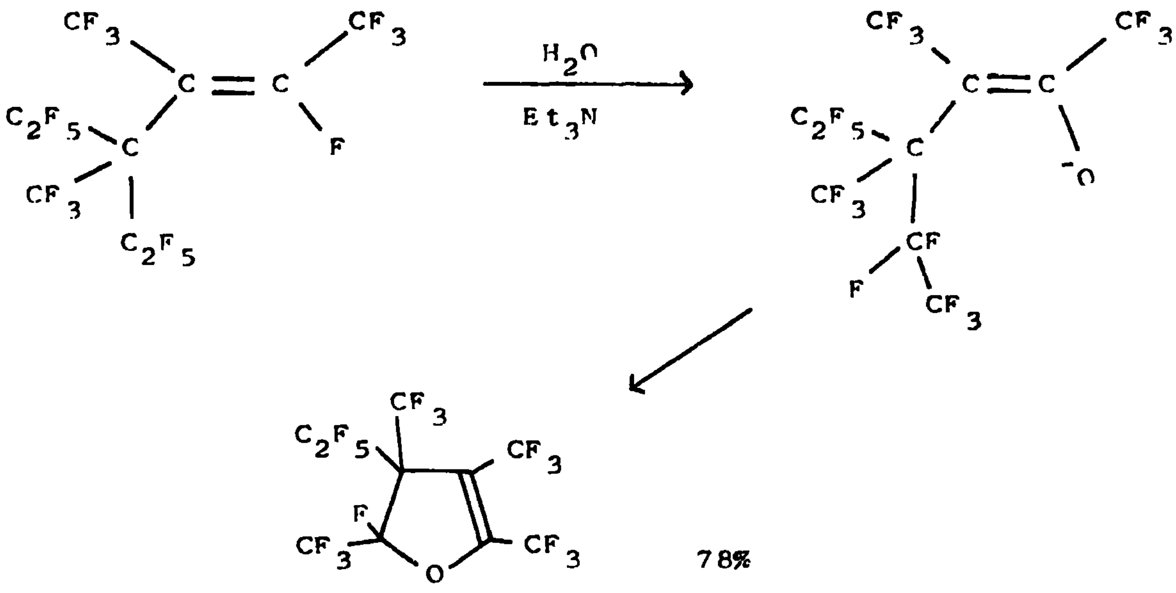
c.f.



M = Na, Li, Mg [250,251]

It can easily be seen that reaction of (125) to give (125a) is another example of this type of ring opening. It seems unlikely that the lifetime of (125a) is very long and reaction of (125) to give (120a) is probably concerted.

Although not a common reaction, intramolecular displacements of fluoride ion from a saturated carbon have been reported, e.g. the reaction of the pentamer, from oligomerisation of F-ethylene, with aqueous base:-[229]

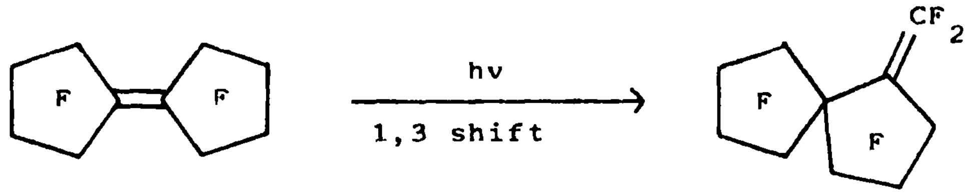


Thus, reaction of (125a) to give (120a) is not without precedent although the reason for displacement of the tertiary fluorine rather than reversion to (18), for example, is not clear. An attempt to trap anionic intermediates by carrying out the reaction in the presence of bromine was unsuccessful.

Obviously, more examples of similar rearrangements are needed before a rationale of the reasons for this reaction can be advanced.

6.F Photochemically Induced Rearrangements

It is reported that photolysis of F-1,2-dialkylcyclopentenes results in high yields of products arising from 1,3-shifts.[32] In particular, photolysis of the F-cyclopentene dimer, (37), is reported to give compound (126) although no experimental details were given. This reaction cannot be repeated in the Durham laboratories.[233]



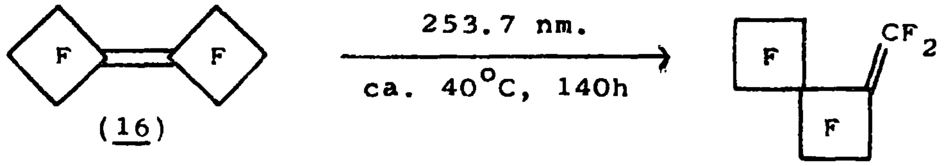
(37)

(126)

6.F.1 Photolysis of F-Methylenecyclobutanes

6.F.1a Dimer (16)

Dimer (16) undergoes a rapid, near quantitative rearrangement (1,3-shift) upon mercury sensitised photolysis to give compound (127).



(16)

ca. 95%

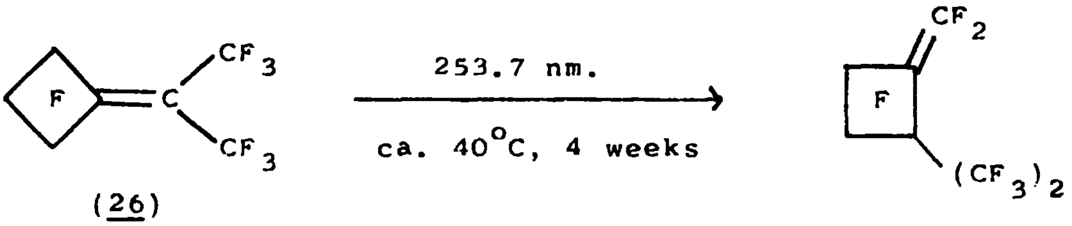
(127)

Compound (127) was identified from its ^{19}F n.m.r. spectrum which shows signals due to a terminal difluoromethylene group, two $-CF_2-$ groups, and a cyclobutane ring (two AB's in the ratio 2:1)

6.F.1b Compounds (26) and (31)

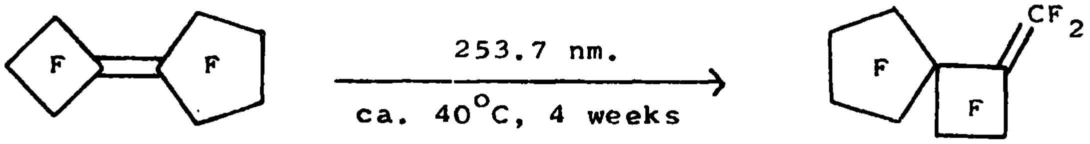
Similar rearrangements occurred for compounds (26) and (31) to give (128) and (129) respectively. However, in both cases, the reactions were far slower; this is presumably a measure of the angle strain present in the starting alkenes. Compound (129) was assigned the structure shown, rather than the alternative (129a), since the C=C absorption in the infrared spectrum occurs in the same position as that for compound (127), and it is well known that the absorption frequency of exocyclic double bonds decreases with increasing ring size.[252]

It seems probable that this type of rearrangement is general to all F-methylenecyclobutanes.



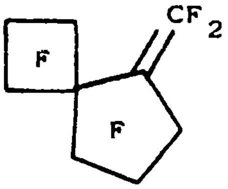
(26)

(128) ca. 90%



(129) ca. 90%

not

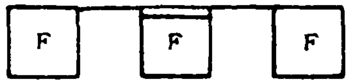


(129a)

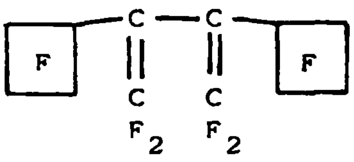
6.F.2 Other Photolysis Reactions

An attempt was made to repeat the reported photolysis of compound (37), but it was not successful.

Photolysis of diene (117) gave a highly complex mixture, whilst trimer (18) and diene (116) were unaffected by prolonged irradiation.

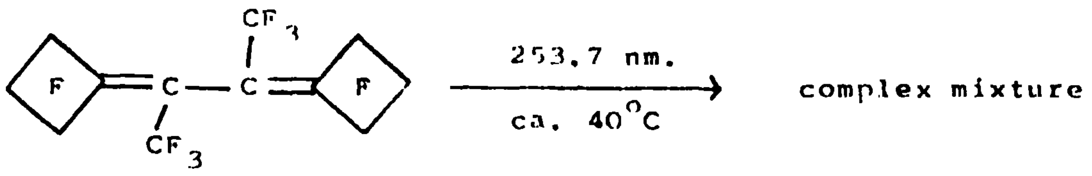


(18)



(116)

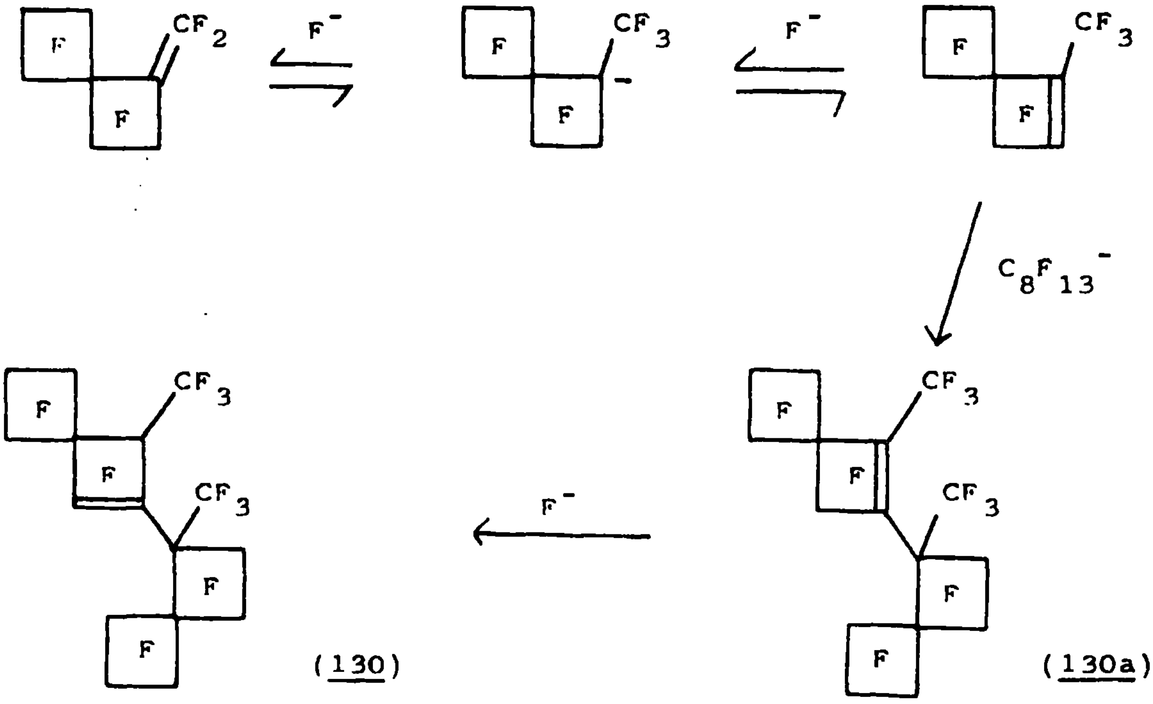
$\xrightarrow[\text{ca. } 40^{\circ}\text{C}]{253.7 \text{ nm.}}$ no reaction



(117)

6.F.3 Dimerisation of Compound (127)

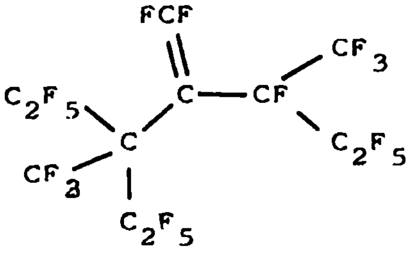
With fluoride ion, compound (127), unexpectedly dimerised to give a product tentatively assigned structure (130).



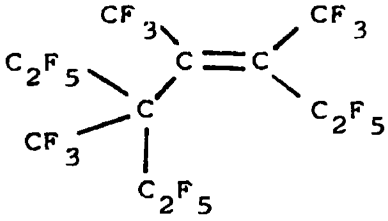
(130)

(130a)

The reason why structure (130), with a destabilising vinylic fluorine, is adopted in preference to (130a) is puzzling. It is possible that structure (130) has fewer eclipsing interactions than (130a) and that this is why it is preferred. Unfortunately, the situation is not clarified by the use of space-filling models. A similar situation exists for the hexamer of F-ethylene, which adopts structure (131) rather than the expected (131a), since the former minimises eclipsing interactions.



(<u>131</u>)



(<u>131a</u>)

6.G <u>Conclusion</u>

It can be seen, in conclusion, that F-cyclobutene oligomers undergo several types of rearrangements which are interesting, not only from a mechanistic point of view, but also from a synthetic standpoint. Thus, for example, the rearrangement of trimer (<u>18</u>) provides a facile route to a crowded diene (i.e. <u>117</u>), or, with fluoride ion, a facile route into a fully fluorinated seven-membered ring system (i.e. <u>120</u>).

EXPERIMENTAL

Chemicals

The caesium fluoride used was reagent grade, and was dried by strong heating (ca. 180°C) under high vacuum with frequent agitation and periodic grinding in a glove bag. It was stored under dry nitrogen. Potassium fluoride was dried by strong heating in air followed by grinding and then heating under vacuum.

Pyridine was redistilled and stored over type 4A molecular sieve under nitrogen.

Perfluorocyclobutene was prepared by the standard route.[13] Thus, in a typical experiment, Arcton 113 ($CF_2ClCFCl_2$) (800 ml) was added to a well stirred suspension of zinc dust (500g) in refluxing meths (800 ml). The rate of addition was such as to maintain reflux. The evolved gas, chlorotrifluoroethylene, was trapped out by passing it through two liquid air traps. When the addition was complete, the mixture was refluxed for one hour and then the contents of the cold traps (410g) transferred, under vacuum, to a one litre, stainless steel bomb. This was heated for 24h at 125°C, 24h at 150°C, 24h at 175°C, 24h at 200°C and 24h at 225°C. The bomb was allowed to cool and then vented; there was little, if any, gas remaining. The liquid contents (402g) were poured out and shown by g.l.c. analysis to be mainly dichlorohexafluorocyclobutane. This was dechlor--inated in an analagous way to the Arcton 113, using zinc dust (200g) and meths (500 ml). The gaseous product was redistilled at ca. 5°C to give perfluorocyclobutene (230g, 81% based on chlorotrifluoroethylene).

Solvents

Dimethylformamide (DMF) was fractionally distilled under vacuum, the middle fraction being collected over dry molecular sieve (type 4A) and stored under nitrogen.

Tetraglyme was purified by stirring with sodium metal at 95°C for 24h, followed by fractional distillation under vacuum, the middle fraction being collected over molecular sieve (type 4A) and stored under nitrogen.

Any other solvents used, e.g. ether, were pre-dried by standard methods.

Instrumentation

Infrared spectra were recorded on a Perkin-Elmer 457 Grating Infrared Spectrophotometer using conventional techniques.

Raman spectra were recorded using a Cary 82 Laser Raman Spectrophotometer with a Spectra-Physics Model 164 Ar/Kr laser at 19436.3 cm.$^{-1}$ (green).

Ultraviolet spectra were recorded using a Unicam SP 8000 Spectrophotometer and spectrosol grade solvents.

Mass spectra were recorded on an A.E.I. M.S. 9 Spectrometer, or on a V.G. Micromass 12B Spectrometer fitted with a Pye 104 gas chromatograph.

Proton (^{1}H) and fluorine (^{19}F) nuclear magnetic resonance spectra were recorded on a Varian A56/60D spectrometer, operating at 60 and 56.4 MHz respectively. Chemical shifts are quoted relative to external T.M.S. and $CFCl_3$. Variable temperature facilities permitted spectra to be recorded at temperatures other than the standard probe temperature of 40^{o}C. Carbon (^{13}C) n.m.r. spectra were recorded on a Joel 100 Spectrometer by Dr. J. Wood of I.C.I. Mond Division.

Quantitative gas line chromatographic analysis was carried out using a Griffin and George D6 Gas Density Balance or a Varian Aerograph Model 920, using columns packed with 30% silicone gum rubber SE-30 on chromosorb P (column O), 20% di-isodecyl phthalate on chromosorb P (column A), and 17% 2-cyanomethyl--silicone on chomosorb P (column Z). Preparative scale gas line chromatography was carried out on a Varian Aerograph Model 920 using columns O, A, Z, or D (30% dinonyl-phthalate on chromosorb P).

Fractional distillations of product mixtures were carried out using a small or large concentric tube; Fischer-Spaltrohr MS 200 and HMS 500 systems.

Carbon, nitrogen and hydrogen analyses were obtained using a Perkin-Elmer 240 Elemental Analyser. Analyses for halogens were performed by the literature method.[253]

Unless otherwise stated, boiling points were determined by Siwoloboff's method and are uncorrected.

CHAPTER 7

EXPERIMENTAL TO CHAPTER 2

7.A Oligomerisation of F-Cyclobutene

7.A.1 With Fluoride Ion

7.A.1a

A nickel tube containing a mixture of F-cyclobutene (38.9g, 240.1 mmol), caesium fluoride (6.2g, 40.8 mmol) and DMF (30 ml) was rotated at room temperature for 72h. The tube was opened and the volatiles transferred to a cold trap under vacuum. The lower fluorocarbon layer was removed, washed with water, dried (P_2O_5) and then transferred under vacuum to a cold trap. The resultant liquid (36.7g, 94% recovery) was shown by g.l.c. (cols O and Z) to be a five component mixture subsequently identified as: F-cyclobutylidene (16), (11%); F-1-cyclobutyl-cyclobutene (17), (10%); F-1-(1'-cyclobutylcyclobutyl)cyclobutene (19), (67%); F-1-(1'-cyclobutylcyclobutyl)-2-cyclobutylcyclobutene (22), (8%); and a component (4%) which was not characterised but was identified as a $C_{12}F_{18}$ isomer by g.l.c.-ms.. Fractional distillation gave fractions boiling at: 79-80°C, shown to be pure compound (16); 80-84°C, shown to be a mixture of compounds (16) and (17); 84-85°C, shown to be pure compound (17);higher boiling fractions shown to be mainly compound (19). The pot residue consisted of compounds (19) and (22) and these were separated by preparative scale g.l.c. (col O). The compound (22) thus obtained contained a minor impurity, identified by g.l.c.-ms. as $C_{16}F_{22}$ (ca. 5%). This was removed by preparative g.l.c. using column Z.

For compound (16): (Found: F,70.6%; M^+,324. C_8F_{12} requires: F,70.37%; M,324); I.r. spectrum no. 1, n.m.r. spectrum no. 1. A Raman spectrum contained a C=C stretch at 5.68µm.

For compound (17): (Found: F, 70.8%; M^+, 324. C_8F_{12} requires: F, 70.37%; M, 324); I.r. spectrum no. 2, n.m.r. spectrum no.2.

For compound (19): I.r. spectrum no. 3, n.m.r. spectrum no. 3.

For compound (22): (Found: C, 29.7; F, 69.07; M^+, 648. $C_{16}F_{24}$ requires: C, 29.63; F, 70.37%; M, 648); I.r. spectrum no. 4, n.m.r. spectrum no. 4.

7.A.1b

A mixture of caesium fluoride (6.0g, 39.5 mmol) and tetraglyme (30 ml) was placed in a flask fitted with a variable gas reservoir. The system was evacuated and F-cyclobutene (12.1g, 74.7 mmol) vented in. The mixture was stirred at room temperature for 18h and then flash distilled to give a product (8.5g) shown by g.l.c. analysis (col O) to be a mixture of F-cyclobutene and its oligomers with trimer (19) forming 60% of the mixture.

7.A.1c

In similar reactions F-cyclobutene was only very slowly oligomerised on stirring at atmospheric pressure and room temperature with KF and tetraglyme, KF and DMF, or CsF and sulpholan.

At higher temperatures oligomerisation was more rapid but trimer (19) was always the major product.

There was no detectable reaction when F-cyclobutene was rotated at room temperature in a nickel tube in the presence of acetonitrile and CsF.

7.A.1d Dimerisation of Compounds (16) and (17)

A mixture of CsF (0.31g, 2.04 mmol), dimers (16) and (17) (3.11g, 9.60 mmol), and DMF (10 ml) was stirred for 100h at room temperature. The volatiles were then transferred under vacuum to a cold trap and the lower fluorocarbon layer removed, washed with water, dried (P_2O_5), and transferred to a cold trap under vacuum. The resultant liquid (2.43g, 78% recovery) was shown by g.l.c. (cols O and Z) to be essentially a mixture of dimers (16) and (17) and two other components which were identified by g.l.c.-ms. as a tetramer, $C_{16}F_{24}$ (ca. 80%) and a defluorinated tetramer, $C_{16}F_{22}$ (ca. 5%). A sample of the tetrameric product was seperated by preparative scale g.l.c. and identified as compound (22) by comparison of spectra.

7.A.1e Reaction of Compound (22) with Excess Fluoride Ion

A mixture of compound (22) (0.72g, 1.11 mmol), excess caesium fluoride , and DMF (5 ml) was stirred for 24h at room temperature. The volatiles were transferred under vacuum to a cold trap and the lower fluorocarbon layer (0.47g) removed. This was shown by g.l.c. (col O) and infrared spectroscopy to be essentially a mixture of dimers (16) and (17).

7.A.1f Reaction of Trimer (19) with Fluoride Ion

A mixture of CsF (3.8g, 25.0 mmol), trimer (19) (1.94g, 3.99 mmol), and DMF (10 ml) was stirred for 200h at room temperature. The volatiles were then transferred under vacuum to a cold trap and the lower fluorocarbon layer (1.17g, 60% recovery) shown by infrared spectroscopy and g.l.c. (col O) to be unchanged trimer (19).

Similar reactions were carried out at temperatures of up to 100°C in both DMF and tetraglyme as solvent. However, in all cases, only unchanged trimer (19) was detected in the resulting fluorocarbon.

7.A.2 With Pyridine

General Procedure

A mixture of pyridine and F-cyclobutene was placed in an evacuated tube fitted with a 'rotaflow' tap and a side-arm. The tap was closed and the mixture stirred at room temperature. The progress of the reaction was checked by fitting the side-arm to a variable gas reservoir at atmospheric pressure and carefully opening the 'rotaflow' tap: if the reservoir was inflated then the reaction was not complete and the F-cyclobutene was returned to the tube by cooling it in liquid air; if the reservoir was unaffected then, again, reaction was incomplete, since the tube contained an atmosphere of F-cyclobutene; if the reservoir deflated then reaction was complete (or nearly so) since the tube was under a vacuum.

When the reaction was complete the volatiles were transferred out under vacuum to a cold trap. Throughout this transference the tube was maintained at ca. 40°C (or, initially, below this) and the contents were stirred. When this transference was complete the cold traps were changed and the reaction tube heated to ca. 100°C when a further small amount of product was obtained. This fraction was heavily contaminated with pyridine and was very difficult to purify. The first fraction was washed with water, dried (P_2O_5) and transferred under vacuum to a cold trap.

7.A.2a

A mixture of pyridine (1.2g, 15.2 mmol) and F-cyclobutene (38.0g, 234.6 mmol) was stirred for 130h to give a product (30.8g, 81% recovery) which was shown by g.l.c. to be a four component mixture subsequently identified as: F-cyclobutene (3%); compound (16) (35%); compound (17) (29%); and F-1,2-dicyclobutylcyclobutene (18) (33%). Fractional distillation gave fractions boiling at: 79-80°C, shown to be pure compound (16); 80-84°C, shown to be a mixture of compounds (16) and (17); 84-85°C, shown to be pure compound (17); 85-147°C (small), shown to be a mixture of compounds (17) and (18); 147-148°C, shown to be pure compound (18): (Found: F, 70.0%; M^+, 486. $C_{12}F_{18}$ requires: F, 70.37%; M, 486); I.r. spectrum no.5, n.m.r. spectrum no. 5. A Raman spectrum contained a C=C stretch at 6.01μm.

A similar reaction, for 15h, between pyridine (2.1g, 26.6 mmol) and F-cyclobutene (38.0g, 234.6 mmol) gave a mixture containing compounds: (16) (11%); (17) (10%); and (18) (79%); with a 67% recovery of fluorocarbon.

A third reaction, for 336h, between pyridine (1.35g, 17.1 mmol) and F-cyclobutene (54.4g, 335.8 mmol) did not reach completion. The volatiles were transferred under vacuum to a cold trap and then maintained for 2h at ca. 50°C with stirring. The evolved gas (18.1g) was collected in a liquid air trap and shown by infrared spectroscopy to be F-cyclobutene. The residue (22.2g) was shown by g.l.c. to be a mixture of F-cyclobutene (9%), compounds (16) and (17) (66%), and compound (18) (25%).

Examples of other reactions are given in scheme 5 (pg. 50).

7.A.2b Reaction of Pyridine with a Mixture Containing Dimers (16) and (17) and F-Cyclobutene

A mixture of F-cyclobutene (3.41g, 21.0 mmol), dimers (16) and (17) (3.35g, 10.3 mmol) and pyridine (0.6g, 7.6 mmol) was stirred at room temperature for 6h. The volatiles were transferred under vacuum to a cold trap and the upper pyridine layer removed. The residue (5.94g) was shown by g.l.c. (col O) to be a mixture of compounds (16) and (17) (32%) and compound (18) (68%); 68% of 5.94g is 4.04g i.e. greater than the weight of F-cyclobutene added.

7.A.2c Reaction of Dimer (16) or (17) with Pyridine

A mixture of pyridine (2 drops) and dimer (16) was stirred for 10 minutes at room temperature. The resultant fluorocarbon layer was shown by g.l.c. to be an equilibrium mixture of dimers (16) and (17) (ca. 11:9). A similar reaction with dimer (17) gave an identical ratio of dimers (16) and (17).

7.A.2d Oligomerisation with DMF as Solvent

A mixture of pyridine (1.4g, 17.7 mmol), F-cyclobutene (9.1g, 56.2 mmol) and DMF (10 ml) was stirred, in a sealed tube, at room temperature for 24h. The tube was opened and the lower fluorocarbon layer (6.3g, 69% recovery) removed. This was shown by g.l.c. to be a mixture of dimers (16) and (17) (19%) and trimer (18). No trimer (19) could be detected.

7.B Fluoride Ion Induced Co-oligomerisation Reactions

7.B.1 F-Cyclobutene with F-Propene

A mixture of F-cyclobutene (18.3g, 113.0 mmol), F-propene (17.2g, 114.7 mmol), CsF (8.7g, 57.3 mmol) and DMF (20 ml) was stirred at atmospheric pressure (in a flask fitted with a variable gas reservoir) for 3h. The flask became very hot during the reaction and the gas reservoir was fully deflated after ca. 1h. Volatile material was transferred under vacuum to a cold trap, the lower fluorocarbon layer removed and washed with water, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (33.2g, 90% recovery) was shown by g.l.c.-ms. to be a highly complex mixture containing compounds: (26), C_7F_{12}; (27), $C_{10}F_{18}$; (28), $C_{10}F_{18}$, (>20%); (29), $C_{11}F_{18}$, (>30%); oligomers of F-propene; and trace amounts of material with MW 500, which were not identified.

Fractional distillation gave: pure compound (26) (2.1g, 6%) b.p. 68-69°C; a small intermediate fraction b.p. 69-113°C; and various fractions b.p. 113-141°C shown by g.l.c. to be mixtures of compounds (27) - (29) and F-propene trimers in varying proportions. Samples of compounds (27) - (29) were obtained by preparative scale g.l.c. of enriched distillation fractions.

Compound (26) was identified as F-2-propylidenecyclobutane: (Found: F, 72.5%; M^+, 312. C_7F_{12} requires: F, 73.08%; M, 312);

I.r. spectrum no. 6, n.m.r. spectrum no. 6.

Compound (27) was identified as F-2 cyclobutenyl-2-methyl-pentane: b.p. 112°C; (Found: F, 74.0%; M^+, 462. $C_{10}F_{18}$ requires: F, 74.03%; M, 462); I.r. spectrum no. 7, n.m.r. spectrum no. 7.

Compound (28) was identified as F-2-cyclobutenyl-2,3-dimethyl-butane: b.p. 120°C; (Found: F, 74.4%; M^+, 462. $C_{10}F_{18}$ requires: F, 74.03%; M, 462); I.r. spectrum no. 8, n.m.r. spectrum no. 8.

Compound (29) was identified as F-2-cyclobutenyl-2-cyclo-butylpropane: b.p. 140°C; (Found: F, 71.9%; M^+, 474. $C_{11}F_{18}$ requires: F, 72.15%; M, 474); I.r. spectrum no. 9, n.m.r. spectrum no. 9.

A similar reaction in acetonitrile as solvent was much slower (72h) and gave a mixture containing compound (28) (ca. 50%) and compound (29) (ca. 40%) with small amounts of other components.

7.B.2 F-Cyclobutene with F-2-Butene

A mixture of F-cyclobutene (18.9g, 116.7 mmol), F-2-butene (21.0g, 105.0 mmol), CsF (6.0g, 39.5 mmol) and DMF (30 ml) was stirred at room temperature and atmospheric pressure for 10 days. Gaseous material (8.1g) was removed from the variable gas reservoir and shown to be a mixture of F-cyclobutene and F-2-butene by infrared spectroscopy. Volatile material was then transferred under vacuum from the reaction flask to a cold trap. The lower fluorocarbon layer was removed, washed with water, dried (P_2O_5) and transferred under vacuum to a cold trap. Distillation gave a fraction (12.1g) b.p. 75-85°C shown by ^{19}F n.m.r. spectroscopy to be mainly (ca. 80%) F-2-butylidenecyclobutane (30), containing small amounts of compounds (16), (17) and (40) (F-3,4-dimethylhex-3-ene). The pot residue was shown by g.l.c.-ms. to consist mainly of two $C_{12}F_{20}$ isomers (which were not characterised) together with a small amount of trimer (19) and other unidentified species. A pure sample of compound (30) was obtained by a combination of repeated fractional distillation and preparative scale g.l.c. (cols O and Z): b.p. 85-86°C; (Found: C, 26.3; F, 73.2%; M^+, 362. C_8F_{14} requires: C, 26.52; F, 73.48%; M, 362); I.r. spectrum no. 10, n.m.r. spectrum no. 10.

A similar reaction at 70°C gave a much greater proportion of higher molecular weight material and little compound (30).

7.B.3 F-Cyclobutene with F-Cyclopentene

A mixture of F-cyclo-butene (8.4g, 51.0 mmol), F-cyclopentene (10.5g, 49.5 mmol), CsF (4.5g, 29.6 mmol) and DMF (20 ml) was stirred at atmospheric pressure and room temperature for 150h. Volatile material was transferred under vacuum to a cold trap. The lower fluorocarbon layer was removed, washed with water, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (15.8g, 83% recovery) was shown by g.l.c.-ms. to be a highly complex mixture with the major product being a mixture of $C_{13}F_{20}$ isomers. A small C_9F_{14} fraction was isolated by fractional distillation and shown by g.l.c. (col O) to be a mixture of two (or more) compounds in the approximate ratio 20:1. The major isomer was separated by preparative scale g.l.c. and identified as F-cyclobutylidenecyclopentane (31): b.p. 103°C; (Found: C, 28.7; F, 70.6%; M^+, 374. C_9F_{14} requires: C, 28.88; F, 71.12%; M, 374); I.r. spectrum no. 11, n.m.r. spectrum no. 11. A Raman spectrum contained a C=C stretch at 5.72 μm.

7.B.4 F-Cyclobutene with F-Cyclohexene

A mixture of F-cyclobutene (19.4g, 119.8 mmol), F-cyclohexene (25.8g, 98.5 mmol), CsF (6.3g, 41.5 mmol) and DMF (20 ml) was stirred at room temperature and atmospheric pressure for 48h. Volatile material was transferred under vacuum to a cold trap. The lower fluorocarbon layer was removed, washed with water, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (40.2g, 89% recovery) was shown by g.l.c. (col O) to be a mixture containing F-cyclohexene, F-cyclobutene oligomers and one other component subsequently identified by g.l.c.-ms. as a $C_{14}F_{22}$ fraction. This was obtained by a combination of fractional distillation and preparative scale g.l.c. and the resultant liquid (1.1g, 3%) shown by ^{19}F n.m.r. spectroscopy to be a mixture of isomers: (Found: C, 28.9; F, 71.8%. $C_{14}F_{22}$ requires: C, 28.67; F, 71.33%).

7.B.4 a F-Cyclobutene Dimers, (16) and (17), with F-Cyclohexene

A mixture of dimers (16) and (17) (1.41g, 4.35 mmol), F-cyclohexene (3.68g, 14.04 mmol), CsF (2.72g, 17.9 mmol) and DMF (10 ml) was stirred for 120h at room temperature. Volatile material was then transferred under vacuum to a cold trap. The resultant liquid (4.17g, 82% recovery) was shown by g.l.c. (col O) to be a mixture of dimers (16) and (17) and F-cyclo-hexene together with one other major component and several trace components which were not identified. The major new component was separated by preparative scale g.l.c. and the resultant low-melting solid (0.74g) shown to be a single $C_{14}F_{22}$ isomer, F-1-(1'-cyclobutylcyclobutyl)cyclohexene (32), (29%): (Found: F, 70.9%; M^+, 586. $C_{14}F_{22}$ requires: F, 71.33%; M, 586); I.r. spectrum no. 12, n.m.r. spectrum no. 12.

Compound (32) was identified as the major isomer present in the $C_{14}F_{22}$ fraction from the previous experiment by comparison of the ^{19}F n.m.r. spectra.

7.B.5 F-Cyclopentene with F-Propene

A mixture of F-cyclopentene (9.6g, 45.3 mmol), F-propene (9.4g, 62.7 mmol), CsF (5.6g, 36.9 mmol) and DMF (30 ml) was stirred for 3h at atmospheric pressure. The reaction flask became hot and the variable gas reservoir was deflated after ca. 1½h. Volatile material was transferred under vacuum to a cold trap. The lower fluorocarbon layer was removed, washed with water, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (17.9g, 94% recovery) was shown by g.l.c. (col O) to be a mixture of several components. Fractional distillation gave: F-cyclopentene (2.1g) containing traces of F-propene and its dimer; a fraction (9.8g) b.p. 83-84°C, identified as F-1-isopropylcyclopentene (33); and a residue (4.3g) shown by g.l.c. to be a mixture of compound (33), F-propene trimers and one other component subsequently identified as F-1,2-di-isopropylcyclopentene (34). A pure sample of compound (34) was obtained by preparative scale g.l.c.. Yields of compounds (33) and (34) were ca. 74 and 10% respectively, based on F-cyclopentene consumed.

For compound (33): (Found: F, 73.8%; M^+, 362. C_8F_{14} requires: F, 73.48%; M, 362); I.r. spectrum no. 13, n.m.r. spectrum no. 13.

For compound (34): (Found: C, 25.9; F, 74.7%; M^+, 512. $C_{11}F_{20}$ requires: C, 25.78; F, 74.22%; M, 512); I.r. spectrum no. 14, n.m.r. spectrum no. 14.

7.B.6 F-Cyclohexene with F-Propene

A mixture of F-propene (12.3g, 82.0 mmol), F-cyclohexene (12.7g, 48.5 mmol), CsF (7.1g, 46.7 mmol) and DMF (30 ml) was stirred at room temperature for 6h. Volatile material was then transferred under vacuum to a cold trap. The lower fluorocarbon layer was removed, washed with water, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (23.7g, 95% recovery) was shown by g.l.c. (cols O and A) to be a mixture of F-cyclohexene, oligomers of F-propene and one other component subsequently identified as F-1-isopropyl-cyclohexene (35). A ^{19}F n.m.r. spectrum of the product mixture indicated that compound (35) was the major component. A pure sample was obtained by a combination of fractional distillation and preparative scale g.l.c. (col A): b.p. 108-109°C; (Found: F, 74.0%; M^+, 412. C_9F_{16} requires: F, 73.79%; M, 412); I.r. spectrum no. 15, n.m.r. spectrum no. 15.

7.B.7 F-Cyclohexene with F-Cyclopentene

A mixture of F-cyclopentene (8.1g, 38.2 mmol), F-cyclohexene (13.6g, 51.9 mmol), CsF (5.8g, 38.2 mmol) and DMF (20 ml) was stirred at ca. 80°C for 120h in a sealed tube. The tube was allowed to cool and the volatiles transferred under vacuum to a cold trap. The lower fluorocarbon layer was removed, washed with water, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (19.2g, 88% recovery) was shown by g.l.c. (col Z) to be a mixture of F-cyclohexene (36%) and three other components subsequently identified as F-cyclopentene dimer (37) (17%), F-cyclohexene dimer (38) (8%), and F-1-cyclohexylcyclopentene (36) (39%). The yield of compound (36) was 61% based on F-cyclohexene consumed. Fractional distillation gave a fraction, b.p. 145-146°C, shown to be pure compound (36): (Found: C, 27.6; F, 72.6%; M^+, 474. $C_{11}F_{18}$ requires: C, 27.85; F, 72.15%; M, 474); I.r. spectrum no. 16, n.m.r. spectrum no. 16.

Compounds (37) and (38) were identified by comparison of their I.r. and ^{19}F n.m.r. spectra with those of authentic samples.[148]

A similar reaction was carried out at ca. 110°C in sulpholan as solvent. The product (91% recovery) was shown by g.l.c. (col O) to be a mixture of F-cyclopentene (4%), F-cyclohexene (31%), compound (37) (27%), compound (36) (36%), and compound (38)

(2%). The yield of (<u>36</u>) was 66%, based on consumed F-cyclo-hexene.

7.C Attempted Oligomerisations with Pyridine

7.C.1 With F-Ethylene

Pyridine (40 ml) was placed in a steel autoclave (300 ml capacity) which was then charged with stabilised F-ethylene to a pressure, at 10°C, of 150 psi. The mixture was stirred at room temperature for 2h then at 100°C for 1h. The autoclave was allowed to cool (the pressure was 147 psi) and then vented. The contents were poured into water but no lower layer seperated.

A similar reaction using DMF as solvent whilst heating for 24h at 100°C, produced analagous results. A ^{19}F n.m.r. spectrum of the product liquid did not indicate the presence of any dissolved fluorocarbon.

7.C.2 With F-Propene

A mixture of pyridine (1.7g, 21.5 mmol) and F-propene (8.8g, 58.7 mmol) was stirred for 48h at room temperature in a sealed tube. The tube was opened and the volatiles transferred under vacuum to a cold trap. The resultant gas (7.2g, 81% recovery) was identified as F-propene by infrared spectroscopy. The residue in the reaction tube was a black tarry substance and was not investigated.

7.C.3 With F-2-Butene

A mixture of pyridine (1.0g, 12.7 mmol) and F-2-butene (12.1g, 60.5 mmol) was stirred for 96h at room temperature in a sealed tube. The tube was opened and the volatiles transferred under vacuum to a cold trap. The resultant gas (10.7g, 88% recovery) was identified as F-2-butene by infrared spectroscopy. The residue in the reaction tube was shown to contain pyridine (by i.r.) but no oligomerisation could be detected.

7.C.4 With F-Cyclopentene

A mixture of pyridine (1.3g, 16.9 mmol) and F-cyclopentene (13.4g, 63.2 mmol) was stirred at ca. 80°C for 24h in a sealed tube. The volatiles (11.1g, 83% recovery) were transferred under vacuum to a cold trap and shown by g.l.c. to be unchanged F-cyclopentene.

7.C.5 With F-Cyclohexene

A mixture of pyridine (1.3g, 16.9 mmol) and F-cyclohexene (15.0g, 57.3 mmol) was stirred at ca. 95°C for 24h in a sealed tube. The volatiles (13.1g, 87% recovery) were transferred under vacuum to a cold trap and shown by g.l.c. to be unchanged F-cyclohexene.

7.C.6 With Chlorotrifluoroethylene

A mixture of pyridine (1.43g, 18.1 mmol) and chlorotrifluoroethylene (9.2g, 79.0 mmol) was stirred at room temperature for 200h in a sealed tube. The mixture was homogeneous and no tarring was observed. The tube was opened and the volatiles (9.9g) transferred under vacuum to a cold trap. These separated into a gas and a liquid identified as C_2F_3Cl and pyridine, respectively, by infrared spectroscopy.

7.D Attempted Co-oligomerisations with Pyridine

7.D.1 F-Cyclobutene with F-Cyclopentene

A mixture of pyridine (3.0g, 38.0 mmol), F-cyclopentene (33.3g, 157.1 mmol) and F-cyclobutene (5.2g, 32.1 mmol) was placed in a tube fitted with a 'rotaflow' tap and stirred at room temperature. Further F-cyclobutene (20.0g, 123.4 mmol) was added in five portions over the following 5h and the mixture then stirred for another 24h. The volatiles were transferred under vacuum to a cold trap and distilled using a small Vigreux column to give F-cyclo-pentene (18.9g) and a residue which was washed with water, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (27.9g) was shown by g.l.c. (col O) to be a mixture of F-cyclopentene (19%), compound (16) (15%), compound (17) (13%), compound (18) (12%), and F-cyclobutylidenecyclopentane (31) (41%). These were separated by fractional distillation and the compound (31) thus obtained shown by g.l.c. (col Z) to contain ca. 5% of an isomer which was not identified (c.f. co-oligomerisation with fluoride ion 7.B.3). The yield of compound (31), based on consumed F-cyclopentene, was 71%.

In a second reaction pyridine (2.4g, 30.4 mmol), F-cyclo-butene (17.6g, 108.6 mmol) and F-cyclopentene (27.0g, 127.4

mmol) gave a liquid (28.4g) containing ca. 26% of compound (31) together with F-cyclopentene and the expected F-cyclobutene oligomers, (16)-(18). Also obtained was unchanged F-cyclo-pentene (11.1g).

7.D.2 F-Cyclobutene with F-Propene

A mixture of F-cyclobutene (11.6g, 71.6 mmol), pyridine (1.0g, 12.7 mmol) and F-propene (9.1g, 60.7 mmol) was stirred at room temperature in a sealed tube for 42h. The tube was opened and a gaseous fraction (7.9g) collected and shown by infrared spectroscopy to be F-propene (86% recovery). Volatile material in the residue was transferred under vacuum to a cold trap, washed with water (there was some effervescence, probably due to residual F-propene), dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (7.1g) was shown by g.l.c. (col O) to be a typical mixture of F-cyclobutene oligomers, (16)-(18); no co-oligomers could be detected.

7.D.3 F-Cyclobutene with F-2-Butene

A mixture of pyridine (1.2g, 15.2 mmol), F-cyclobutene (13.8g, 85.2 mmol) and F-2-butene (23.2g, 116.0 mmol) was stirred at room temperature for 72h. The tube was opened and a gaseous fraction (11.4g) removed. This was shown by infrared spectroscopy to be F-2-butene. Volatile material in the residue was transferred under vacuum to a cold trap and then maintained at ca. 40°C for 1h with stirring, when a further amount of F-2-butene was obtained (7.2g). The residue was washed with water, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid was shown by g.l.c. (col O) to be a mixture of the expected F-cyclobutene oligomers, (16)-(18), and F-2-butene. No co-oligomers could be detected.

7.D.4 F-Cyclobutene with F-Cyclohexene

A mixture of F-cyclo-butene (15.3g, 94.4 mmol), F-cyclohexene (18.6g, 71.0 mmol) and pyridine (1.2g, 15.2 mmol) was stirred for 48h at room temperature. Volatile material was transferred under vacuum to a cold trap, washed with water, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (31.5g) was shown by g.l.c. (col O) to be a mixture of F-cyclobutene oligomers, (16)-(18), and F-cyclohexene; no co-oligomers could be detected.

7.D.5 F-Cyclobutene with Chlorotrifluoroethylene

A mixture of pyridine (3.19g, 40.4 mmol), F-cyclobutene (13.4g, 82.7 mmol) and chlorotrifluoroethylene (11.9g, 102.2 mmol) was stirred at room temperature for 180h. The volatiles were transferred under vacuum to a cold trap and then stirred for 1h at ca. 40°C. The evolved gas (10.5g) was shown by infrared spectroscopy to be unchanged C_2F_3Cl. The residue was washed with water, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (7.1g) was shown by g.l.c. (col O) to be the expected oligomer mixture, (16)-(18). No co-oligomers could be detected.

CHAPTER 8

EXPERIMENTAL TO CHAPTER 3

8.A Anion from F-Cyclobutene Dimers, (16) and (17)

8.A.1 Trapping with Bromine

A mixture of CsF (4.5g, 29.6 mmol), dimers (16) and (17) (3.4g, 10.5 mmol) and DMF (20 ml) was stirred at room temperature for 10 minutes. Stirring was then discontinued and the mixture allowed to stand for 30 minutes. A small sample of the resultant liquid was removed and its ^{19}F n.m.r. recorded at various temperatures. The solution was found to contain the F-1-cyclobutylcyclobutyl anion (23): n.m.r. spectrum no. 17.

To the residue was added bromine (1.7g, 10.6 mmol) and the mixture stirred for 1h. The volatiles were then transferred under vacuum to a cold trap and poured into water. The lower fluorocarbon layer was removed, washed with water, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (4.0g) was shown by g.l.c. (col O) to be a single component identified as 1-bromo-F-1-cyclobutylcyclobutane (45) (90%): (Found: C, 22.5; F, 58.6; Br, 19.6%; M^+, 424 (^{81}Br). $C_8F_{13}Br$ requires: C, 22.70; F, 58.41; Br, 18.89%; M, 424 (^{81}Br)); b.p. 125°C; I.r. spectrum no. 17, n.m.r. spectrum no. 18.

Similar reactions were carried out using KF instead of CsF and tetraglyme instead of DMF. In both cases the spectrum of anion (23) was relatively unchanged and compound (45) was obtained on quenching with bromine.

8.A.2 Attempted Trapping with Iodine

A mixture of CsF (3.2g, 21.1 mmol), dimers (16) and (17) (2.5g, 7.7 mmol), iodine (2.0g, 7.9 mmol) and tetraglyme (10 ml) was stirred at room temperature for 1 week and then at ca. 60°C for a further week. Volatile material (1.9g) was transferred under vacuum to a cold trap and shown by g.l.c. (col O) to be a mixture of dimers (16) and (17) (73%) and iodine. The residue was poured into water (100 ml), decolourised with sodium thiosulphate and ether extracted but no tractable products were obtained.

8.A.3 Attempted Trapping with F-Diazines

A mixture of dimers (16) and (17) (2.28g, 7.04 mmol), CsF (3.8g, 25.0 mmol), F-pyrimidine (0.51g, 3.36 mmol) and DMF (20 ml) was stirred for 66h at room temperature. The volatiles were transferred under vacuum to a cold trap and the lower fluorocarbon layer removed (1.42g). This was shown to be mainly a mixture of dimers (16) and (17) by g.l.c.. The upper layer was shown by n.m.r. spectroscopy to contain dimers (16) and (17) and F-pyrimidine, in DMF.

The experiment was repeated at ca. 80°C using sulpholan as a solvent. Again no F-alkylation of the F-pyrimidine was observed.

Similar results were obtained for reactions using F-pyrid--azine instead of F-pyrimidine.

8.A.4 Estimation of Fluoride Ion Present in Anion (23)

A mixture of dimers (16) and (17) (2.56g, 7.90 mmol), excess CsF and DMF (20 ml) was stirred for 30 minutes at room temperature and then filtered under partial vacuum through a Schlenk tube. Volatile material was then transferred under vacuum from the filtrate to a cold trap, to leave CsF (1.17g, 7.70 mmol). Thus, within experimental error, the ratio of fluoride ion to F-cyclobutene dimer present in anion (23) is 1:1. The cold trap contents separated into a lower layer (1.53g), shown by g.l.c. (col O) to be a mixture of dimers (16) and (17), and an upper, DMF, layer shown by ^{19}F n.m.r. spectroscopy to contain some dissolved dimers.

8.B Anion from F-2-Propylidenecyclobutane (26)

A mixture of CsF (1.24g, 8.16 mmol), compound (26) (0.72g, 2.31 mmol) and DMF (5 ml) was stirred for 15 minutes at room temperature. A small sample of the liquid was removed and its ^{19}F n.m.r. spectrum recorded at various temperatures. The solution was found to contain the F-1-isopropylcyclobutane anion (47): n.m.r. spectrum no. 19.

To the residue was added bromine (0.43g, 2.69 mmol) and the mixture stirred at room temperature for 2h. The volatiles were then transferred under vacuum to a cold trap and shaken with water. The lower layer was removed, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid was shown by g.l.c. (col O) to consist of one major component and several minor ones which were not identified. The major component (0.54g) was separated by preparative scale g.l.c. and identified as <u>1-bromo-F-1-isopropylcyclobutane (49)</u>, (57%): b.p. 110°C; (Found: C, 20.2; Br, 20.1; F, 59.5%; M^+, 412 (^{81}Br). $C_7F_{13}Br$ requires: C, 20.44; Br, 19.46; F, 60.10%; M, 412 (^{81}Br)); I.r. spectrum no. 18, n.m.r. spectrum no. 20.

8.C <u>Anion from F-2-Butylidenecyclobutane (30)</u>

The procedure was as for 8.B. Thus, a mixture of CsF (3.07g, 20.21 mmol), compound (<u>30</u>) (2.08g, 5.75 mmol) and DMF (10 ml) gave a solution containing the <u>F-1-isobutylcyclobutyl anion (48)</u>: n.m.r. spectrum no. 21. Quenching with bromine (1.17g, 7.31 mmol) gave a product (2.46g) shown by g.l.c. (col O) to consist essentially of compound (<u>30</u>) (ca. 10%) and one other component which was separated by preparative scale g.l.c. and identified as <u>1-bromo-F-1-isobutylcyclobutane (50)</u>, (1.54g, 58%): (Found: C, 21.2; F, 62.8; Br, 16.7%; M^+, 462 (^{81}Br). $C_8F_{15}Br$ requires: C, 20.82; F, 61.82; Br, 17.36%; M, 462 (^{81}Br)); I.r. spectrum no. 19, n.m.r. spectrum no. 22.

8.D <u>F-Cyclopentene Dimer, (37), with Fluoride Ion</u>

Compound (<u>37</u>) did not dissolve CsF (or KF) in the presence of DMF or tetraglyme, nor was its ^{19}F n.m.r. spectrum altered by interaction with these systems.

8.E <u>Anions from F-Cyclobutylidenecyclopentane (31)</u>

The procedure was as for 8.B. Thus, a mixture of CsF (2.00g, 13.16 mmol), compound (<u>31</u>) (2.50g, 6.68 mmol) and DMF (10 ml) gave a solution thought to contain the F-1-cyclopentylcyclobutyl anion (<u>52</u>) together with the F-1-cyclobutylcyclopentyl anion (<u>53</u>) in the approximate ratio 6:1 (at 0°C; ratio obtained by integration of the respective low-field difluoromethylene signals in the ^{19}F n.m.r. spectrum of the anion mixture): n.m.r. spectrum no. 23. Quenching with bromine (1.07g, 6.69 mmol) gave a product (2.75g) shown by g.l.c. (col O) to be a mixture containing compound (31) (ca. 10%), one major component and three minor components which were not identified but which were shown to contain chlorine by g.l.c.-ms.. A sample of this mixture (2.47g) was purified by preparative scale g.l.c. and the major component (1.49g) shown by ^{19}F n.m.r. spectroscopy to be a mixture of 1-bromo-F-cyclo- pentylcyclobutane (54) and -butylcyclopentane (55) in the approximate ratio 3:1 (52%): (Found: C, 23.1; F, 59.4; Br, 17.7%; M^+, 474 (^{81}Br). $C_9F_{15}Br$ requires: C, 22.83; F, 60.25; Br, 16.91%; M, 474 (^{81}Br)); n.m.r. spectrum no. 24.

8.F Anion from F-Cyclohexene Dimer (38)

A mixture of CsF (2.7g, 17.8mmol), F-cyclohexene dimer (38) (1.43g, 2.73 mmol) and DMF (15 ml) was stirred for 1h at room temperature. A small sample of the resultant solution was removed and its ^{19}F n.m.r. spectrum recorded at various temperatures. These indicated the presence of the F-1-cyclohexylcyclohexyl anion (56) in solution: n.m.r. spectrum no. 25.

Chlorine gas (ca. 1.4g) was bubbled through the residue and the resultant solution stirred until it had cooled to room temperature. Volatile material was then transferred under vacuum to a cold trap and filtered under suction to give a white solid (1.22g). This was shown by g.l.c. (col O, ethereal solution) to be a single component with traces of DMF as impurity. A sample was purified by dissolving in ether, washing with water, drying ($MgSO_4$) and removal of the ether. The resultant solid was identified as 1-chloro-F-1-cyclohexylcyclohexane (57), (77%): m.p. 80-81°C; (Found: C, 24.9; F, 68.6; Cl, 6.6%; M^+, not observed, highest peak at M/e = 559 (^{35}Cl, M^+-19). $C_{12}F_{21}Cl$ requires: C, 24.89; F, 68.97; Cl, 6.14%; M, 578 (^{35}Cl)); I.r. spectrum no. 20, n.m.r. spectrum no. 26.

In a similar reaction trapping with bromine was attempted. Thus, to a mixture of CsF (2.45g, 16.13 mmol), compound (38) (2.17g, 4.14 mmol) and DMF (15 ml) was added bromine (0.67g, 4.19 mmol) and the resultant mixture stirred for 30h at room temperature. After this time a ^{19}F n.m.r. spectrum of the mixture still indicated the presence of anion (56) in solution. The volatiles were transferred under vacuum to a cold trap and the lower fluorocarbon layer (1.79g) was removed. This was shown by g.l.c. (col O) to be mainly compound (38) with a small amount of one other component. This minor component was separated by preparative scale g.l.c. and identified as the chloro-derivative, (57), by comparison of spectra with an authentic sample.

8.G Anion from F-1-Cyclohexylcyclopentene

The procedure was as for 8.F. Thus, a mixture of CsF (2.1g, 13.8 mmol), compound (36) (1.30g, 2.74 mmol) and DMF (10 ml) gave the F-1-cyclohexyl--cyclopentyl anion (58) in solution: n.m.r. spectrum no. 27. Quenching with chlorine gave a low-melting white solid, identified as 1-chloro-F-1-cyclohexylcyclopentane (59), (1.06g, 73%): m.p. 45°C; (Found: C,24.8; F, 68.8; Cl, 6.6%; M^+, 528 (^{35}Cl). $C_{11}F_{19}Cl$ requires: C, 24.98; F, 68.31; Cl, 6.72%; M, 528 (^{35}Cl)); I.r. spectrum no. 21, n.m.r. spectrum no. 28.

In a similar reaction trapping with bromine was attempted. The recovered fluorocarbon was shown by g.l.c.-ms. (col O) to be a mixture of compound (36) together with a small amount of the chloro-derivative (59).

CHAPTER 9

EXPERIMENTAL TO CHAPTER 4

9.A Reactions with Alcohols

9.A.1 Dimer (16) with Neutral Ethanol

Dimer (16) (1.2g, 3.7 mmol) was stirred with ethanol (5 ml) for two minutes. The fluorocarbon rapidly dissolved in the ethanol which became very warm. The mixture was poured into water, the lower fluorocarbon layer removed, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid was shown by g.l.c. (col O) to be essentially a single compound with traces of ethanol and other, unidentified species. The major component was separated by preparative scale g.l.c. and identified as 1-ethoxy-F-cyclobutenylcyclobutane (60), (1.0g, 78%): b.p. 131°C; (Found: C, 34.6; H, 1.6; F, 59.4%; M^+, 350. $C_{10}F_{11}OH_5$ requires : C, 34.29; H, 1.43; F, 59.71%; M, 350); I.r. spectrum no. 22, n.m.r. spectrum no. 29.

In an analogous reaction compound (16) (1.4g, 4.3 mmol) was stirred for 18h with ethanol (5 ml) at room temperature. The mixture was poured into water, the lower layer removed, dried (P_2O_5) and transferred to a cold trap under vacuum. The resultant liquid (1.5g) was shown by g.l.c. (cols O and Z) to be a complex mixture. The three main components were identified by g.l.c.-ms. as disubstituted compounds, $C_8F_{11}(OEt)_2$. The major component was separated by preparative scale g.l.c. and identified as 1-(1'-ethoxyhexafluorocyclobutyl)-2-ethoxytetra-fluorocyclobutene (61), (1.0g, 65%): b.p. 192°C; (Found: C, 38.4; H, 2.5; F, 50.3%; M^+, 376. $C_{12}F_{10}O_2H_{10}$ requires: C, 38.30; H, 2.66; F, 50.53%; M, 376); I.r. spectrum no. 23, n.m.r. spectrum no. 30.

9.A.1a Anion from Compound (60)

A mixture of compound (60) (0.76g, 2.17 mmol), CsF (1.43g, 9.4 mmol) and DMF (5 ml) was stirred at room temperature for 30 minutes. A small sample of the resultant solution was removed and its ^{19}F n.m.r. spectrum recorded at various temperatures. These indicated the presence of the 1-(1'-ethoxy-F-cyclobutyl)-F-cyclobutyl anion (62) in solution: n.m.r. spectrum no. 31. The residue was quenched with bromine (0.35g, 2.19 mmol) and stirred at room temperature for 1h. The volatiles were then transferred under vacuum to a cold trap and shaken with water. The lower layer was removed, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (0.72g) was shown by g.l.c. (col O) to be a single compound identified as 1-ethoxy-1-(1'-bromo-F-cyclo-butyl)-F-cyclobutane (63), (79%): b.p. 169°C; (Found: C, 26.5; F, 51.5; Br, 17.1%. $C_{10}F_{12}OH_5Br$ requires: C, 26.73; F, 50.78; Br, 17.82%); I.r. spectrum no. 24, n.m.r. spectrum no. 32.

9.A.2 Dimer (17) with Neutral Ethanol

A mixture of compound (17) (1.1g, 3.4 mmol) and ethanol (5 ml) was stirred at room temperature for 18h. The mixture was poured into water and the lower layer removed, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (1.0g) was shown by g.l.c.-ms. (col O) to be a mixture of two monosubstituted compounds, an addition product and two disubstituted compounds. The major monosubstituted compound (0.61g, 60%) was separated by preparative scale g.l.c. and identified as 1-ethoxy-F-2-cyclobutylcyclobutene (64). Also separated was the addition product (< 0.1g, ca. 8% by g.l.c.) which was identified as 1-ethoxy-2-hydro-F-2-cyclobutylcyclobutane (65). Other components were not characterised.

For compound (64): b.p. 154°C; (Found: C, 34.1; H, 1.0; F, 59.5%; M^+, 350. $C_{10}F_{11}OH_5$ requires: C,34.29; H, 1.43; F, 59.71%; M,350); I.r. spectrum no. 25, n.m.r. spectrum no. 33.

For compound (65): (Found: C, 32.4; H, 1.4%; M^+, 370. $C_{10}F_{12}OH_6$ requires: C, 32.43; H,1.62%; M, 370); I.r. spectrum no. 26, n.m.r. spectrum no. 34

In a similar reaction a mixture of compound (17) and ethanol (5 ml) was stirred for three minutes. The reaction was exothermic and the fluorocarbon was rapidly dissolved into the ethanol. The reaction mixture was treated as before and the resultant liquid (0.94g) shown by g.l.c. to be a mixture of several components, the major one of which was identified as compound (64) by ^{19}F n.m.r. spectroscopy.

9.A.3 Dimers (16) and (17) with Ethoxide Ion

Sodium metal (0.9g, 39.1 mmol) was added to dry ethanol (20 ml) and when reaction was complete a mixture of dimers (16) and (17) (2.6g, 8.0 mmol) was slowly added. There was a vigorous reaction with the formation of a white precipitate. The mixture was left stirring overnight and the ethanol removed under reduced pressure. The residue was distilled in vacuo (up to 90°C, ca. 0.1 mm Hg) to give a colourless liquid (2.3g), shown by g.l.c. (col O) to be a single compound identified as 1-(1'-ethoxyhexafluorocyclo-butyl)-2,3,3-triethoxy-4,4-difluorocyclobutene (66), (67%): b.p. >200°C; (Found: C,44.6; H, 5.0; F, 35.0%; M^+, 428. $C_{16}F_8O_4H_{20}$ requires: C, 44.85; H, 4.67; F, 35.51%; M, 428); I.r. spectrum no. 27, n.m.r. spectrum no. 35.

9.A.4 Trimer (19) with Neutral Ethanol

Trimer (19) (2.0g, 4.1 mmol) was stirred with ethanol (10 ml) for 8h at room temperature. The mixture was then poured into water and the lower layer removed, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (1.8g) was shown by g.l.c. (col O) to be a mixture of trimer (19) (ca. 6%), two mono-substituted products (ca. 90%) in the ratio 8:1, and traces of a disubstituted compound (identified by g.l.c.-ms.). The monosubstituted products were separated by preparative scale g.l.c. and identified as 1-ethoxy-F-2-(1'-cyclobutylcyclobutyl)-cyclobutene (67), (major product), and 4-ethoxy-F-1-(1'-cyclo-butylcyclobutyl)cyclobutene (68).

For compound (67): b.p. 202°C; (Found: C, 32.5; H, 0.7; F, 62.7%; M^+, 512. $C_{14}F_{17}OH_5$ requires: C, 32.81; H, 0.98; F, 63.09%; M, 512); I.r. spectrum no. 28, n.m.r. spectrum no. 36.

For compound (68): (Found: C, 32.7; H, 0.8%; M^+, not observed, peak at M/e = 483 i.e. M^+-29 (ethyl). $C_{14}F_{17}OH_5$ requires: C, 32.81; H, 0.98%; M, 512); I.r. spectrum no. 29, n.m.r. spectrum no. 37.

9.A.5 Trimer (19) with Methoxide Ion

Sodium metal (0.6g, 26.1 mmol) was dissolved in methanol (20 ml) and when the resultant solution had cooled to room temperature, trimer (19) (4.2g, 8.6 mmol) was added. There was an exothermic reaction. The mixture was stirred for 16h at room temperature and then the methanol was removed under reduced pressure. Volatile material in the residue was transferred under vacuum to a cold trap and the resultant liquid shown by g.l.c. (col A) to consist of two components in the approximate ratio 3:1 (3.6g). These were separated by preparative g.l.c. to give a liquid and a solid.

The liquid (major product) was identified as 1,3,3 -tri-methoxy-F-2-(1'-cyclobutylcyclobutyl)cyclobutene (69): b.p. >210°C; (Found: C, 34.7; H, 1.9; F, 54.2%; M^+, 522. $C_{15}F_{15}O_3H_9$ requires: C, 34.48; H, 1.72; F, 54.60%; M, 522); I.r. spectrum no. 30, n.m.r. spectrum no. 38.

The solid was recrystallised from carbon tetrachloride and identified as 1-methoxy-F-2-(1'-cyclobutylcyclobutyl)cyclobuten-3-one (70): m.p. 53-54°C; (Found: F, 59.7%; M^+, 476. $C_{13}F_{15}OH_3$ requires: F, 59.87%; M,476); I.r. spectrum no. 31, n.m.r. spectrum no. 39.

A sample of compound (70) was left open to the atmosphere for 8 days to give the corresponding hydroxy-derivative, (72), identified by comparison of its infrared spectrum with that of an authentic sample (see 9.B.2).

9.A.6 Trimer (18) with Neutral Ethanol

Trimer (18) was stirred for several days with ethanol. The two layers did not homogenise and after two weeks g.l.c. (col O) did not indicate the presence of any products in either layer.

9.A.7 Trimer (18) with Sodium Ethoxide

Sodium metal (0.65g, 28.3 mmol) was added to ethanol (20 ml) and when reaction was complete trimer (18) (2.6g, 5.4 mmol) was added and the mixture stirred overnight at room temperature. The ethanol was removed under reduced pressure and the residue sublimed in vacuo (ca. 60°C, .1 mm Hg) to give a solid (2.0g) which was recrystallised from methanol (at low temperature) and identified as 1,3-diethoxy-2-(1'-ethoxyhexafluorocyclobutyl)-F-3-cyclobutylcyclobutene (73) (66%): m.p. 52-53°C; (Found: C,38.4; H, 2.7; F, 50.4%; M^+, 564. $C_{18}F_{15}O_3H_{15}$ requires: C, 38.30; H, 2.66; F, 50.53%; M, 564); I.r. spectrum no. 32, n.m.r. spectrum no. 40.

9.B Reactions with Water

9.B.1a Dimers (16) and (17) with Excess Water

A mixture of dimers (16) and (17) (3.0g, 9.3 mmol) and aqueous acetone (20 ml) was stirred at room temperature for 24h. The acetone was removed under reduced pressure and the residue molecular distilled (ca. 60°C, 0.1 mm Hg) to give a pale yellow, viscous liquid (1.9g) identified as 1-hydroxy-2-(1'-hydroxyhexafluorocyclobutyl)-4,4-difluorocyclobuten-3-one (74), (69%): (Found: F, 51.1%. $C_8F_8O_3H_2$ requires: F, 51.01%); I.r. spectrum no. 33, n.m.r. spectrum no. 41. Compound (74) decomposes on strong heating.

Similar reactions with the separate dimers, (16),(17), also gave compound (74).

9.B.1b Dimer (16) with an Equivalent of Water

Dimer (16) (1.70g, 5.25 mmol) was dissolved in ether (10 ml) and water (94μl, 5.22 mmol) was added. The mixture was stirred for 2h at room temperature and then the ether removed by distillation to leave a colourless liquid (2.06g) shown by g.l.c. (col O) to consist of ether and two other components. These were separated by preparative scale g.l.c. to give 1-hydro-1-(1'-hydroxy-F-cyclo--butyl)-F-cyclobutane (75), (0.59g, 33%), and 1-hydroxy-F-1-cyclobutenylcyclobutane (76), (0.24g, 14%). Yields by g.l.c. were 46 and 24% respectively.

For compound (75): b.p. 107°C; (Found: C, 28.1; H, 0.7; F, 67.0%; M^+, not observed, highest peak at M/e = 322 i.e. M^+-20 (HF). $C_8F_{12}OH_2$ requires: C, 28.07; H, 0.58; F, 66.67%; M, 342); I.r. spectrum no. 34, n.m.r. spectrum no. 42.

For compound (76): b.p. 111°C; (Found: C, 29.6; H, 0.2; F, 64.7%; M^+, 322. $C_8F_{11}OH$ requires: C, 29.81; H, 0.31; F, 64.91%; M,322); I.r. spectrum no. 35, n.m.r. spectrum no. 43.

When stirred overnight in aqueous acetone, both compound (75) and (76) were hydrolysed to compound (74).

9.B.1c Dimer (17) with an Equivalent of Water

Dimer (17) (1.53g 4.72 mmol) was dissolved in ether (10 ml) and water (85μl, 4.72 mmol)added. the mixture was stirred at room temperature for 2h and then left standing overnight. The ether was removed by distillation and shown by ^{19}F n.m.r. spectroscopy to contain dimer (17) and a little dimer (16). The residue was shown by infrared and ^{19}F n.m.r. (in ether) spectroscopy to be mainly compound (74) with a minor component which was not identified.

9.B.2 Trimer (19) with Water

A mixture of trimer (19) (5.6g, 11.5 mmol) and aqueous acetone (20 ml) was stirred for 24h at room temperature. The acetone was removed under reduced pressure and the residue sublimed in vacuo (90°C, 0.1 mm Hg) to give a white solid (4.8g) identified as 1-hydroxy-2-(1'-F-cyclobutylcyclobutyl)-4,4-difluorocyclobuten-3-one (72), (90%): m.p. 181-183°C; (Found: C, 31.1; F, 62.0%; M^+, 462. $C_{12}F_{15}O_2H$ requires: C, 31.17; F, 61.69%; M, 462); I.r. spectrum no. 36, n.m.r. spectrum no. 44.

9.B.3 Trimer (18) with Water

Stirring trimer (18) in aqueous acetone at room temperature did not lead to any detectable reaction. However, addition of the trimer (3.4g) to a mixture of sodium carbonate (3.4g, 30.2 mmol), acetone (15 ml) and water (5 ml) resulted in an exothermic reaction. The mixture was left stirring overnight and then acidified (dilute HCl). The lower layer was removed and dissolved in ether (50 ml). The upper layer was ether extracted (2x50 ml) and the extracts combined with the lower layer. The solution was then washed with water, dried ($MgSO_4$) and the ether removed on a rotary evaporator to leave a yellow liquid (2.0g). A ^{19}F n.m.r. spectrum indicated this to be a mixture. Attempts to seperate components by molecular distillation, preparative scale g.l.c., and t.l.c. were unsuccessful and the reaction was not pursued further.

9.C Reactions with Amines

9.C.1a Dimer (16) with Dimethylamine

Dimer (16) (1.4g, 4.3 mmol) and dimethylamine (1.4g, 31.1 mmol) were transferred under vacuum to a Carius tube. The tube was sealed and allowed to warm; there was a vigorous exothermic reaction. When the tube had cooled to room temperature it was opened and the contents were shaken with water. The lower layer was removed and molecular distilled (ca. 65°C, 0.1 mm Hg) to give a pale yellow liquid (1.4g) shown by g.l.c.-ms. (col O) to be a mixture of a mono- and a di-substituted compound (46 and 54% respectively). These were separated by preparative scale g.l.c..

The monosubstituted compound (a liquid) was identified as 1-dimethylamino-F-2-cyclobutylcyclobutene (79): (Found: C, 35.5; N, 4.1; F, 59.5%; M^+, 349. $C_{10}F_{11}NH$ requires: C, 34.38; N, 4.01; F, 59.89%; M, 349); I.r spectrum no. 38, n.m.r.spectrum no. 46.

The disubstituted compound (a solid) was identified as 1-dimethylamino-2-(1'-dimethylamino-F-cyclobutyl)-F-cyclobutene (78): (Found: C, 38.2; N, 7.9; H, 3.5; F, 51.3%; M^+, 374. $C_{12}F_{10}N_2H_{12}$ requires: C, 38.50; N, 7.49; H, 3.21; F, 50.80%; M, 374); I.r. spectrum no. 37, n.m.r.spectrum no. 45.

9.C.1b Dimer (17) with Dimethylamine

In a similar reaction to the above, dimer (17) (1.7g, 5.2 mmol) and dimethylamine (0.9g, 20.0 mmol) gave a mixture (1.5g) of compound (79) (83%) and compound (78) (17%).

9.C.1c Dimer (17) with Diethylamine

Dimer (17) (1.4g, 4.3 mmol) was added slowly to diethylamine (5 ml) with stirring and external cooling (ice-bath). When the addition was complete, the mixture was shaken with water and the lower layer removed and molecular distilled (ca. 85°C, 0.1 mm Hg) to give a colourless liquid (1.2g) which rapidly darkened. This was identified as 1-diethylamino-2-F-cyclobutylcyclobutene (80), (74%): (Found: F, 55.0%; M^+, 377. $C_{12}F_{11}NH_{10}$ requires: F, 55.44%; M, 377); I.r. spectrum no. 39, n.m.r. spectrum no. 47.

9.C.2 Trimer (19) with Diethylamine

Trimer (19) (3.4g, 7.0 mmol) was slowly added to diethylamine (5 ml) with stirring and external cooling (ice-bath). A vigorous reaction occurred with precipitation of diethylaminehydrofluoride. This was removed by filtration and the filtrate washed with water. The lower layer was removed and molecular distilled (0.1 mm Hg, up to 90°C) to give a pale yellow liquid (2.8g) identified as 1-diethylamino-2-(1'-F-cyclobutylcyclobutyl)-F-cyclobutene (81), (73%): (Found: F, 60.3%; M^+, 539. $C_{16}F_{17}NH_{10}$ requires: F, 59.93%; M, 539); I.r. spectrum no. 40, n.m.r. spectrum no. 48.

9.C.3 Trimer (18) with Diethylamine

The procedure was as for 9.C.2. Thus, trimer (<u>18</u>) (3.3g, 6.8 mmol) and diethylamine (10 ml) gave a pale yellow liquid (1.7g) which gave two peaks on g.l.c. (cols O and Z). The larger peak was separated by preparative scale g.l.c. and shown by ^{19}F n.m.r. spectroscopy to be a complex mixture. The smaller peak was not eluted from a preparative g.l.c. column and this suggests that it was heat sensitive. An attempt to seperate components of the mixture by t.l.c. was unsuccessful and so the reaction was not pursued further.

9.C.4 Dimer (17) with Triethylamine

Dimer (<u>17</u>) (1.42g, 4.38 mmol) was dissolved in ether (5 ml) and cooled at -18°C whilst a solution of triethylamine (1.05g, 10.40 mmol) in ether (10 ml) was added slowly. The mixture was filtered under nitrogen to give a white solid (0.46g), shown to be a quaternary ammonium salt (extremely soluble in water and resultant solution shows only a resonance corresponding to F^- in its ^{19}F n.m.r. spectrum). The ether was removed from the filtrate on a rotary evaporator and the resultant oil shown by ^{19}F n.m.r. spectroscopy to be a complex mixture. Attempts to separate components by molecular distillation and t.l.c. were unsuccessful and the reaction was not pursued further.

9.C.5 Trimer (19) with Tertiary Amines

Trimer (<u>19</u>) (2.0g, 4.1 mmol) and trimethylamine (1.3g, 22.0 mmol) were sealed in a Carius tube and allowed to stand at room temperature for 18h. The tube was opened and the volatiles transferred under vacuum to a cold trap (there was no residue). On warming, these gave a gas, shown by infrared spectroscopy to be trimethylamine, and a liquid (1.6g) shown by g.l.c. (col O) to be trimer (<u>19</u>) containing a small amount of dissolved amine. A small amount (ca. 0.1g) of a white solid was recovered from the neck of the cold trap but was not characterised: an infrared spectrum showed a strong 'amine salt band' at ca. 2700 $cm.^{-1}$.

A mixture of pyridine (0.6g, 7.6 mmol) and trimer (<u>19</u>) (2.6g, 5.3 mmol) was stirred at room temperature for 18h. The lower layer was removed, washed with water, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (1.8g) was shown to be trimer (<u>19</u>) by g.l.c. (col O) and infrared spectroscopy. The upper (brown) layer was shown to be pyridine, i.e. no reaction could be detected.

9.C.6 <u>Trimer (18) with Tertiary Amines</u>

A mixture of pyridine (0.5g, 6.3 mmol) and trimer (<u>18</u>) (2.1g, 4.3 mmol) was stirred for 18h at room temperature. The mixture was homogenous and, initially, a bright red in colour, but it rapidly turned black. The mixture was poured into water and the lower layer removed, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (1.2g) was shown by g.l.c. (col O) and infrared spectroscopy to be trimer (<u>18</u>) (57% recovery).

A similar reaction occurred with triethylamine.

9.D.1 <u>Trimer (19) with Sodium Borohydride</u>

To a suspension of sodium borohydride (2.3g, 53.7 mmol) in tetraglyme (20 ml) was added slowly compound (<u>19</u>) (6.0g, 12.3 mmol) with rapid stirring and external cooling. When the addition was complete the mixture was heated for 1h on a steam bath and then left stirring at room temperature overnight. The lower layer (3.1g) was removed and the residue flash distilled to give a liquid (1.1g) shown by g.l.c. to be identical with the lower layer. The two fractions were combined and identified as <u>1-(1'-F-cyclo-butylcyclobutyl)-3,3-difluorocyclobutene (82)</u>, (79%): b.p. 164°C; (Found: C, 33.3; H, 0.7; F, 65.6%; M^+, 432. $C_{12}F_{15}H_3$ requires: C,33.33; H, 0.69; F, 65.97%; M, 432); I.r. spectrum no. 41, n.m.r. spectrum no. 49.

9.D.2 <u>Trimer (18) with Sodium Borohydride</u>

To a suspension of sodium borohydride (1.0g, 25.6 mmol) in tetraglyme (20 ml) at -18°C was added slowly trimer (<u>18</u>) (3.3g, 6.8 mmol) with rapid stirring. When the addition was complete the mixture was stirred at room temperature for 1h and then carefully poured into water (100 ml) and ether extracted (3x50 ml). The ether extracts were bulked, washed with water, dried ($MgSO_4$) and the ether removed by distillation to leave a colourless liquid (3.1g) shown by g.l.c. (col O) to be a mixture of ether and ca. 20 other components.

In a similar reaction, after the addition was complete the mixture was stirred for 1h on a steam bath and then flash distilled to give a small amount of a colourless liquid which was shown by g.l.c. (col O) to be a highly complex mixture. In view of the low recovery and the complexity of the product the reaction was not pursued.

9.E.1a Trimer (19) with F-Propene and Fluoride Ion

A mixture of CsF (2.0g, 13.2 mmol) and tetraglyme (20 ml) was placed in a flask fitted with a variable gas reservoir. The apparatus was evacuated and trimer (19) (5.4g, 11.1 mmol) and F-propene (5.3g, 35.3 mmol) transferred in under vacuum. The mixture was stirred at room temperature for 18h and then flash distilled to give a colourless liquid (8.9g) shown by g.l.c. (col O) to be a complex mixture of F-propene oligomers, trimer (19) and other, unidentified components. Material boiling below 130°C was removed by distillation and was not investigated further (mainly F-propene trimers). The residue (4.8g) was shown by g.l.c. to be a mixture of three components subsequently identified as trimer (19) (58%), F-2-methyl-3-(1'-cyclobutyl-cyclobutyl)pent-2-ene (84) (12%) and F-1-isopropyl-2-(1'-cyclo-butylcyclobutyl)cyclobutene (83) (30%). These were separated by preparative scale g.l.c..

For compound (83) (a low melting solid): b.p. 192°C; (Found: F, 72.3%; M^+, 636. $C_{15}F_{24}$ requires: F, 71.70%; M, 636); I.r. spectrum no. 42, n.m.r. spectrum no. 50.

For compound (84): b.p. 180°C; (Found: C, 27.2; F, 72.6%; M^+, 624. $C_{14}F_{24}$ requires: C, 26.92; F, 73.08%; M, 624); I.r. spectrum no. 43, n.m.r. spectrum no. 51.

9.E.1b Dimers (16) and (17) with F-Propene and Fluoride Ion

A mixture of CsF (5.0g, 32.9 mmol) and DMF (10 ml) was placed in a flask fitted with a variable gas reservoir. The apparatus was evacuated and a mixture of dimers (16) and (17) (2.3g, 7.1 mmol) and F-propene (10.9g, 72.7 mmol) was transferred in under vacuum. The mixture was stirred overnight at room temperature (there was a very exothermic initial reaction and the gas reservoir was fully deflated after ca. 30

minutes). Volatile material was transferred under vacuum to a cold trap and the lower layer removed. This was washed with water, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (11.9g) was shown by g.l.c. to be a highly complex mixture. Much of the lower boiling material (7.3g) was removed by distillation and was not investigated further (g.l.c. indicated the presence of F-propene oligomers and dimers (16) and (17)). The residue (4.2g) was shown by g.l.c.-ms. to be a mixture of F-propene trimers (73%), a $C_{11}F_{18}$ compound (4%) which was not characterised, compound (84) (22%) and traces of two other unidentified species. Compound (84) was separated by preparative scale g.l.c. and its identity confirmed by comparison of spectra.

9.E.2 Trimer (19) with F-Phenyl Lithium

Pentafluorobromobenzene (5.3g, 21.5 mmol) was dissolved in a mixture of ether (18 ml) and hexane (12 ml) and cooled, under nitrogen, to -30°C. ^{n}Butyl lithium (13ml of a 1.65M solution, 21.5 mmol) was added slowly, the temperature being maintained between -20 and -30°C. When the addition was complete trimer (19) (3.70g, 7.61 mmol) was added slowly and the resultant mixture allowed to warm to room temperature and left stirring overnight. Water (50 ml) was added, the aqueous layer separated, ether extracted (2x20 ml) and the extracts combined with the organic layer. This was then washed with water, dried ($MgSO_4$) and the ether removed on a rotary evaporator. The residue was molecular distilled (<0.1 mm, 80°C) to give a pale yellow liquid (1.17g) and a white solid (2.41g). The liquid was shown by g.l.c. (col O) to be >90% of a single compound, the solid being the same, pure compound. The solid was recrystallised from ether and identified as F-1-parabiphenyl-2-(1'-cyclobutylcyclobutyl)cyclobutene (85), (ca. 58%): m.p. 107-108°C; (Found: C, 36.9; F, 62.8%; M^+, 782. $C_{24}F_{26}$ requires: C, 36.83; F, 63.17%; M, 782); I.r. spectrum no. 44, n.m.r. spectrum no. 52.

9.F Dimer (16) with Lithium Chloride

A mixture of lithium chloride (1.22g, 28.80 mmol), dimer (16) (2.49g, 7.69 mmol) and DMF (10 ml) was stirred at room temperature for 3h. The volatiles were transferred under vacuum to a cold trap. The lower fluorocarbon layer was removed, washed with water, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (2.11g) was shown by g.l.c. (col O) to be a single compound identified as 1-chloro-2-(1'-chloro-F-cyclo--butyl)-F-cyclobutene (86), (77%); b.p. 129°C; (Found: C, 26.7; F, 52.5; Cl, 20.5%; M^+, 356 (^{35}Cl). $C_8F_{10}Cl_2$ requires: C, 26.89; F, 53.22; Cl, 19.89%; M, 356); I.r. spectrum no. 45, n.m.r. spectrum no. 53.

9.G Dimer (16) with Ethylene Glycol

A solution of dimer (16) (1.89g, 5.83 mmol) in ether (10 ml) was slowly added to a mixture of ethylene glycol (0.35g, 5.65 mmol) and ether (20 ml) and the mixture stirred until an homogeneous solution was obtained. This was allowed to stand at room temperature for 48h and then the ether was removed on a rotary evaporator. Vacuum sublimation of the residue gave a white solid which was recrystallised from CCl_4 at 0°C to give large rhombohedral crystals identified as bicyclo-(5.2)-2-spirohexafluorocyclo--butyl-3,6-dioxa-8,8,9,9-tetrafluoronon-1,7-ene (87), (60%): m.p. 54-55°C; (Found: C, 34.4; H, 1.1; F, 55.3%; M^+, 346. $C_{10}F_{10}O_2H_4$ requires: C, 34.68; H, 1.16; F, 54.91%; M, 346); I.r. spectrum no. 46, n.m.r. spectrum no. 54.

CHAPTER 10

EXPERIMENTAL TO CHAPTER 5

10.A.1 Fluorination of F-Cyclobutene Dimers

A mixture of dimers (16) and (17) (1.81g, 5.59 mmol) was passed over a mixture of cobalt trifluoride and calcium fluoride, at ca. 150°C, in a stream of dry nitrogen. The product (1.24g) was separated from the eluted gases by passing them through a liquid air trap. It was shown by ^{19}F n.m.r. spectroscopy to consist of compounds (16), (17) and F-bicyclobutyl (46). The mixture could not be separated by preparative scale g.l.c. and hence was stirred with methanol (5 ml) for 1h. The lower fluorocarbon layer was removed, washed with water, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (0.74g) was shown to be pure compound (46) by comparison of its spectra with those of an authentic sample.[175] I.r. spectrum no. 47, n.m.r. spectrum no. 55.

10.A.2 Fluorination of Trimer (19)

Trimer (19) (4.8g, 9.9 mmol) was passed over a mixture of cobalt trifluoride and calcium fluoride, at ca. 180°C, in a stream of dry nitrogen. The product (obtained as in 10.A.1) (4.2g) was shown by g.l.c. (col O) to be a mixture two compounds susequently identified as trimer (19) (20%) and F-1,1 - dicyclobutylcyclobutane (89) (80%). These were separated by preparative g.l.c. to give compound (89) as a low melting solid: b.p. 161°C; (Found: F, 72.2%; M^+, not observed, highest peak at M/e = 505 (M^+-19). $C_{12}F_{20}$ requires: F, 72.52%; M, 524); I.r. spectrum no. 48, n.m.r. spectrum no. 56.

A similar reaction at 210°C gave ca. 90% fluorination.

10.A.3 Thermal Behaviour of Compound (89)

Compound (89) was recovered unchanged after heating, in a Carius tube, with iron filings for 100h at ca. 320°C. Similarly, it was unaffected by passage through a platinum lined tube at ca. 600°C.

10.B.1 Addition of Bromine to Dimer (16)

A mixture of dimer (16) (2.13g, 6.57 mmol) and bromine (1.05g, 6.57 mmol) was allowed to stand for 24h at room temperature when a pale yellow solid was obtained. This was then maintained at ca. 60°C for a further 4h to give a colourless liquid which solidified on cooling. The product was identified as the expected 1-bromo-1-(1'-bromo-F-cyclobutyl)-F-cyclobutane (90): b.p. 165°C; (Found: C, 19.7; F, 46.6; Br, 33.5%; M^+, not observed, highest peak at M/e = 405 (^{81}Br, M^+- Br). $C_8F_{12}Br_2$ requires: C, 19.83; F, 47.11; Br, 33.06%; M, 486); I.r. spectrum no. 49, n.m.r. spectrum no. 57.

10.B.2 Other Attempted Bromine Additions

No addition of bromine was observed for corresponding reactions with the other F-cyclobutene oligomers, (17)-(19), nor with compound (40), F-2,3-dimethylhex-3-ene.

10.C Co-Polymerisation Reactions

10.C.1a Dimer (16) with 1,3-Butadiene

A mixture of dimer (16) (0.97g, 2.99 mmol) and 1,3-butadiene (1.50g, 27.78 mmol) was sealed in a Carius tube and irradiated with gamma rays for 28h. Initially the two compounds formed an homogeneous mixture. The tube was opened and volatile material (1.13g) transferred under vacuum to a cold trap. This was shown by infrared spectroscopy to be unchanged 1,3-butadiene. The residual white solid in the reaction tube was removed and pumped under vacuum for 4h to give a fluffy white powder (1.15g) identified as a co-polymer: (Found: C, 45.8; H, 2.9%); I.r. spectrum no.50.

A reference experiment using only 1,3-butadiene showed little, if any, polymerisation after 28h.

10.C.1b Compound (40) with 1,3-Butadiene

A mixture of 1,3-butadiene (2.34g, 43.33 mmol) and F-2,3-dimethylhex-3-ene (40) (3.12g, 7.80 mmol) was irradiated with gamma rays for two weeks at room temperature in a sealed tube. The tube was opened and volatile material transferred under vacuum to a cold trap;

there was very little solid residue. The contents of the cold trap were heated to ca. 40°C to give a gas (2.17g), shown to be 1,3-butadiene, and a liquid (3.05g) shown by g.l.c. (col O) to be compound (40) containing a small amount of dissolved butadiene.

10.C.1c Dimer (17) with 1,3-Butadiene

The procedure was as for 10.C.1b and, again, no co-polymerisation could be detected, both dimer (17) and 1,3-butadiene being recovered unchanged.

10.C.2a Dimer (16) with F-2-Butyne

A mixture of dimer (16) (1.52g, 4.69 mmol) and F-2-butyne (1.61g, 9.94 mmol) was irradiated with gamma rays for three weeks at room temperature in a sealed tube. The tube was opened and the volatiles (3.08g) transferred under vacuum to a cold trap. On warming these separated into a gas and a liquid shown by infrared spectroscopy to be F-2-butyne and dimer (16) respectively. No co-polymer (or polymer) could be detected.

10.C.2b Dimer (16) with F-Ethylene

A mixture of unstabilised F-ethylene (1.55g, 15.50 mmol) and dimer (16) (2.48g, 7.65 mmol) was sealed, at -173°C, in a Carius tube. The tube was placed in a metal sleeve, allowed to warm to room temperature and then irradiated with gamma rays for 100h. The tube was opened and the volatiles (3.43g) transferred under vacuum to a cold trap. The residual solid was pumped under vacuum for 1h to give a solid (0.12g) shown by elemental analysis to be P.T.F.E.. The volatiles separated into a gas and a liquid shown by infrared spectroscopy to be F-ethylene and dimer (16), respectively.

In a similar reaction, using only a small amount of dimer (16), the amount of P.T.F.E. formed was much greater.

10.D Oxidation Reactions

General Procedure

The fluorocarbon, dissolved in acetone, was slowly added to a mixture of potassium permanganate and acetone.

In all but one case (compound (72)) there was a vigorous reaction. When the addition was complete the mixture was allowed to stir at room temperature for ca. 2h and then poured into water, decolourised with SO_2 and the bulk of the acetone removed on a rotary evaporator. The residual solution was ether extracted, the extracts washed with water, dried (P_2O_5) and the ether removed on a rotary evaporator to leave the product as a solution in acetone.

10.D.1 Dimer (16)

Dimer (16) (2.1g, 6.5 mmol) in acetone (20 ml) was added to potassium permanganate ($KMnO_4$) (1.7g, 10.8 mmol) in dry acetone (70 ml). After the work-up the product (3.2g) was shown by g.l.c. (col O) to be a mixture of acetone and one other compound identified subsequently as 1-hydroxy-1-(1'-hydroxy-F-cyclobutyl)-F-cyclobutane (91) (yield by g.l.c. was ca. 90%). Compound (91) was separated by preparative scale g.l.c. and recrystallised from CCl_4 to give colourless needles: m.p. 59-60°C; (Found: C, 27.1; H, 0.9; F, 64.2%; M^+, not observed, highest peak at M/e = 338 (M^+- 20). $C_8F_{12}O_2H_2$ requires: C, 26.82; H, 0.56; F, 63.69%; M, 358); I.r. spectrum no. 51, n.m.r. spectrum no. 58.

10.D.2a Trimer (19)

Trimer (19) (3.0g, 6.2 mmol) in acetone (20 ml) was added to $KMnO_4$ (1.8g, 11.4 mmol) in acetone (70 ml). After work-up the product (2.7g) was shown by g.l.c. (col O) to be a mixture of actone and compound (91) (61% yield based on g.l.c.). The mixture was separated by preparative scale g.l.c. and the identity of (91) verified by comparison of spectra.

10.D.2b Compound (82)

This also gave compound (91) upon oxidation, together with a small amount of a very hydroscopic solid which was not identified.

10.D.2c Compound (72)

Compound (72) was recovered unchanged when treated with $KMnO_4$ in acetone.

10.D.2d Compound (91) with Phosphorus Pentoxide

A small sample of compound (91) was heated to 100°C with P_2O_5 and then allowed to cool to room temperature. Volatile material was transferred under vacuum to a cold trap and identified by infrared spectroscopy as unchanged (91).

10.D.3 Trimer (18)

Trimer (18) (3.5g, 7.2 mmol) in acetone (20 ml) was added to $KMnO_4$ (1.6g, 10.1 mmol) in acetone (70 ml). After work-up, the product (2.0g) was shown by g.l.c. (col O) and ^{19}F n.m.r. spectroscopy to be a mixture of compounds containing a small amount of acetone. The mixture was treated with a slight excess of diazomethane in ether and the ether removed on a rotary evaporator to leave a liquid (1.7g) shown by g.l.c. (col Z) to be a mixture of two major products with a small amount of acetone and two other unidentified components. The two major products were separated by preparative scale g.l.c. to give (93a),(0.38g, 16%), and (93b), (0.99g, 42%). These were identified as 1-methoxy-F-1-cyclobutylcyclopropane and 1-methoxy-F-1-cyclopropylcyclobutane, although it is not clear from the available data which isomer is which.

For (93a): b.p. 203°C; (Found: C,29.3; H, 1.1; F, 64.0%; M^+, 324. $C_8F_{11}OH_3$ requires: C, 29.63; H, 0.93; F, 64.51%; M, 324); I.r. spectrum no. 52, n.m.r. spectrum no. 59.

For (93b), a low melting solid: b.p.> 210°C; (Found: C, 29.6; H, 1.2; F, 64.2%; M^+, 324. $C_8F_{11}OH_3$ requires: C, 29.63; H, 0.93; F, 64.51%; M, 324); I.r. spectrum no. 53, n.m.r. spectrum no. 60.

10.E.1a Attempted Difluorocarbene Addition to Dimer (16)

A mixture of dimer (16) (1.5g, 4.6 mmol) and sodium chloro-difluoroacetate (2.9g, 19.0 mmol) was heated at ca. 200°C for 40h in a sealed tube. The tube was opened and volatile material transferred under vacuum to a cold trap. The cold trap was allowed to warm to room temperature and evolved gas allowed to escape. The residue (1.5g) was shown by g.l.c. (col O) to be a mixture of dimers (16) and (17), one other major component and several trace ones. These were separated by preparative scale g.l.c. to give dimers (16) and (17)

(0.7g, 47% recovery) and 1-chloro-F-1-cyclobutenylcyclobutane (95), (0.4g, 25%): b.p. 106°C; (Found: C, 28.1; F, 60.8; Cl, 11.0%; M^+, 340 (^{35}Cl). $C_8F_{11}Cl$ requires: C, 28.19; F, 61.38; Cl, 10.43%; M, 340 (^{35}Cl)); I.r. spectrum no. 54, n.m.r. spectrum no. 61.

10.E.1b Attempted Difluorocarbene Addition to Trimer (19)

A mixture of trimer (19) (6.3g, 13.0 mmol) and sodium chlorodifluoroacetate (4.0g, 26.2 mmol) was heated at 240°C for 60h in a sealed tube. The tube was opened and volatile material transferred under vacuum to a cold trap. The cold trap contents were warmed to room temperature and evolved gas allowed to escape. The residue (5.9g) was shown by g.l.c. (col O) to be mainly trimer (19) with small amounts of other compounds, of lower retention time, which were not identified.

10.E.2 Attempted (2+2) Cycloadditions

10.E.2a Dimer (16) with F-Ethylene

A mixture of dimer (16) (1.89g, 5.83 mmol) and stabilised F-ethylene (4.31g, 43.10 mmol) was heated, in a nickel tube, at ca. 230°C for 24h. The tube was allowed to cool and the volatiles transferred under vacuum to a cold trap (6.07g). On warming a gas (3.98g) was evolved and shown by infrared spectroscopy to be F-cyclobutane. The residue (1.42g) was shown by g.l.c. to be a mixture of dimer (16), dissolved F-cyclobutane and a minor component identified by g.l.c.-ms. as a C_8F_{10} isomer (presumably the nickel surface of the tube causes this defluorination). No addition products derived from dimer (16) could be detected.

10.E.2b Dimer (16) with F-2-Butyne

A mixture of dimer (16) (1.73g, 5.34 mmol) and F-2-butyne (4.31g, 26.60 mmol) was heated at ca. 250°C for 48h in a sealed tube. The tube was opened and volatile material transferred under vacuum to a cold trap. On warming a gas (3.78g) was evolved and identified as F-2-butyne by infrared spectroscopy. The residue (1.44g) was shown by g.l.c. (col O) to be dimer (16) containing a trace of dissolved F-2-butyne. The residue in the Carius tube was extracted with ether and its ^{19}F n.m.r. spectrum recorded. This indicated the presence of F-hexamethylbenzene (from trimerisation of F-2-butyne) but no other fluorine containing material could be detected.

10.E.3a Dimer (16) Heated with 1,3-Butadiene

A mixture of dimer (16) (2.15g, 6.64 mmol) and 1,3-butadine (1.90g, 35.2 mmol) was heated at 80°C for 60h in a sealed tube. The tube was opened and volatile material transferred under vacuum to a cold trap. On warming a gas was evolved and this was allowed to escape. The resultant liquid (3.11g) was shown by g.l.c. (cols O and Z) to be a mixture 1,3-butadiene and its dimer with one other component. These were separated by preparative scale g.l.c. to give a low melting solid identified as 4,5-dispiro(hexafluorocyclobutyl)cyclohexene (96), (1.74g, 69% separated yield; 99% yield by g.l.c.): b.p. 181°C; (Found: C, 37.9;H, 1.7; F, 60.7%; M^+, 378. $C_{12}F_{12}H_6$ requires: C, 38.10; H, 1.59; F, 60.32%; M, 378); I.r. spectrum no. 79, n.m.r. spectrum no. 62.

10.E.3b Dimer (17) Heated with 1,3-Butadiene

A mixture of dimer (17) (1.24g, 3.83 mmol) and 1,3-butadiene (2.10g, 38.89 mmol) was heated at 150°C for 24h in a Carius tube. The tube was opened and volatile material was transferred under vacuum to a cold trap. On warming a gas was evolved (shown to be 1,3-butadiene) and the liquid residue separated into two layers. The lower layer (2.11g) was shown by g.l.c. (col O) to be mainly dimer (17) with small amounts of 1,3-butadiene and its dimer. The upper layer (0.85g) was similarly shown to be mainly 1,3-butadiene dimer. No Diels Alder adduct of dimer (17) could be detected.

10.E.3c Other F-Alkenes with 1,3-Butadiene

Similar reactions to 10.E.3c were carried out with trimer (18), F-cyclopentene dimer (37) and F-ethylene tetramer (40). In no case could a Diels Alder adduct of these compounds be detected and in all cases there was a good recovery of starting material.

10.E.4 Reactions Involving Diazomethane

General Procedure

An ethereal solution of diazomethane was prepared by the standard literature method.[254] In all cases an excess of this solution was added (i.e. until mixture remained coloured) to the fluorocarbon reactant and the resultant mixture stirred at room temperature for a few hours. The ether was then removed by distillation to leave the product.

10.E.4a With F-2,3-Dimethylbut-2-ene

F-2,3-Dimethylbut-2-ene (1.45g, 4.83 mmol) and excess diazomethane gave a solid residue which was sublimed in vacuo to give a white solid (0.93g), recrystallised from CCl_4/CH_2Cl_2 and identified as 4,4,5,5-tetrakis(trifluoromethyl)-2-pyrazoline (98), (56%). This material has been obtained before but was assigned a different structure[238]: I.r. spectrum no. 55, n.m.r. spectrum no. 63; m.p. 84-85°C.

10.E.4b With Dimer (16)

A mixture of dimer (16) (1.71g, 5.28 mmol) and excess diazomethane gave a liquid (1.57g) shown by g.l.c. (col O) to be a mixture of one major and several minor components. The major component (1.11g) was separated by preparative g.l.c. and identified as 4,5-dispiro(hexafluoro-cyclobutyl)-2-pyrazoline (99), (57%): m.p. 37°C; (Found: C, 29.8; H, 0.8; N, 8.0; F, 62.9%; M^+, 366. $C_9F_{12}N_2H_2$ requires: C, 29.51; H, 0.56; N, 7.65; F, 62.30%; M, 366); I.r. spectrum no. 56, n.m.r. spectrum no. 64.

10.E.4c With Trimer (18)

Trimer (18) (2.63g, 5.41 mmol) with excess diazomethane gave a solid product which was sublimed in vacuo to give a white solid (2.11g). This was recrystallised from chloroform and identified as 1-methyl-3,6-di(heptafluoro-cyclobutyl)-4,4,5,5-tetrafluoro-1,2-diazepine (100), (72%): m.p. 85-86°C; (Found: C, 30.8; H,1.2; N, 4.8; F, 62.6%; M^+, 542. $C_{14}F_{18}N_2H_4$ requires: C, 31.00; H, 0.74; N, 5.17; F, 63.10%; M, 542); I.r. spectrum no. 57, n.m.r. spectrum no. 65.

10.E.4d With F-Cyclopentene Dimer (37)

Compound (37) (2.29g, 5.40 mmol) and excess diazomethane gave a product which was sublimed in vacuo to give a white solid (2.01g). This was recrystallised from CCl_4 and identified as 4,5-dispiro(octa--fluorocyclopentyl)-2-pyrazoline (102), (79%): m.p. 81-82°C; (Found: C, 28.0; H, 0.3; N, 6.1; F, 65.5%; M^+, 466. $C_{11}F_{16}N_2H_2$ requires: C, 28.32; H, 0.43; N, 6.01; F, 65.24%; M, 466); I.r. spectrum no. 58, n.m.r. spectrum no. 66.

CHAPTER 11

EXPERIMENTAL TO CHAPTER 6

General Procedure for Flow Pyrolyses

The material to be pyrolysed was placed in a two-necked flask. This flask was maintained at different temperatures, depending on the material being pyrolysed: -18°C for F-cyclobutene, (b.p. 0°C); room temperature for F-cyclobutene dimers, (16) and (17), (b.p. 78 and 84°C); and ca.80°C for F-cyclobutene trimers, (18) and (19), (b.p. 148 and 149°C). Dry nitrogen was bubbled into the material at a fairly constant, known rate and the resultant gas passed through the pyrolysis tube which was heated by an electrical furnace. Four tubes were used: one lined with platinum and packed with platinum foil; one packed with coarse iron filings which were changed after pyrolysis of ca. 40g of material; one packed with caesium fluoride (CsF); and one packed with potassium fluoride (KF). For all but the platinum tube the average contact time during pyrolysis followed simply from a knowledge of the nitrogen flow rate and the volume of packing material. The product was trapped out by passing the effluent gases through two liquid air traps; little, if any, material was ever recovered from the second trap. When the pyrolysis was complete the cold trap contents were transferred under vacuum to a flask fitted with a variable gas reservoir. For pyrolyses involving F-cyclobutene dimers, (16) and (17), or trimers, (18) and (19), any gaseous material in the product was not investigated.

11.A. Thermal Behaviour of F-Cyclobutene

11.A.1a Over Platinum

Passage of F-cyclobutene (4.5g, 27.8 mmol) over platinum at ca. 640°C (residence time ca. 50 seconds) gave a product gas (3.1g) shown by g.l.c. (col O) and infrared spectroscopy to be mainly unchanged F-cyclobutene (69% recovery) together with trace amounts of other, unidentified, components.

A similar reaction at 670°C gave analagous results.

11.A.1b Over Fluoride Ion

Passage of F-cyclobutene (5.91g, 36.48 mmol) over CsF at ca. 510°C (contact time ca. 20 secs.) gave a product gas (4.72g, 80% recovery) shown by g.l.c. (col O) and infrared spectroscopy to be a mixture of unchanged F-cyclobutene (60%) and F-2-butyne (40%).

A similar reaction at 590°C (4.01g of F-cyclobutene) gave a product (2.87g, 72% recovery) identified as F-cyclobutene (10%) and F-2-butyne (90%).

Over KF at ca. 510°C, F-cyclobutene gave a mixture (4.76g, 76% recovery) of F-cyclobutene (90%) and F-2-butyne (10%).

A similar reaction at 570°C with a longer contact time (30 seconds) gave a mixture of F-cyclobutene (25%) and F-2-butyne (75%).

11.A.2a Heating F-Cyclobutene with CsF in a Nickel Tube

A mixture of F-cyclobutene (5.77g, 35.62 mmol) and CsF (4.61g, 30.35 mmol) was heated at ca. 300°C in a nickel tube for 24h. Volatile material was transferred under vacuum to a cold trap. The product (3.36g, 58% recovery) was mostly gaseous at room temperature although there was a small amount of liquid ($<$ 0.1g). Both the gaseous and the liquid fraction were shown by g.l.c. (cols O and Z) to be complex mixtures. A ^{19}F n.m.r. spectrum of the gas (under pressure) showed the presence of F-cyclobutene and a small amount of F-2-butyne together with other, unidentified compounds.

11.A.2b Heating F-Cyclobutene in a Carius Tube

F-Cyclobutene (6.11g, 37.72 mmol) was heated at ca. 360°C for 66h in a Carius tube. Volatile material was transferred under vacuum to a cold trap to give, on warming, a gas (0.91g) and a liquid (4.72g). The gas was shown by infrared spectroscopy and g.l.c. (col O) to be mainly F-cyclobutene containing small amounts of silicon tetrafluoride and other, unidentified components. The liquid was shown by g.l.c. (cols O and Z) to be a very complex mixture from which two compounds were isolated by preparative scale g.l.c.. These were identified as F-norbornene (0.4g, 8%) and F-tricyclo(2.2.^{1,5}0.^{2,6}0)octane (<u>106</u>) (2.54g, 49%). Other components of the mixture were identified by g.l.c.-

ms. as dissolved F-cyclobutene and four (or more) C_8F_{12} isomers which were not characterised.

F-Norbornene was identified by comparison of spectra with those of authentic sample.[56]

Compound (<u>106</u>) has been prepared previously [246,247] but no spectral data has been published: m.p. 40°C, b.p. 79°C; literature: m.p. 40°C, b.p. 80°C; (Found: C, 29.7; F, 70.2%; M^+, 324. C_8F_{12} requires: C, 29.63; F, 70.37%; M, 324): I.r. spectrum no. 59, n.m.r. spectrum no. 67.

At 430°C F-cyclobutene (5.0g, 30.9 mmol) gave a gaseous (2.61g) and a liquid (1.50g) product. The gas was shown by g.l.c. (col O) and infrared spectroscopy to be mainly silicon tetrafluoride with a small amount of F-cyclobutene. The liquid was shown by g.l.c. (col O) to be a similar mixture to that obtained at 360°C.

A similar reaction occurred at 360°C in a nickel tube but the recovery of material (23%) was low.

11.A.2c <u>Heating F-Cyclobutene with KF in a Carius Tube</u>

A mixture of KF (1.6g, 27.5 mmol) and F-cyclobutene (6.5g, 40.1 mmol) was heated at 360°C for 66h in a Carius tube. Volatile material was transferred under vacuum to a cold trap and gave, on warming, a gas (1.0g) and a liquid (4.2g). The gas was shown by infrared spectroscopy to be mainly F-cyclobutene, whilst the liquid was shown by g.l.c. (col O) to be a mixture comparable to that obtained in the abscence of KF.

11.B <u>Thermal Behaviour of F-Cyclobutene Dimers (16) and (17)</u>

11.B.1a <u>Over Platinum</u>

Passage of dimer (<u>16</u>) (0.41g) over platinum at 510°C (residence time ca. 30 secs.) gave a product (0.28g) shown by g.l.c. (col O) to be a mixture of dimers (<u>16</u>) and (<u>17</u>) (in the approximate ratio 2:3) with small amounts of four (or more) other compounds which were identified by g.l.c.-ms. as C_8F_{12} isomers. The identity of the dimers was verified by ^{19}F n.m.r. spectroscopy.

In a similar reaction, at 510°C, dimer (<u>17</u>) (0.21g) gave a product (0.11g) shown by g.l.c. (col O) to be a mixture of dimers (<u>16</u>) and (<u>17</u>) (ca. 1:7) together with small amounts of other, unidentified species.

Passage of a mixture of dimers (1.5g) over platinum at 550°C gave a product (1.2g) containing dimers (16) and (17) (85%, ca. 1:6) and rearranged compounds (15%).

In a similar reaction at 570°C, dimer mixture (3.5g) gave a product (1.5g) containing five or more rearranged products (ca. 30%) together with dimers (16) and (17) (70% ca. 1:6).

11.B.1b Over Iron Filings

Passage of dimer (17) (2.3g) over iron filings at 480°C (contact time ca. 30 secs.) gave a product (1.7g) shown by g.l.c.-ms. (col Z) to consist of a mixture of dimer (16) (10%), dimer (17) (80%), rearranged products (3%) and two defluorinated products (6 and 1%). The mixture was recirculated at 550°C when the amount of the major defluorinated compound in the product mixture was increased to 15%.

In a similar reaction, at 550°C, dimer (16) (1.0g) gave a product (0.6g) shown by g.l.c. (col Z) to be a mixture of dimer (16) (24%), dimer (17) (52%), rearranged products (5%) and two defluorinated products (16 and 3%).

The major defluorinated product was separated by preparative scale g.l.c. and identified as F-bicyclobutenyl (107): b.p. 108°C; (Found: C, 33.6; F, 66.8%; M^+, 286. C_8F_{10} requires: C, 33.57; F, 66.43%; M, 286); I.r. spectrum no. 60, n.m.r. spectrum no. 68.

11.B.1c Over Fluoride Ion

Passage of dimer (16) (0.55g) over CsF at 420°C (contact time ca. 25 secs.) gave a product (0.38g) shown by g.l.c. (col O) to be a mixture of dimers (16) and (17) (ca. 85% in the ratio 3:4) and rearranged products (15%).

In a similar reaction dimer (17) gave, within experimental error, the same product mixture.

A mixture of dimers (16) and (17) (15.3g) was passed over CsF at 510°C (contact time ca. 30 secs.) to give a product liquid (14.0g, 92% recovery) shown by g.l.c. (col Z) to be a highly complex mixture with four major components. Three of these were separated by a combination of fractional distil-lation and preparative scale g.l.c. (cols D and Z) and subsequently identified as: a mixture of cis- and trans-

F-ethylidene-2,3-dimethylcyclobutene (108) (ca. 40% by g.l.c.); F-methylene-2,3,4-trimethylcyclobutene (109) (ca. 25% by g.l.c.); and F-2-propylidene-(3'-methyl)cyclobutene (110) (ca. 10% by g.l.c.). The fourth major component, (111), could not be isolated on the available praparative scale g.l.c. apparatus and it disappeared on distillation. Many of the minor components of the mixture were identified by g.l.c.-ms. as C_8F_{12} isomers but these were not isolated.

For compound (108): I.r. spectrum no. 61, n.m.r. spectrum no. 69.

For compound (109): (Found: C, 29.4; F, 70.2%; M^+, 324. C_8F_{12} requires: C, 29.63; F, 70.37%; M, 324); I.r. spectrum no. 62, n.m.r. spectrum no. 70.

For compound (110): (Found: C, 29.7; F, 70.0%; M^+, 324. C_8F_{12} requires: C, 29.63; F, 70.37%; M, 324); I.r. spectrum no. 63, n.m.r. spectrum no. 71.

In a similar reaction dimer mixture (1.61g) was passed over KF at 510°C (contact time ca. 20 secs.) and the product (1.35g, 84% recovery) shown by g.l.c. (col Z) and ^{19}F n.m.r. spectro-scopy to be mainly (ca. 70%) compound (108) with small amounts of compounds (109)-(111) and other unidentified species.

Recirculation at ca. 570°C increased the proportion of compounds (109)-(111).

11.B.1d Addition of Bromine to Compound (108)

A mixture of compound (108) (1.01g, 3.12 mmol) and bromine (0.50g, 3.13 mmol) gave, on standing in visible light, a single compound which was identified as 3-bromo-1-(2'-bromo-F-ethyl)-F-2,3-dimethyl-cyclobutene (113): b.p. 147°C; (Found: C, 19.9; F, 47.9; Br, 32.5%; M^+, 486 (^{81}Br). $C_8F_{12}Br_2$ requires: C, 19.84; F, 47.13; Br, 33.03%; M, 486 (^{81}Br)); I.r. spectrum no. 64, n.m.r. spectrum no. 72.

11.B.1e Addition of Bromine to Compound (110)

A mixture of compound (110) (0.47g, 1.45 mmol) and bromine (0.23g, 1.44 mmol) gave, on standing in visible light, a single compound which was identified as 3-bromo-1-(2'-bromo-F-2'-methylethyl)-F-3-methyl-cyclobutene (114): (Found: C, 20.1; F, 46.4; Br, 33.8%;

M^+, 486 (^{81}Br). $C_8F_{12}Br_2$ requires: C, 19.84; F, 47.13; Br, 33.03%; M, 486); I.r. spectrum no. 65, n.m.r. spectrum no. 73.

11.B.2 Heating Dimers (16) and (17) with CsF in a Nickel Tube

A mixture of dimers (16) and (17) (2.17g, 6.70 mmol) and CsF (2.91g, 19.09 mmol) was heated at 290°C for 20h in a nickel tube. Volatile material was transferred under vacuum to a cold trap. The resultant liquid was shown by g.l.c.-ms. (col Z) to be a complex mixture of C_8F_{14} and C_8F_{12} compounds. Preparative scale g.l.c. gave: a C_8F_{14} compound shown to be F-2-butylidene cyclobutene (30), (40% by g.l.c.), identified by comparison of its spectra with those of an authentic sample; a mixture of C_8F_{14} isomers (22% by g.l.c.) tentatively identified as F-1,2,3,4-tetramethylcyclobutene (115) and F-1,2,3,4-tetra-methyl-1,3-butadiene by comparison of spectra of the mixture with those of authentic pure samples [26]; a C_8F_{12} compound (22% by g.l.c.) identified as compound (108) by infrared spectroscopy; and a second C_8F_{12} isomer (10% by g.l.c.) identified as compound (110) by infrared spectroscopy.

11.C Thermal Behaviour of F-Cyclobutene Trimers (18) and (19)

11.C.1a Trimer (18) Over Platinum

Passage of trimer (18) (1.5g) over platinum at 510°C (residence time ca. 30 secs.) gave a liquid (1.1g) shown by g.l.c.-ms. (col O) to be a mixture of: trimer (18) (ca. 30%); compound (116) subsequently identified as F-2,3-dicyclobutyl-1,3-butadiene (ca. 15%); compound (117) subsequently identified as F-2,3-di(methylenecyclobutyl)butane (ca. 40%); and small amounts of several $C_{10}F_{14}$ isomers which were not separated. Samples of compounds (116) and (117) were separated by preparative scale g.l.c..

For compound (116): b.p. 148°C; (Found: C, 29.9; F, 69.9%; M^+, 486. $C_{12}F_{18}$ requires: C, 29.63; F, 70.37%; M, 486); I.r. spectrum no. 66, n.m.r. spectrum no. 74.

For compound (117): b.p. 134°C; (Found: C, 29.9; F, 70.0%; M^+, 486. $C_{12}F_{18}$ requires: C, 29.63; F, 70.37%; M, 486); I.r. spectrum no. 67, n.m.r. spectrum no. 75.

A similar reaction at 550°C gave a more complex mixture but compound (117) was still the major product.

11.C.1b Trimer (18) Over Iron Filings

Passage of trimer (18) (1.3g) over iron filings at 480°C (contact time ca. 30 secs.) gave a liquid (0.9g) shown by g.l.c.-ms (col O) to be a mixture of trimer (18) (ca. 75%), compounds (116) and (117) (ca. 10% each) and a defluorinated product, $C_{12}F_{16}$ (ca. 5%), which was not isolated.

11.C.1c Trimer (18) Over CsF

Passage of trimer (18) (1.8g) over CsF at 515°C (contact time ca. 20 secs.) gave a product (1.3g) shown by g.l.c. (col O) and ^{19}F n.m.r. spectroscopy to be largely (>90%) compound (117) with small amounts of compound (116) and other unidentified components.

11.C.2a Heating Trimer (18) in a Carius Tube

Trimer (18) (2.75g) was heated in a Carius tube for 24h at 300°C. Volatile material was transferred under vacuum to a cold trap and shown by g.l.c. (col O) to be a mixture of trimer (18) (ca. 80%) and diene (116) (ca. 20%) (2.61g, 95% recovery).

11.C.2b Heating Trimer (18) with Fluoride Ion in a Nickel Tube

A mixture of trimer (18) (8.25g, 16.98 mmol) and CsF (3.12g, 20.54 mmol) was heated at 300°C in a nickel tube for 14h. Volatile material was transferred under vacuum to a cold trap and the resultant liquid (8.14g) shown by g.l.c. (col O) and ^{19}F n.m.r. spectroscopy to be a mixture of diene (117) (>90%) with small amounts of trimer (18), diene (116) and other unidentified species.

A similar reaction, with KF instead of CsF, for 24h at 300°C gave virtually pure diene (117) with a 96% recovery.

11.C.3a Trimer (19) Over Platinum

Passage of trimer (19) (3.9g) over platinum at 610°C (residence time ca. 30 secs.) gave a product (1.6g) shown by g.l.c. (col O) to be a highly complex mixture. The major product (ca. 30% by g.l.c.) was isolated by preparative scale g.l.c. and identified as F-methyl-cyclobutyl-methylenecyclobutane (118): b.p. 117°C; (Found: C, 31.0; F, 69.0%; M$^+$, 386. $C_{10}F_{14}$ requires: C, 31.09; F, 68.91%; M, 386);

I.r. spectrum no. 68, n.m.r. spectrum no. 76.

Other components of the product mixture were identified by g.l.c.-ms. as being mainly $C_{10}F_{14}$ isomers.

A similar reaction at 560°C gave a less complex product mixture but the conversion of trimer (<u>19</u>) was only about 50% and the major product was still compound (<u>118</u>).

11.C.3b <u>Trimer (19) Over Iron Filings</u>

Passage of trimer (<u>19</u>) (3.0g) over iron filings at 480°C (contact time ca. 25 secs.) gave a product (2.1g) shown by g.l.c. (col O) and ^{19}F n.m.r. spectroscopy to be unchanged trimer.

A similar reaction at 525°C gave a mixture containing trimer (<u>19</u>) (>80%) with small amounts of other components identified by g.l.c.-ms. (col O) to be $C_{10}F_{14}$ isomers, i.e. pyrolysis products; no defluorinated material could be detected.

11.C.3c <u>Trimer (19) Over CsF</u>

Passage of trimer (<u>19</u>) (2.4g) over CsF at 550°C (contact time ca. 25 secs.) gave a product (1.4g) shown by g.l.c. (col O) to be a highly complex mixture with the major component being unchanged trimer (<u>19</u>).

11.C.3d <u>Heating Trimer (19) with Iron Filings in a Carius Tube</u>

A mixture of trimer (<u>19</u>) (3.5g) and iron filings (washed in pet. ether and chloroform) (10g) was heated at 300°C for 72h. Volatile material (3.1g) was transferred under vacuum to a cold trap and shown by g.l.c. (col O) and infrared spectros--copy to be unchanged trimer (89% recovery).

11.D.1 <u>Defluorination of F-1-Isopropylcyclopentene (33)</u>

Passage of compound (<u>33</u>) (2.99g) over iron filings at 640°C (contact time ca. 25 secs) gave a product (1.56g) shown by g.l.c. (col O) to be a mixture of unchanged compound (<u>33</u>) (ca. 60%) and compound (<u>119</u>) (ca. 35%) with small amounts of two other compounds which were not identified. Compound (<u>119</u>) was separated by preparative scale g.l.c. and identified as <u>F-2-(cyclopenten-1'-yl)-propene</u>: (Found: F, 70.2%; M^+, 324. C_8F_{12} requires: F, 70.37%; M, 324); I.r. spectrum no. 78, n.m.r. spectrum no. 77.

A similar reaction at 690°C gave compound (119) as the major product but it was accompanied by significant amounts of other, unidentified compounds.

11.D.2 Attempted Defluorination of F-1-Isopropylcyclohexene (35)

Passage of compound (35) (1.9g) over iron filings at 600°C (contact time ca. 30 secs.) gave a product (1.2g) shown by g.l.c.-ms. (col A) to be a complex mixture, the two major products being F-cyclohexane and a C_9F_{16} compound (not (35)). A ^{19}F n.m.r. spectrum of the product mixture did not indicate the presence of any benzylic fluorines.

11.D.3 Pyrolysis of Compounds (28) and (29)

Passage of compound (28) over platinum at 550°C gave a complex mixture which was not investigated. In a similar reaction at 510°C, compound (28) was largely unaffected.

Pyrolysis of compound (29) over platinum at 490°C (residence time ca. 30 secs.) also gave a complex mixture which was not investigated.

11.E Reaction of Trimer (18) with CsF

A mixture of trimer (18) (4.1g, 8.4 mmol), CsF (2.2g, 14.5 mmol) and DMF (15 ml) was stirred at room temperature for 24h. Volatile material was transferred under vacuum to a cold trap. The lower layer was removed, washed with water, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (3.4g) was shown by g.l.c. (col O) to be a single compound subsequently identified as F-spiro(cyclobutane-1',2-bicyclo(5.2.0)non-1,7-ene) (120), (83%): b.p. 148°C; (Found: C, 29.4; F, 70.2%; M^+, 486. $C_{12}F_{18}$ requires: C, 29.63; F, 70.37%; M, 486); I.r. spectrum no. 69, n.m.r. spectrum no. 78.

11.E.1a Pyrolysis of Compound (120)

Passage of compound (120) (6.65g) over platinum at 590°C (residence time ca. 30 secs.) gave a product (3.94g) shown by g.l.c. (cols O and A) to be a complex mixture with four major components separated by preparative scale g.l.c. and subsequently identified as: F-bicyclo(5.2.0)-2-methylnona-(1,7),(2,3)-diene (121), (1.57g, 30%); F-1,2-dimethylene-3-methylcyclohept-3-ene (122), (0.41g, 8%); F-3-methylene-2,4-dimethylcyclohepta-1,4-diene (123), (0.29g, 5%); and a component (0.55g) shown by ^{19}F n.m.r. spectroscopy to be a mixture consisting mainly (>90%) of compound (124) which was tentatively identified as F-o-methylbenzocyclobutane.

For compound (121): b.p. 126°C; (Found: C,31.1; F, 69.3%; M^+, 386. $C_{10}F_{14}$ requires: C, 31.09; F, 68.91%; M, 386); l_{max} (cyclohexane) 245 nm., log ε = 4.13; I.r. spectrum no. 70, n.m.r. spectrum no. 79.

For compound (122): (Found: F, 68.4%; M^+, 386. $C_{10}F_{14}$ requires: F, 68.91%; M, 386); l_{max} (cyclohexane) 228 nm., log ε = 3.60; I.r. spectrum no. 71, n.m.r. spectrum no. 80.

For compound (123): (Found: C, 30.9%; M^+, 386. $C_{10}F_{14}$ requires: C, 31.09%; M, 386); l_{max} (cyclohexane) 241 nm., log ε = 3.68, and ca. 255 nm., log ε = ca. 3.48; I.r. spectrum no. 72, n.m.r. spectrum no. 81.

For compound (124): I.r. spectrum no. 73, n.m.r. spectrum no. 82.

11.E.1b Passage of Compounds (121) and (122) Over Platinum

A small amount of compound (121) (0.77g) was passed over platinum at 600°C (residence time ca. 30 secs.) and the product (0.43g) shown by g.l.c.(col A) and ^{19}F n.m.r. spectroscopy to be a mixture of compounds (121)-(124) with compound (124) forming ca. 60% of the mixture

A similar reaction occurred with compound (122); products identified by g.l.c. (col A).

11.E.2 Trimer (18) with CsF and Bromine in DMF

A mixture of CsF (2.9g, 19.1 mmol), bromine (0.8g, 5.0 mmol), trimer (18) (2.4g, 4.9 mmol) and DMF (15 ml) was stirred at room temperature for 48h. The volatiles were transferred under vacuum to a cold trap and the lower fluorocarbon layer removed. This was washed with water, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (1.9g) was shown by g.l.c. (col O) to be a mixture of trimer (18) and compound (120) (ca. 1:2); no bromine containing material could be detected.

11.F Photolysis Reactions

General Procedure

The compound to be photolysed was transferred under vacuum into a scrupulously clean silica tube containing a trace of mercury. The tube was then sealed (under vacuum) and irradiated with ultraviolet light, of wavelength 253.7 nm., in a Rayonet R.P.R. reactor. The ambient temperature of the reactor was about 40°C. The tube was then opened and volatile material was transferred under vacuum to a cold trap.

11.F.1a Dimer (16)

Dimer (16) (1.7g) was irradiated for 140h to give a product shown by g.l.c. (col O) to be a single compound identified as F-spiro(cyclobutane-1$'$,1-(2-methylenecyclobutane)) (127), (1.6g, 94%): b.p. 82°C; (Found: C, 29.5; F, 69.8%; M^{+}, 324. C_8F_{12} requires: C, 29.63; F, 70.37%; M, 324); I.r. spectrum no. 74, n.m.r. spectrum no. 83.

11.F.1b F-2-Propylidenecyclobutane (26)

Compound (26) (1.52g) was irradiated for a total of 500h. The product (1.52g) was shown by g.l.c. to be a mixture of compound (26) (13%) and one other component (82%) separated by preparative scale g.l.c. and identified as F-methylene-2,2-dimethylcyclobutane (128), (82% by g.l.c.): b.p. 67°C; (Found: C, 26.6; F, 73.6%; M^{+}, 312; C_7F_{12} requires: C, 26.92; F, 73.08%; M, 312); I.r. spectrum no. 76, n.m.r. spectrum no. 84.

11.F.1c F-Cyclobutylidenecyclopentane (31)

Compound (31) (1.57g) was irradiated for 180h to give a product (1.54g) shown by g.l.c. (col O) to be a mixture of unchanged compound (31) (10%) and one other component (90%). These were separated by preparative scale g.l.c. and the product (1.14g) was identified as F-spiro(cyclopentane-1$'$,1-(2-methylenecyclobutane)) (129): b.p. 109°C; (Found: F, 71.4%; M^{+}, 374. C_9F_{14} requires: F, 71.12%; M, 374); I.r. spectrum no. 77, n.m.r. spectrum no. 85.

11.F.2 Other Photolysis Reactions

The F-cyclopentene dimer (37) was photolysed under the following conditions: in vacuo with Hg for 140h; in vacuo with Hg and CsF for 150h; and in the presence of oxygen. In each case compound (37) was recovered unchanged.

In separate reactions trimer (18) and diene (116) were recovered unchanged after irradiation for 140 and 250h respectively.

Photolysis of diene (117) (2.17g) for 250h gave a product (1.96g) shown by g.l.c. (col O) to be a complex mixture. The major peak was separated by preparative scale g.l.c. but shown by ^{19}F n.m.r. spectroscopy to be a mixture of several compounds.

11.F.3 Dimerisation of Compound (127)

A mixture of compound (127) (0.71g, 2.19 mmol), CsF (0.9g, 6.6 mmol) and DMF (5 ml) was stirred for 4h. Volatile material was then transferred under vacuum to a cold trap. The lower fluorocarbon layer was removed, washed with water, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (0.46g) was shown by g.l.c. (col O) to be a single compound subsequently identified as F-1-(1'-methyl-2'-spirocyclobutylcyclobutyl)-3--spirocyclobutyl-4-methylcyclobutene (130), (65%): (Found: F, 70.1%; M^+, 648. $C_{16}F_{24}$ requires: F, 70.37%; M, 648); I.r. spectrum no. 75, n.m.r. spectrum no. 86.

APPENDIX I

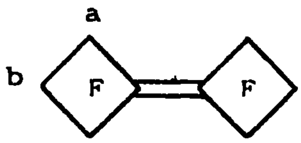
The following abbreviations are used in this appendix:-
S, singlet; D, doublet; T, triplet; Q, quartet; P, pentet.

Unless otherwise stated spectra were recorded at 40°C as neat liquids.

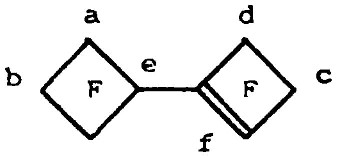
External $CFCl_3$ and TMS were used as references for ^{19}F and ^{1}H spectra respectively.

For ^{1}H spectra downfield shifts are quoted as positive (delta scale), whilst for ^{19}F spectra, upfield shifts are quoted as positive.

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
1. F-bicyclobutylidene (16)			
117.8	S	2	a
132.0	S	1	b



(16)



(17)

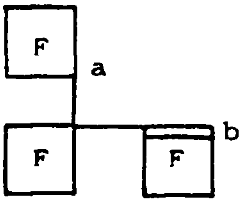
2. F-1-cyclobutylcyclobutene (17)

189.6	S	1	e
134.3	AB J = 232	4	a
128.3			
134.7	AB J = 232	2	b
131.1			
121.7	M	2	c
116.5	M	2	d
98.5	Broad S	1	f

3. F-1-(1'-cyclobutylcyclobutyl)cyclobutene (19)

173.0	Broad S	1	a
91.8	Broad S	1	b

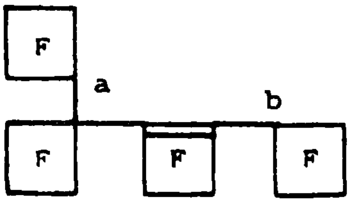
Signals between 110 and 133 p.p.m. (equivalent to 16F) which were not assigned.



(19)

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
4. F-1-(1'-cyclobutylcyclobutyl)-2-cyclobutylcyclobutene (22)			
183.1	Broad D J = 62	1	a
175.3	Broad D J = 62	1	b

Signals between 110 and 138 p.p.m. (equivalent to 22F) which were not assigned.



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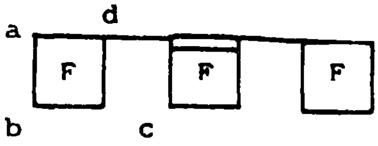


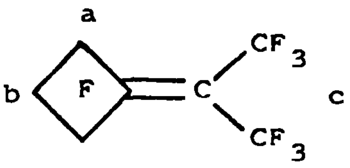
(18)

5. F-1,2-dicyclobutylcyclobutene (18)

180.0	S	1	d
133.0 127.0	AB J = 232	4	a
134.0 130.3	AB J = 230	2	b
112.6	S	2	c

6. F-2-propylidenecyclobutane (26)

132.4	S	1	b
116.9	M	2	a
65.4	D(J = 6) of Q(J =7)	3	c

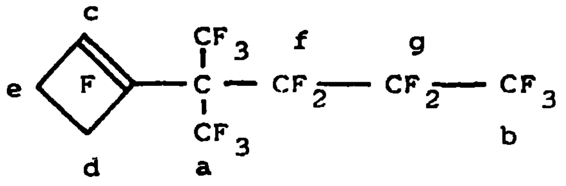


(26)

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment

7. F-2-cyclotutenyl-2-methylpentane (27)

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
64.8	S	6	a
83.0	T J = 12	3	b
95.7	Broad S	1	c
109.2	Broad S	2	d
115.3	Broad S	2	e
125.4	Broad S	2	f
123.9	M	2	g



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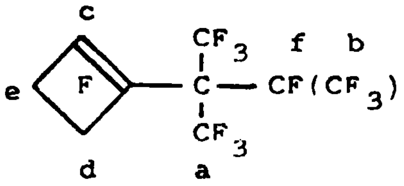


(28)

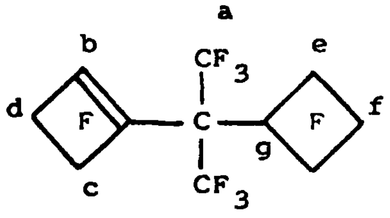
8. F-2-cyclobutenyl-2,3-dimethylbutane (28)

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
63.4	S	6	a
72.0	S	6	b
95.5	Broad S	1	c
115.1	Broad S	2	d
124.5	M	2	e
171.2	Broad S	1	f

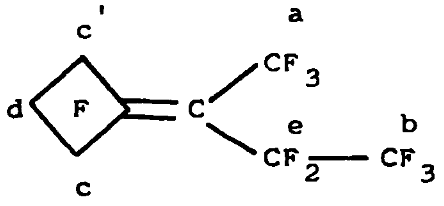
9. F-2-cyclobutenyl-2-cyclobutylpropane (29)

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
65.4	D(J = 5) of Q(J = 13)	6	a
91.2	Broad S	1	b
114.1	Broad S	2	c
124.0	M	2	d
130.5	S	4	e
130.3 134.2	AB J = 223	2	f
179.9	Broad S	1	g

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment



(29)



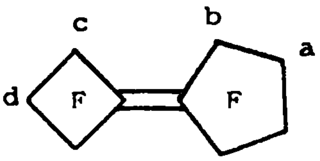
(30)

10. F-2-butylidenecyclobutane (30)

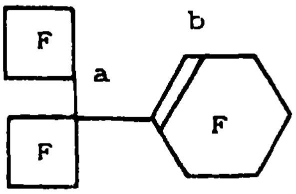
Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
63.0	M	3	a
84.7	M	3	b
116.8	Q(J =13) of Q(J = 2)	2	e
114.8	Broad M	4	c & c'
132.6	S	2	d

11. F-cyclobutylidenecyclopentane (31)

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
136.9	S	2	a
132.1	S	1	d
117.1	S	2	c
114.2	S	2	b



(31)



(32)

12. F-1-(1'-cyclobutylcyclobutyl)cyclohexene (32)

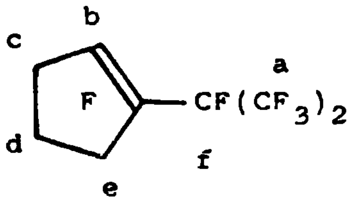
Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
181.0	Broad S	1	a
86.8	Broad S	1	b

Signals between 110 and 142 p.p.m. (equivalent to 20F) which were unassigned. Run as solution in ether

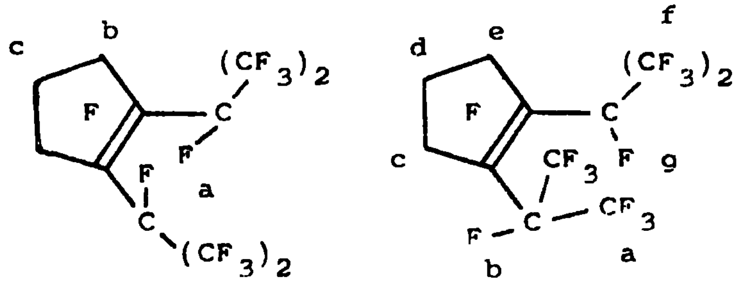
Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment

13. F-1-isopropylcyclopentene (33)

77.1	M	6	a
107.5	Broad S	2	c
111.4	Broad S	1	b
122.1	D J = 15	2	e
132.4	S	2	d
189.2	M	1	f



(33)



A B

(34)

14. F-1,2-di-isopropylcyclopentene (34) - A:B = ca. 2:5

Rotamer A

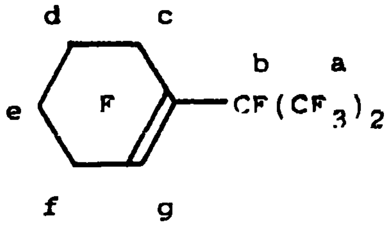
110.6	M	2	b
137.2	S	1	c
169.0	S	1	a

CF_3 resonance(s) hidden under those of rotamer B.

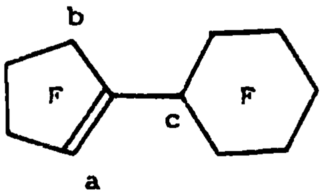
Rotamer B

72.7	D $J_{a,g}$ = 48	6	a
73.7	S	6	f
109.6	D $J_{b,c}$ = 47	2	c
111.4	S	2	e
136.7	S	2	d
170.5	T $J_{b.c}$ = 47	1	b
175.8	Septet $J_{a,g}$ = 48	1	g

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
15. F-1-isopropylcyclohexene (35)			
78.3	D(J = 25) of Q(J = 37)	6	a
107.2	Broad S	1	g
110.3	D $J_{b,c} = 37$	2	c
123.5	M	2	f
137.1	M	2	d
138.6	M	2	e
186.4	T $J_{b,c} = 37$	1	b



(35)



(36)

16. F-1-cyclohexylcyclopentene (36)

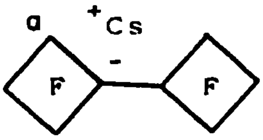
107.3	M	2	b
108.3	Very Broad	1	a
187.4	M	1	c

Signals between 115 and 148 p.p.m. (equivalent to 14F) which were not assigned.

17. F-1-cyclobutylcyclobutyl anion (23)

86.6	D J = 46	4	a

Signals between 119 and 137 p.p.m. (equivalent to 8F) which were unassigned.
Spectrum run in DMF as solvent at 0°C but temperature has no effect on the spectrum below ca. 100°C.

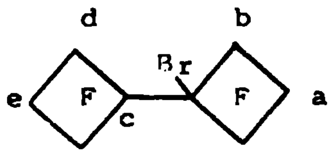


(23)

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment

18. 1-bromo-F-1-cylobutylcyclobutane (45)

108.4 122.1	AB $J = 220$	4	b
126.3	M	4	d
125.5 130.7	AB $J = 230$	2	a
131.1	S	2	e
168.3	M	1	c



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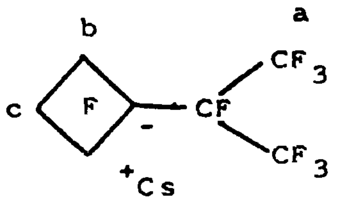


(47)

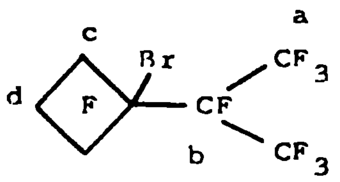
19. F-1-isopropylcyclobutane anion (47)

74.4	M	3	a
88.6	D $J = 46$	2	b
125.3	S	1	c

Spectrum run in DMF as solvent at 0°C but temperature has little effect on the spectrum below ca. 100°C.

20. 1-bromo-F-1-isopropylcyclobutane (49)

72.3	M	6	a
112.1 124.6	AB $J = 220$. $J_{b,c} = 54$	4	c
124.3 128.6	AB $J = 220$	2	d
171.6	T $J_{b,c} = 54$	1	b

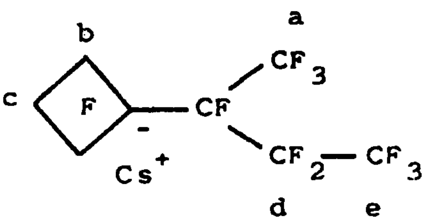


(49)

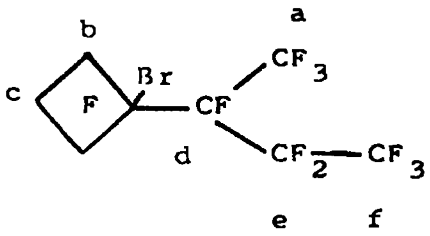
21. F-1-isobutylcyclobutyl anion (48)

Shift p.p.m.	Fine Structure J value in Hz	Relative Intensity	Assignment
74.6	S	3	a
81.2	S	3	e
88.6	D J = 44	4	b
121.2	Very Broad AB	2	d
126.1	Broad S	2	c

Spectrum run in DMF as solvent at 0°C but temperature has little effect on the spectrum below ca. 100°C



(48)



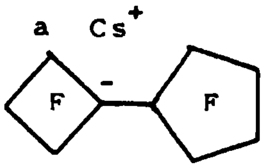
(50)

22. 1-bromo-F-1-isobutylcyclobutane (50)

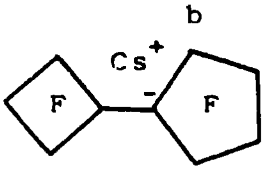
Shift p.p.m.	Fine Structure J value in Hz	Relative Intensity	Assignment
71.3	M	3	a
82.5	M	3	f
113.0	M	2	e
112.1 125.7	AB J = 216	4	b
125.3 129.7	AB J = 224	2	c
170.6	M	1	d

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment

23. <u>Anions from compound (31)</u>



(52)



(53)

The spectrum of these anions was recorded in DMF as solvent; temperature has a considerable effect (see Fig 2 pg. 72). Thus, at 0°C, and below, signals arising from both anions can be observed (a and b; ca. 6:1), but as the temperature is raised broadening occurs and at 80°C a single, sharp resonance is observed.

<u>At 0°C</u>

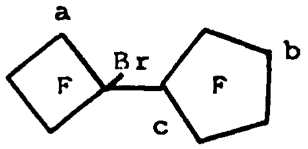
81.8	D J = 46		b
89.4	D J = 44		a

Signals between 117 and 138 p.p.m. (uncertain integration) which were not assigned.

<u>At 80°C</u>

A single signal is observed at 127.7.

24. Compounds (54) and (55)



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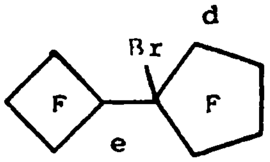


(55)

ca. 3:1

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
106.3	Part of AB J = 248		d
107.7	Part of AB J = 215		a
135.1	S		b
164.2	M		c
168.1	Broad S		e

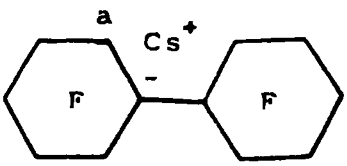
Ratio of d:e is 2:1; of a:b:c: is 2:4:1.
Numerous other signals between 113 and 133 p.p.m. which were not assigned.

25. F-1-cyclohexylcyclohexyl anion (56)

75.8	Broad S		a

Signals between 115 and 143 p.p.m. (uncertain integration) which were not assigned.

Spectrum run in DMF as solvent at 0°C but temperature has little effect on the spectrum below 60°C. Above this temperature the signal at 75.8 p.p.m. rapidly broadens and finally disappears, whilst other signals seem little affected except for some slight broadening.



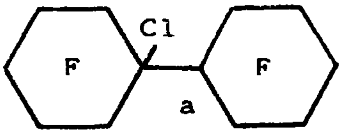
(56)

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment

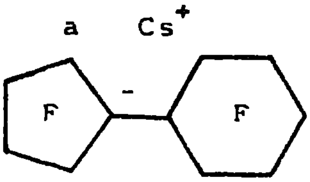
26. 1-chloro-F-1-cyclohexylcyclohexane (57)

166.0	Broad S	1	a

Signals between 101 and 149 p.p.m. (equivalent to 20F) which were not assigned.
Run as solution in ether.



(57)



(58)

27. F-1-cyclohexylcyclopentyl anion (58)

79.0	Broad S		a

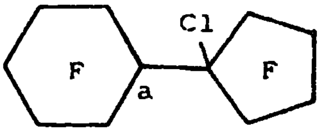
Signals between 110 and 145 p.p.m. (uncertain integration) which were not assigned.

Spectrum run in DMF as solvent at 0°C but temperature has little effect on the spectrum below 40°C. Above this temperature signals slowly start to broaden with the exception of a signal at 129.3 p.p.m. which sharpens. However, the signal at 79.0 p.p.m. never disappears completely and is still visible at 130°C.

28. 1-chloro-F-1-cyclohexylcyclopentane (59)

174.6	Broad M	1	a

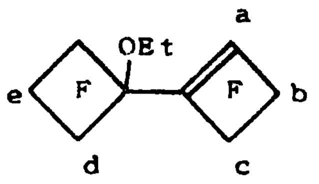
Signals between 101 and 149 p.p.m. (equivalent to 18F) which were not assigned. Run as solution in ether.



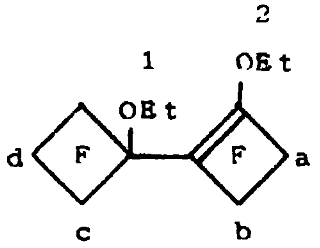
(59)

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
29. 1-ethoxy-F-cyclobutenylcyclobutane (60)			
98.9	T(J = 16) of T(J =18)	1	a
116.1	M	2	c
121.1	M	2	b
123.8 133.3	AB J = 228	4	d
131.5 133.8	AB J = 223	2	e

^{1}H at 1.40 (CH_3, T , J = 7) and 3.97 (CH_2, Q, J = 7)



(60)



(61)

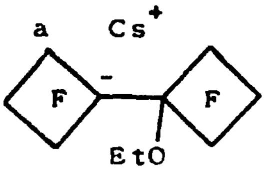
Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
30. 1-(1'-ethoxyhexafluorocyclobutyl)-2-ethoxytetrafluoro-cyclobutene (61)			
111.2	M	2	b
116.1	T J = 4	2	a
123.9 133.3	AB J = 224	4	c
131.7 133.8	AB J = 223	2	d

^{1}H at 1.40 (CH_3 (1), T, J = 7), 1.53 (CH_3 (2), T, J = 7), 3.83 (CH_2 (1), Q, J = 7) and 4.53 (CH_2 (2), Q, J = 7).

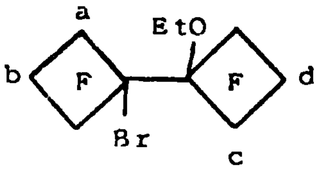
Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
31. 1-(1'-ethoxy-F-cyclobutyl)-F-cyclobutyl anion (62)			
84.0	Very Broad S	3	a

Signals between 119 and 138 p.p.m. (equivalent to 8F) which were not assigned.

Spectrum run in DMF as solvent at 40°C. As temperature is lowered below 10°C extra small peaks appear. As it is raised above 50°C the signal at 84.0 p.p.m. broadens very rapidly and disappears completely at 60°C.



(62)



(63)

32. 1-ethoxy-1-(1'-bromo-F-cyclobutyl)-F-cyclobutane (63)

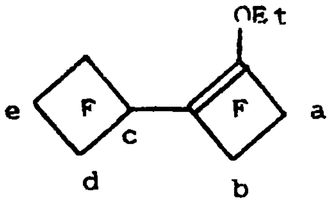
109.7 119.3	AB J = 216	2	a
125.7	Broad Complex Signal	2	c
126.0 128.7	AB J = 221	1	b
131.2	S	1	d

^{1}H at 1.63 (CH_3, T(J = 7) of D(J = 1.5)) and 4.20 (CH_2, Q, J = 7).

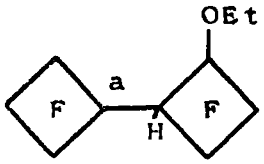
33. 1-ethoxy-F-2-cyclobutylcyclobutene (64)

Shift p.p.m.	Fine Structure J value in Hz	Relative Intensity	Assignment
111.2	M	2	b
116.3	M	2	a
127.2 133.8	AB J = 229	4	d
130.8 134.4	AB J = 229	2	e
179.4	S	1	c

^{1}H at 1.50 (CH_3, T, J = 7) and 4.48 (CH_2, Q, J = 7).



(64)



(65)

34. 1-ethoxy-2-hydro-F-2-cyclobutylcyclobutane (65)

Shift p.p.m.	Fine Structure J value in Hz	Relative Intensity	Assignment
195.5	M	1	a

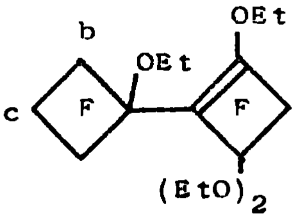
Signals between 113.6 and 138.5 p.p.m. (equivalent to 11F) which were not assigned.

^{1}H at 1.62 (CH_3, T(J = 7) of D(J = 1)), 4.28 (CH_2, Q, J = 7) and 3.48 (CH, very broad).

35. 1-(1'-ethoxyhexafluorocyclobutyl)-2,3,3-triethoxy-4,4-difluorocyclobutene (66)

Shift p.p.m.	Fine Structure J value in Hz	Relative Intensity	Assignment
112.7	S	1	a
122.8 133.1	AB J = 219	2	b
130.5 133.3	AB J = 219	1	c

^{1}H at 3.90, 3.96 and 4.42: all CH$_2$'s, Q, J = 7; ratio 2:1:1. Signal centred at ca. 1.5 due to overlapping CH$_3$ resonances.



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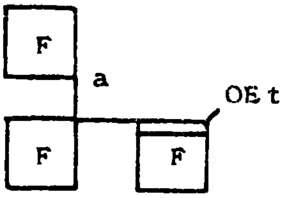

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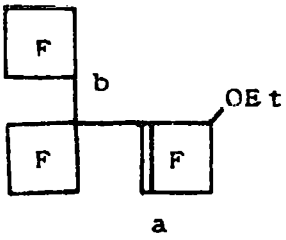


(68)

36. 1-ethoxy-F-2-(1'-cyclobutylcyclobutyl)cyclobutene (67)

174.2	S	1	a

Signals between 108 and 133 p.p.m. (equivalent to 16F) which were not assigned.

^{1}H at 1.60 (CH$_3$, T, J = 7) and 4.58 (CH$_2$, Q, J = 7).

37. 4-ethoxy-F-1-(1'-cyclobutylcyclobutyl)cyclobutene (68)

98.0	S	1	a
174.5	S	1	b

Signals between 112 and 134 p.p.m. (equivalent to 15F) which were not assigned.

^{1}H at 1.53 (CH$_3$, T, J = 7) and 4.22 (CH$_2$, Q, J = 7).

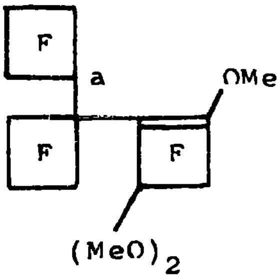
Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment

38. 1,3,3-trimethoxy-F-2-(1'-cyclobutylcyclobutyl)cyclo-butene (69)

172.6	S	1	a

Signals between 111 and 133 p.p.m. (equivalent to 14F) which were not assigned.

^{1}H at 3.75 (S, (1)) and 4.30 (S, (2)).



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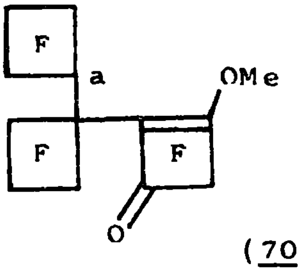


(70)

39. 1-methoxy-F-2-(1'-cyclobutylcyclobutyl)cyclobuten-3-one (70)

178.6	P J = 23	1	a

Signals between 111 and 133 p.p.m. (equivalent to 14F) which were not assigned.

^{1}H at 4.65 (S). Spectrum run in CCl_4 as solvent.

40. 1,3-diethoxy-2-(1'-ethoxyhexafluorocyclobutyl)-F-3-cyclo-butylcyclobutene (73)

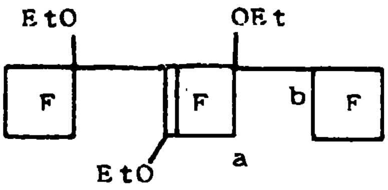
107.9	M	2	a
176.4	Broad M	1	b

Signals between 122 and 136 p.p.m. (equivalent to 12F) which were unassigned.

^{1}H: CH_3's centred at 1.6 p.p.m.; CH_2's at 4.2 p.p.m..

Spectrum run in CCl_4 as solvent.

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment



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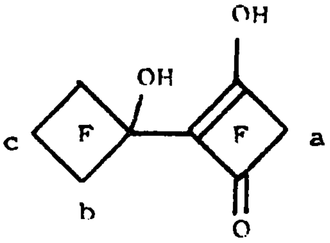


(74)

41. 1-hydroxy-2-(1'-hydroxyhexafluorocyclobutyl)-4,4-difluoro--cyclobuten-3-one (74)

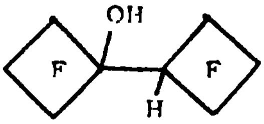
115.3	S	1	a
125.9 132.5	AB J = 222	2	b
131.6	D J = 20	1	c

^{1}H: single sharp peak at 8.25 p.p.m..

42. 1-hydro-1-(1' hydroxy-F-cyclobutyl)-F-cyclobutane (75)

Signals between 110 and 140 p.p.m. all unassigned.

^{1}H: single broad peak at 3.7 p.p.m..



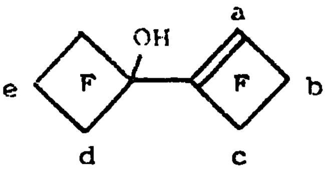
(75)

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment

43. 1-hydroxy-F-1-cyclobutenylcyclobutane (76)

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
99.9	T(J = 15) of T(J = 18)	1	a
116.3	M	2	c
121.5	M	2	b
127.5 134.8	AB J = 225	4	d
132.6	D J = 12	2	e

^{1}H: broad resonance centred at 4.25 p.p.m..



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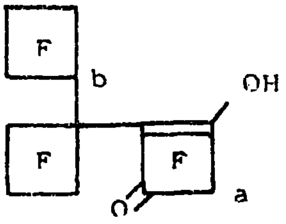


(72)

44. 1-hydroxy-2-($1'$-F-cyclobutylcyclobutyl)-4,4-difluoro-cyclobuten-3-one (72)

119.7	S	2	a
178.2	P J = 22	1	b

Signals between 115 and 137 p.p.m. (equivalent to 12F) which were not assigned.

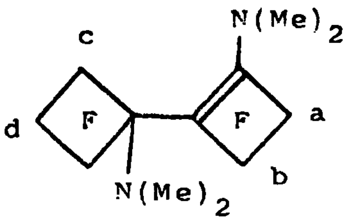
Spectrum run as aqueous solution.

C.f. spectrum no. 39.

45. 1-dimethylamino-2-(1'-dimethylamino-F-cyclobutyl)-F-cyclobutene (78)

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
103.4	T(J = 18) of T(J = 24)	1	b
115.8	S	1	a
111.1 124.9	AB J = 227	2	c
130.6 135.2	AB J = 226	1	d

^{1}H: two singlets (1:1) at 2.72 and 3.13, which were not assigned.



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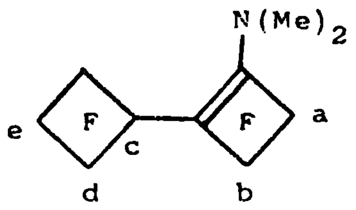


(79)

46. 1-dimethylamino-2-cyclobutylcyclobutene (79)

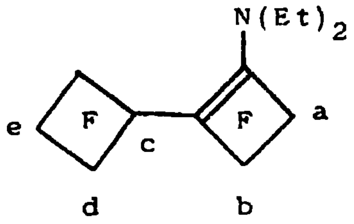
104.4	Broad S	2	b
117.0	S	2	a
125.7 132.8	AB J = 228	4	d
130.6 134.0	AB J = 228	2	e
154.9	Broad S	1	c

^{1}H at 3.31 (S).

47. 1-diethylamino-2-F-cyclobutylcyclobutene (80)

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
104.2	M	2	b
116.0	M	2	a
125.9 132.0	AB J = 226	4	d
130.1 133.6	AB J = 228	2	e
159.2	S	1	c

^1H at 1.42 (CH_3, T, J = 7) and 3.55 (CH_2, Q, J = 7).



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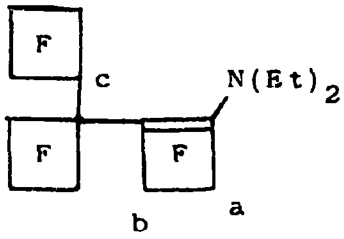


(81)

48. 1-diethylamino-2-($1'$-F-cyclobutylcyclobutyl)-F-cyclobutene (81)

103	Very Broad S	2	b
114.1	Very Broad S	2	a
172.9	S	1	c

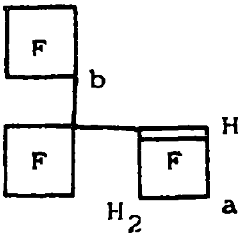
Signals between 115 and 133 p.p.m. (equivalent to 12F) which were not assigned.

^1H at 1.36 (CH_3, T, J = 7) and 3.34 (CH_2, Q, J = 7).

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
49. 1-(1'-F-cyclobutylcyclobutyl)-3,3-difluorocyclobutene (82)			
109.6	S	2	a
176.1	S	1	b

Signals between 118 and 133 p.p.m. (equivalent to 12F) which were not assigned.

^{1}H at 3.35 (CH_2, T, J = 3) and 6.59 (CH, S).



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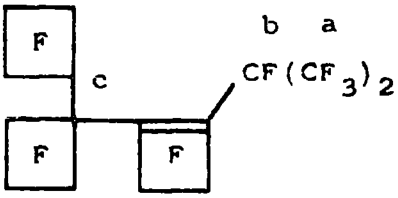


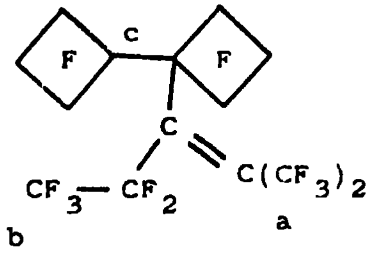
(83)

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
50. F-1-isopropyl-2-(1'- cyclobutylcyclobutyl)cyclobutene (83)			
75.6	S	6	a
173.1	D $J_{b,c}$ = 98	1	b
184.4	D $J_{b,c}$ = 98	1	c

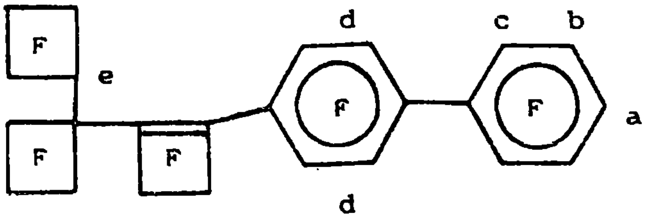
Signals between 110 and 133 p.p.m. (equivalent to 16F) which were not assigned.

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
51. F-2-methyl-3-(1'-cyclobutylcyclobutyl)pent-2-ene (84)			
62.3	M	6	a
82.1	T J = 13	3	b
179.2	P J = 22	1	c

Signals between 106 and 133 p.p.m (equivalent to 14F) which were not assigned.



(84)



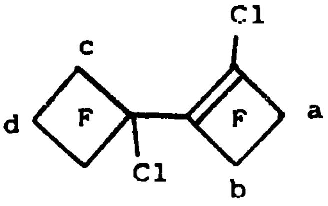
(85)

52. F-1-parabiphenyl-2-(1'-cyclobutylcyclobutyl)cyclobutene (85)			
136.4		4	d
138.1		2	c
150.5		1	a
161.8		2	b
171.7		1	e

Signals between 109 and 128 p.p.m. (equivalent to 16F) which were not assigned.

Spectrum run in ether as solvent by Dr. R.S. Matthews using a Bruker HX90E Spectrometer.

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
53. 1-chloro-2-(1'-chloro-F-cyclobutyl)-F-cyclobutene (86)			
114.1	M	1	b
120.7	M	1	a
121.9	S	2	c
129.6	S	1	d



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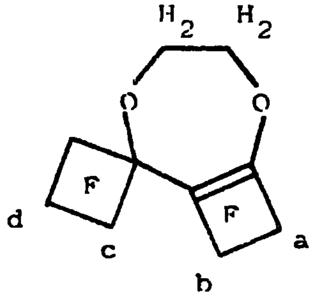


(87)

54. bicyclo-(5.2.0)-2-spirohexafluorocyclobutyl-3,6-dioxa-8,8,9,9-tetrafluoronon-(1,7)-ene (87)			
109.3	Broad S	1	b
121.4	S	1	a
124.9 132.4	AB J = 221	2	c
131.2 133.3	AB J = 224	1	d

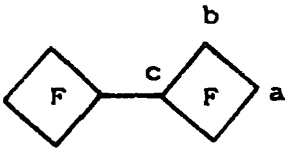
^{1}H: D(J = 22) of M's; unassigned. Possibly overlapping D and D of D's.

Spectrum recorded in CCl_4 as solvent.

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment

55. F-bicyclobutyl (46)

130.7	M	4	b
133.4 136.5	AB $J = 229$	2	a
192.2	Broad S	1	c



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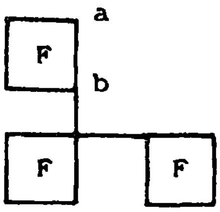


(89)

56. F-1,1-dicyclobutylcyclobutane (89)

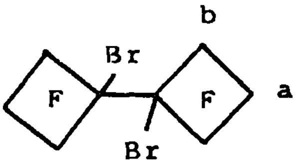
130.5	D $J_{a,b} = 32$	8	a
175.6	P $J_{a,b} = 32$	2	b

Signals between 112 and 129 p.p.m. (equivalent to 10F) which were not assigned.

57. 1-bromo-1-($1'$-bromo-F-cyclobutyl)-F-cyclobutane (90)

103.4 120.3	AX $J = 208$, Very Broad	2	b
123.7 127.8	AB $J = 225$	1	a

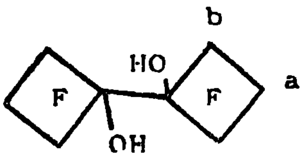
Spectrum recorded at 80°C.



(90)

58. 1-hydroxy-1-(1'-hydroxy-F-cyclobutyl)-F-cyclobutane (91)

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
128.0	S	2	b
131.3 137.6	AB J = 224	1	a



(91)

(93) a and b

1-methoxy-F-1-cyclobutylcyclopropane and 1-methoxy-F--cyclopropylcyclobutane (93) a and b

59. compound (93a)

182.7	Broad S	1	a

Signals between 124 and 138 p.p.m. (equivalent to 10F) which were not assigned.

^1H at 4.07 (S).

60. compound (93b)

185.6	P J = 16	1	a

Signals between 122 and 137 p.p.m. (equivalent to 10F) which were not assigned.

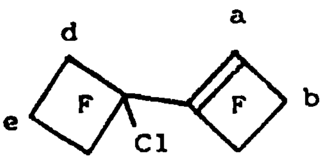
^1H at 4.00 (S).

The CF_2 resonances for both compounds appear as AB's, thus hampering assignment.

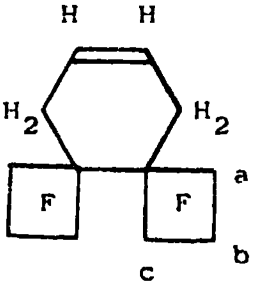
Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment

61. <u>1-chloro-F-1-cyclobutenylcyclobutane (95)</u>

98.6	Broad S	1	a
116.4	M	2	c
122.2	M	2	b
123.1	D J = 8	4	d
129.7	S	2	e



(95)



(96)

62. <u>4,5-dispiro(hexafluorocyclobutyl)cyclohexene (96)</u>

120.7	M	1	a
130.7	S	1	c
130.3	S	1	b

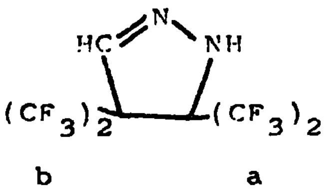
^{1}H at 2.67 (CH_2, S) and 6.67 (CH, S).

63. <u>4,4,5,5-tetrakis(trifluoromethyl)-2-pyrazoline (98)</u>

60.4		1	a
65.9		1	b

^{1}H at 7.17 (CH, Q, J = 5) and 11.0 (NH, very broad S).

Spectrum run in $CDCl_3$ as solvent



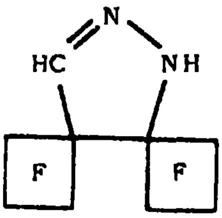
(98)

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment

64. 4,5-dispiro(hexafluorocyclobutyl)-2-pyrazoline (99)

Signals between 119 and 135 p.p.m. which were not assigned.

^{1}H at 3.72 (NH, D, J = 14) and 7.25 (CH, D, J = 34).



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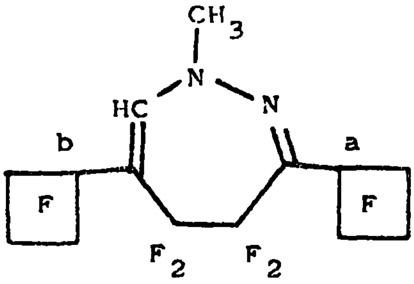


(100)

65. 1-methyl-3,6-di(heptafluorocyclobutyl)-4,4,5,5-tetra-fluoro-1,2-diazepine (100)

154.0	S	1	a
164.1	S	1	b

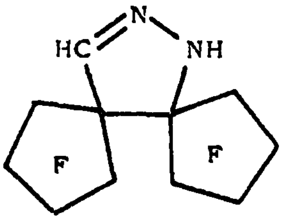
Signals between 120 and 138 p.p.m. (equivalent to 16F) which were unassigned.

^{1}H at 3.83 (CH_3, S) and 6.97 (CH, S). Spectrum run in $CDCl_3$.

66. 4,5-dispiro(octafluorocyclopentyl)-2-pyrazoline (102)

Signals between 108 and 135 p.p.m. which were unassigned.

^{1}H at 7.07 (CH, S) and 8.60 (NH, S). Spectrum run in D_6 acetone.

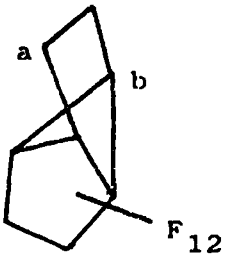


(102)

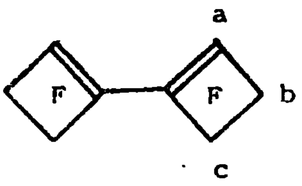
Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment

67. F-tricyclo(2.2.^{1,5}0.^{2,6}0)octane (106)

129.3	S	2	a
220.3	S	1	b



(106)



(107)

68. F-bicyclobutenyl (107)

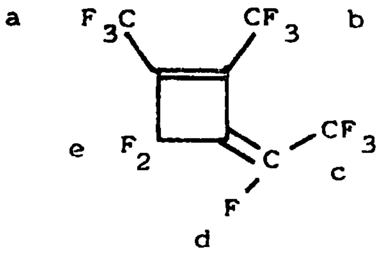
101.1	Broad S	1	a
119.3	M	2	c
121.1	M	2	b

69. F-ethylene-2,3-dimethylcyclobutene (108)

cis-isomer

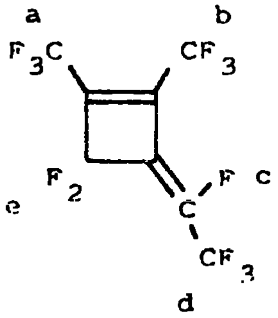
65.1	Q J = 6	3	a
73.9	D($J_{c,d}$ = 10) of Q(J = 10)	3	c
113.8	S	2	e
127.6	Q $J_{c,d}$ = 10	1	d

Resonance due to (b) is hidden under the corresponding resonance for the trans-isomer.

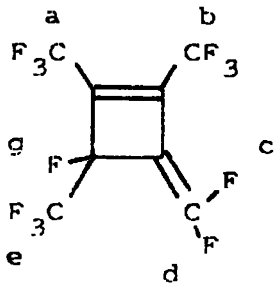


(108)

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
trans-isomer			
65.7	Q J = 6	3	a
68.7	M	3	b
75.3	D(J = 11) of T(J = 6)	3	d
110.9	M	2	e
135.9	M	1	c



trans-(108)

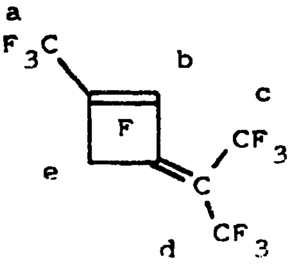


(109)

70. F-methylene-2,3,4-trimethylcyclobutene (109)

65.7	S	3	a
69.3	M	3	b
81.5	M	3	e
83.1	D($J_{c,d}$ = 21) of Q(J = 8)	1	c
84.9	D($J_{c,d}$ = 21) of Q(J = 10)	1	d
178.6	Broad S	1	g

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
71. F-2-propylidene-(3′-methyl)cyclobutene (110)			
62.9	D(J = 23) of Q(J = 8)	3	c
64.3	M	3	d
64.6	D J = 8	3	a
83.3	M	1	b
107.9	D(J = 19) of Q(J = 9)	2	e



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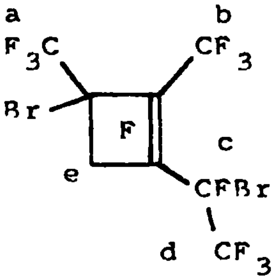

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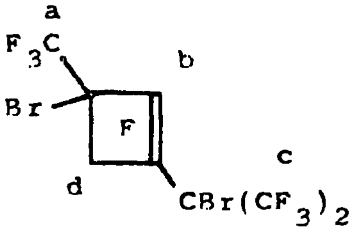


(114)

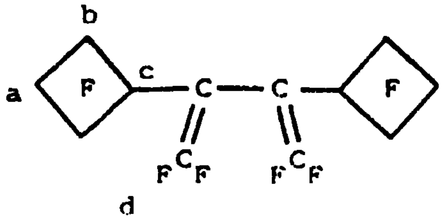
Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
72. 3-bromo-1-(2′-bromo-F-ethyl)-F-2,3-dimethylcyclobutene (113)			
61.6	D J = 17	3	b
69.7	T(J = 19) of Q(J = 3)	3	a
79.8	Q J = 9 (distorted)	3	d
101.8 108.7	AB J = 196	2	e
131.8	Broad M	1	c
73. 3-bromo-1-(2′-bromo-F-2′-methylethyl)-F-3-methylcyclo-butene (114)			
89.4	M	1	b
103.5 110.0	AB J = 184	2	d

Complex resonance at 72.7 (centre) equivalent to 9F (a & c).

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment

74. F-2,3-dicyclobutyl-1,3-butadiene (116)

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
69.8	Broad M	2	d
133.4	S	4	b
129.6 136.5	AB J = 225	2	a
169.0	Broad S	1	c



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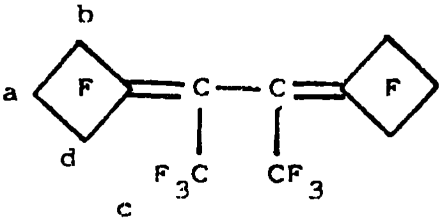


(117)

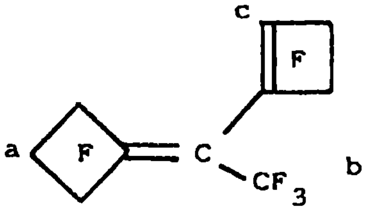
75. F-2,3-di(methylenecyclobutyl)butane (117)

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
65.9	Broad S	3	c
117.8	Q J = 9	2	d
118.6	D J = 25	2	b
133.6	S	2	a

76. F-methyl-cyclobutylmethylenecyclobutane (118)

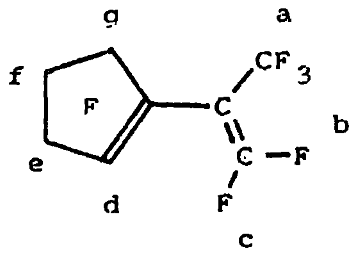
Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
67.5	Broad S	3	b
94.7	Broad S	1	c
132.7	S	2	a

Signals at 115.7 (M), 116.9 (Broad S), 118.6 (M) and 121.9 (M), all equivalent to 2F and all unassigned.



(118)

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
77. F-2-(cyclopenten-1'-yl)-propene (119)			
58.5	Broad M	3	a
65.6	Broad M	1	b
67.4	Broad M	1	c
111.5	Broad S	2	g
119.5	Broad S	1	d
121.4	M	2	e
133.7	Overlapping T's J = 22 & 24	2	f



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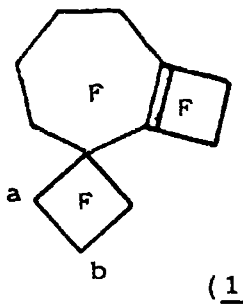


(120)

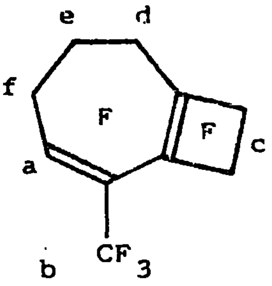
Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
78. F-spiro(cyclobutane-1',2-bicyclo(5.2.0)non-(1,7)-ene) (120)			
113.2 121.0	AB J = 231	4	a
129.8 133.4	AB J = 223	2	b

Signals at 110.2 (Broad), 111.2 (Broad), 115.5 (M), 117.3 (Broad), 127.0 (Broad) and 131.6 (Broad), all equivalent to 2F and all unassigned.

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment

79. F-bicyclo(5,2,0.)-2-methylnona-(1,7),(2,3)-diene (121)

62.1	D(J = 25) of T(J = 10)	3	b
91.2	M (possibly Q of T)	1	a
113.7	M	2	d
114.9	M	2	f
122.0	Broad S	4	c
133.2	Distorted P	2	e



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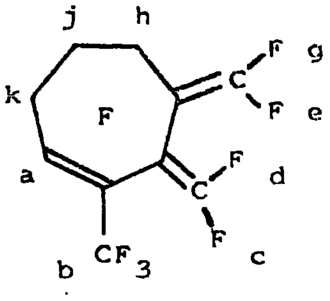
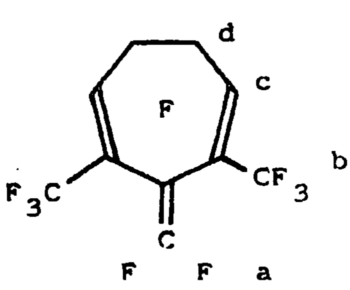


(122)

80. F-1,2-dimethylene-3-methylcyclohept-3-ene (122)

63.6	D(J = 20) of D($J_{b,c}$ = 11)	3	b
69.6	Q $J_{b,c}$ = 11	1	c
69.8	D $J_{d,e}$ = 8	1	d
72.6	T $J_{g,h}$ = 41	1	g
73.2	D $J_{d,e}$ = 8	1	e
105.4	M	1	a
113.4	D $J_{g,h}$ = 41	2	h
118.7	Broad S	2	k
133.7	Broad S	2	a

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
81. F-3-methylene-2,4-dimethylcyclohepta-1,4-diene (123)			
64.5	D(J = 20) of D(J = 12)	3	b
67.6	Broad M	1	a
110.0	Broad M	1	c
124.6	D(J = 52) of M	2	d



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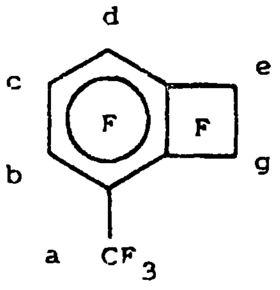


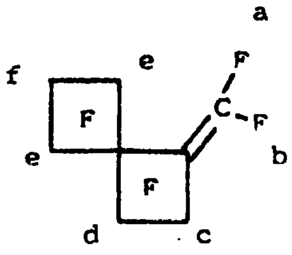
(124)

82. F-o-methylbenzocyclobutane (124)

63.8	M	3	a
108.1	S	2	e
108.5	S	2	g
122.7	Broad M	1	b
126.6	M	1	d
148.7	M	1	c

83. F-spiro(cyclobutane-1',1-(2-methylenecyclobutane)) (127)

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment
66.5	D(J = 7) of T(J = 6)	1	b
69.3	Broad S	1	a
114.5	M	2	c
119.6	T(J = 19) of M	2	d
120.1	AB J = 225	4	e
128.1			
134.1	P J = 21	2	f



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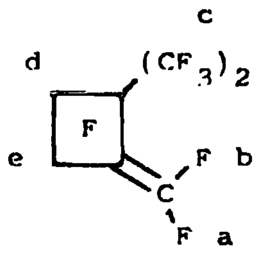

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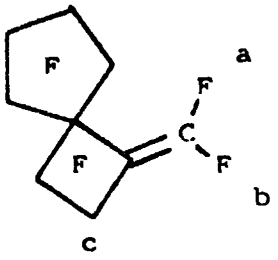


(129)

84. F-methylene-2,2-dimethylcyclobutane (128)

66.5	D(J = 7) of T(J = 6)	1	a
69.1	Q J = 9	6	c
70.0	M	1	b
114.5	S	2	e
120.7	M	2	d

85. F-spiro(cyclopentane-1',1-(2-methylenecyclobutane)) (129)

66.0	D(J = 8) of T(J = 8)	1	b
67.5	Broad S	1	a
116.5	M	2	c

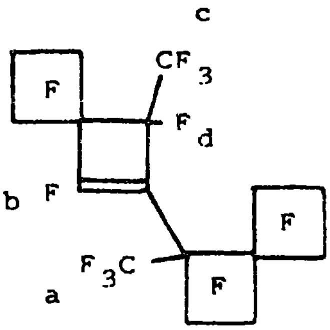
Signals between 119 and 135 p.p.m. (equivalent to 10F) which were not assigned.

Shift p.p.m.	Fine Structure J values in Hz	Relative Intensity	Assignment

86. F-1-(1'-methyl-2'-spirocyclobutylcyclobutyl)-3-spiro--cyclobutyl-4-methylcyclobutene (130)

63.2	Broad S	3	a
75.6	Broad S	3	c
97.3	Broad S	1	b
184.4	Broad S	1	d

Signals between 104 and 133 p.p.m. (equivalent to 16F) which were not assigned.



(130)

APPENDIX II

INFRARED SPECTRA

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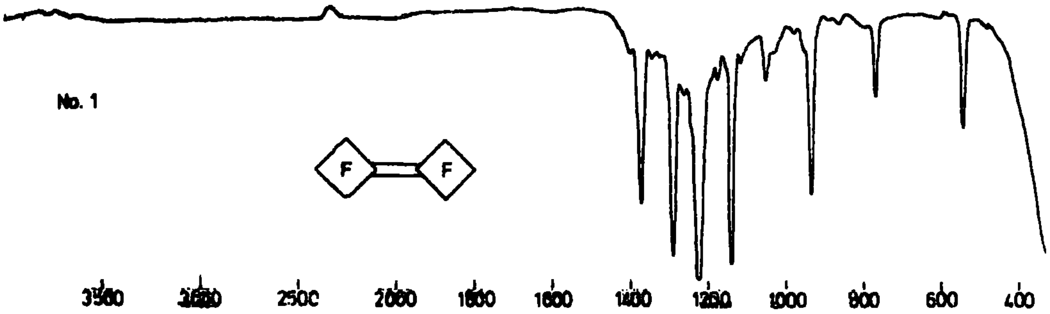

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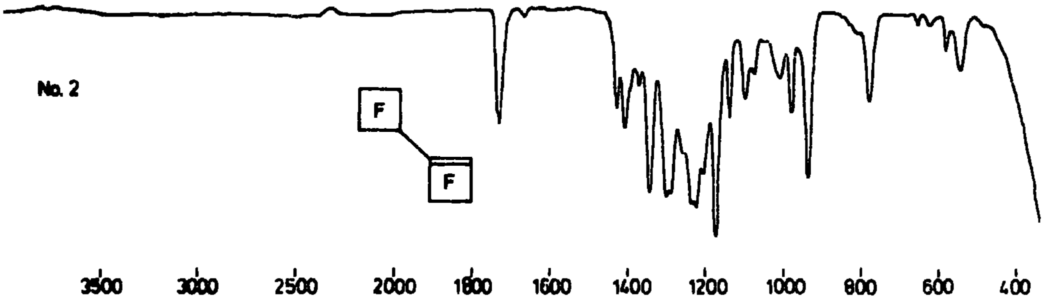

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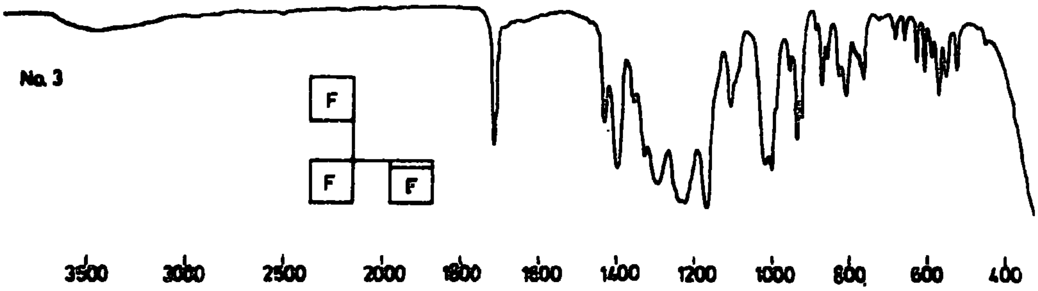

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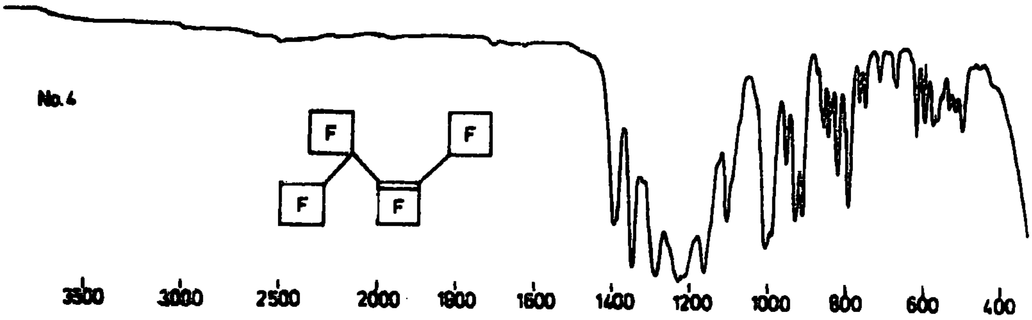

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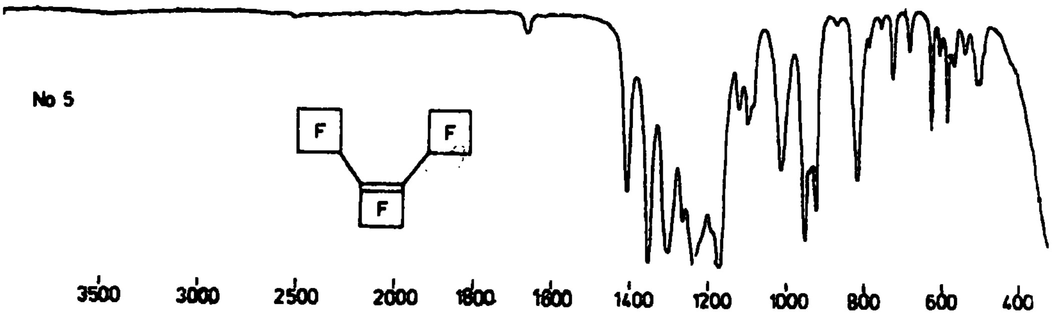

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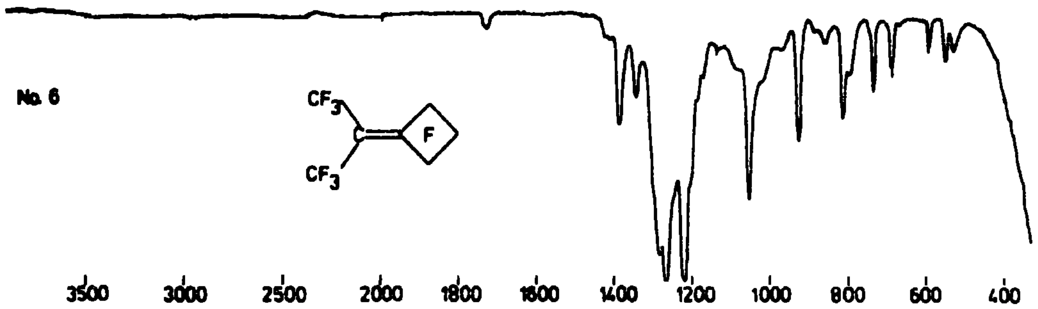

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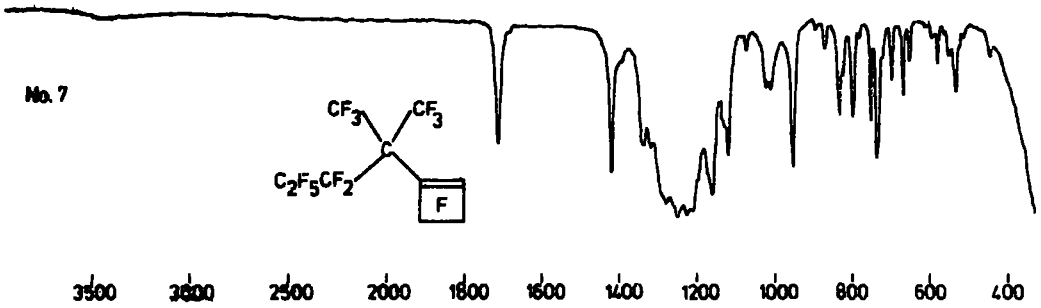

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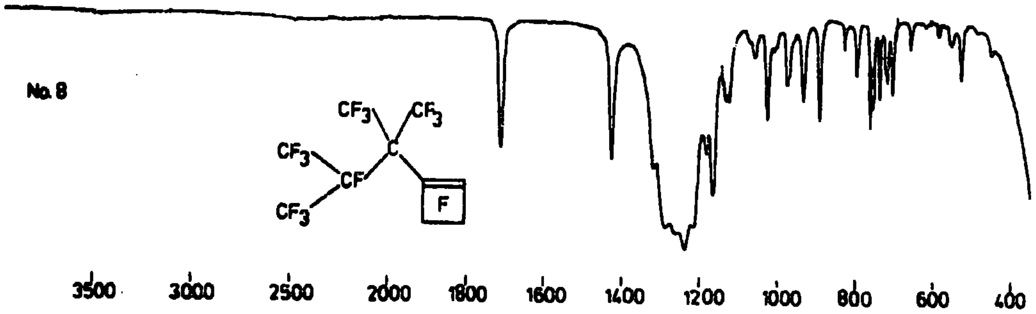

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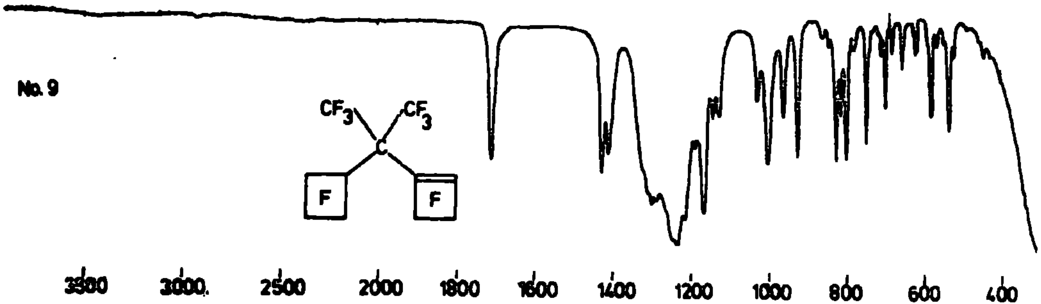

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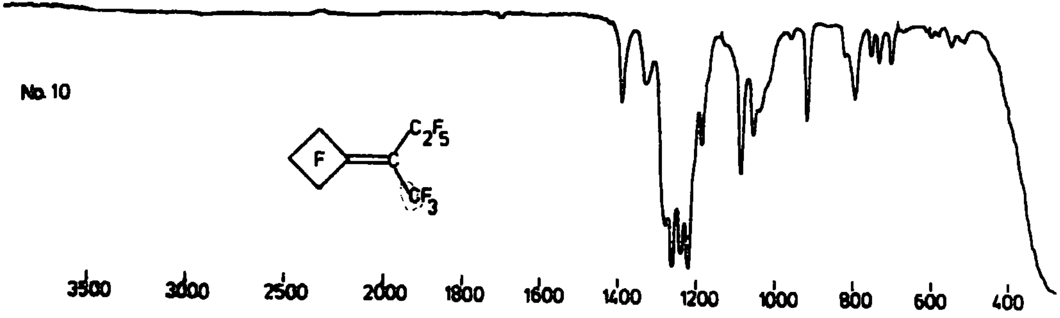

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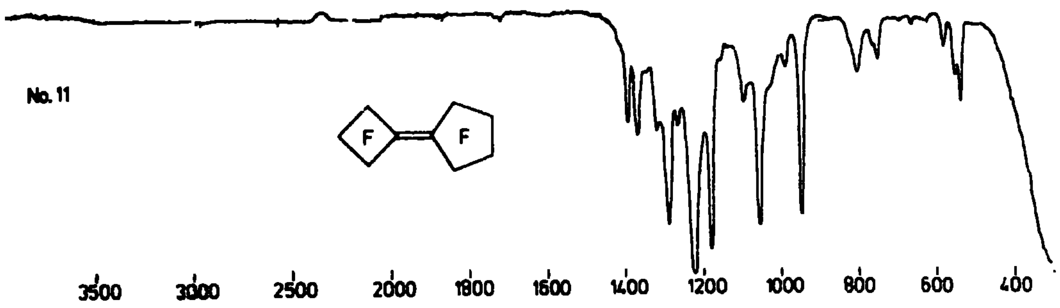

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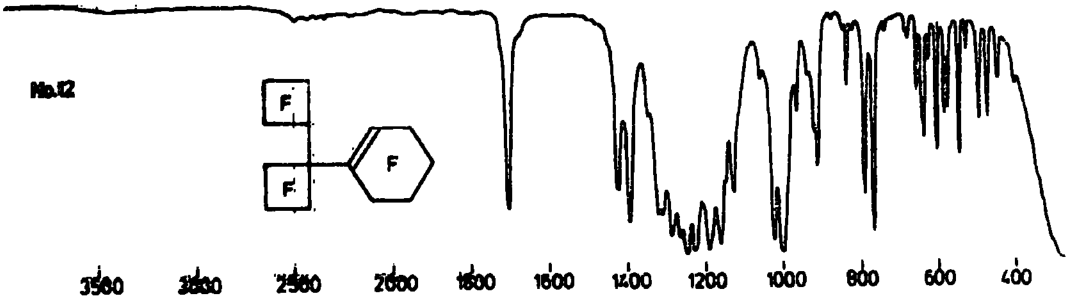

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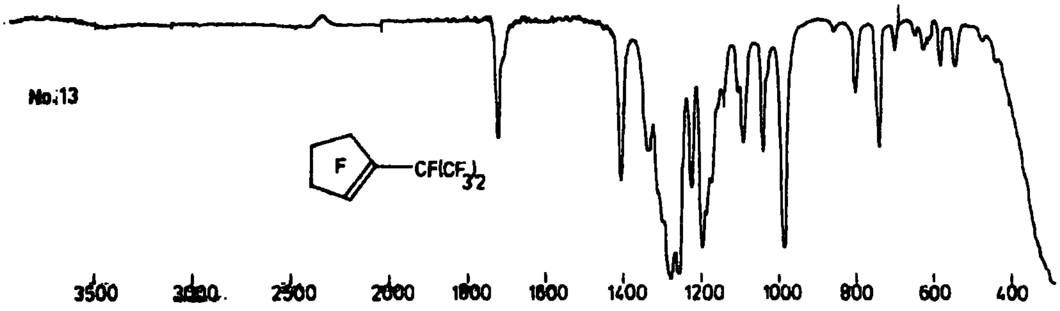

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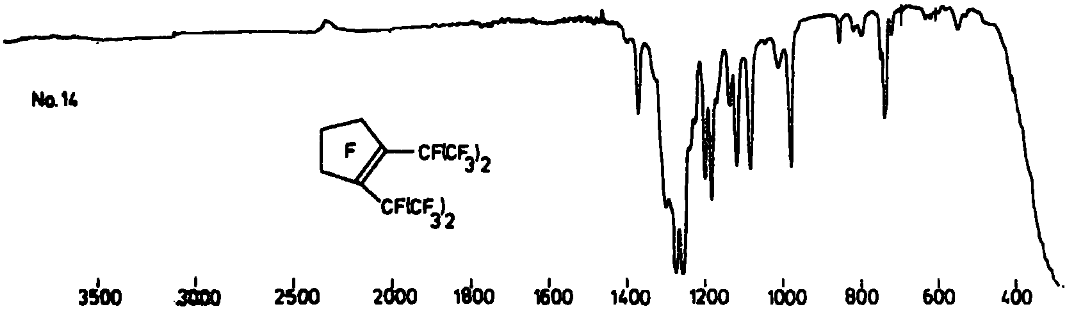

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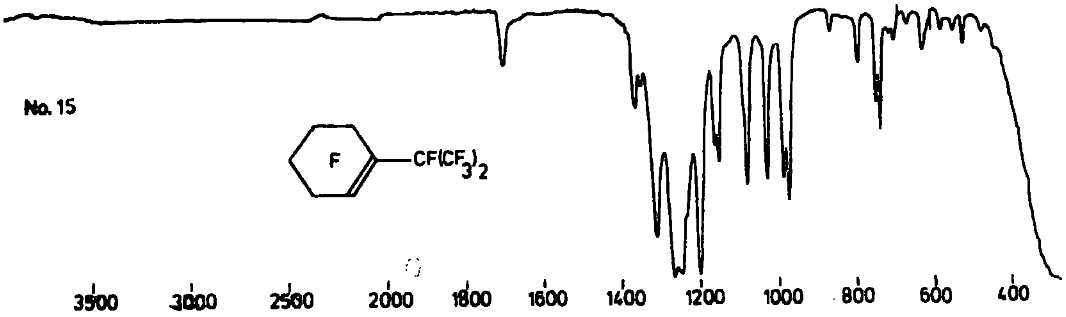

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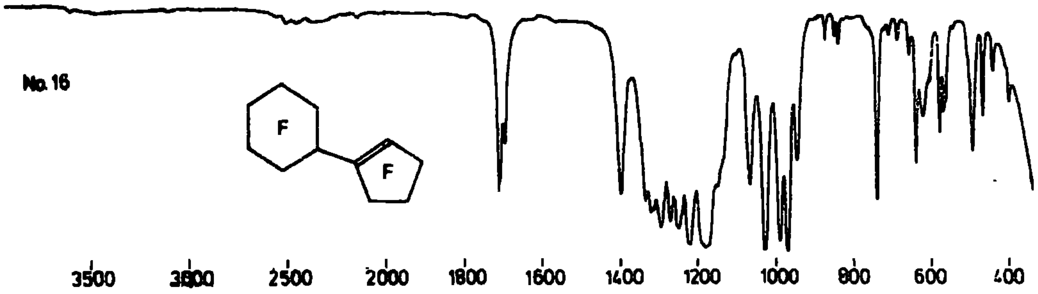

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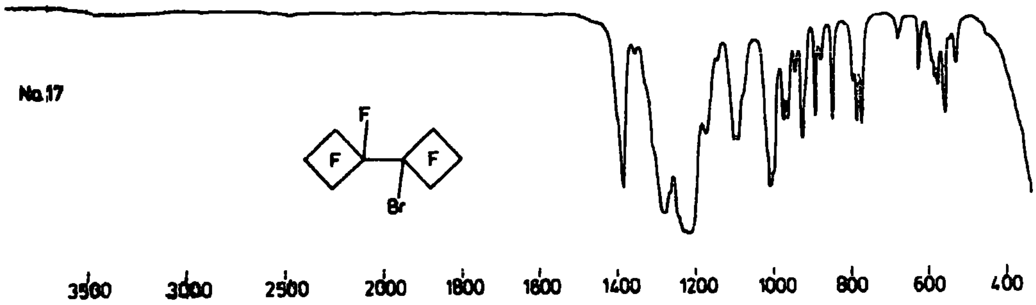

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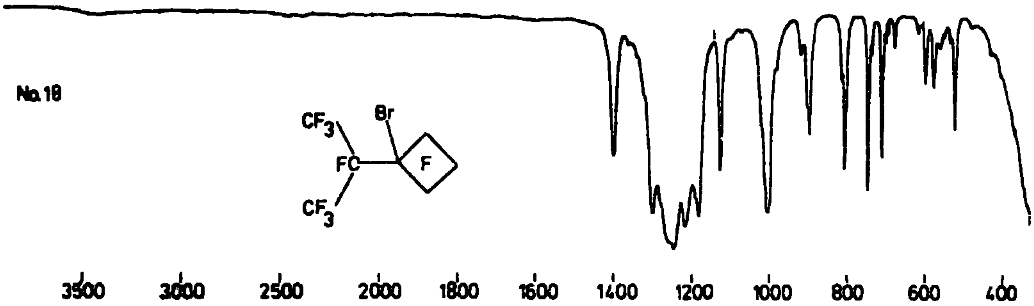

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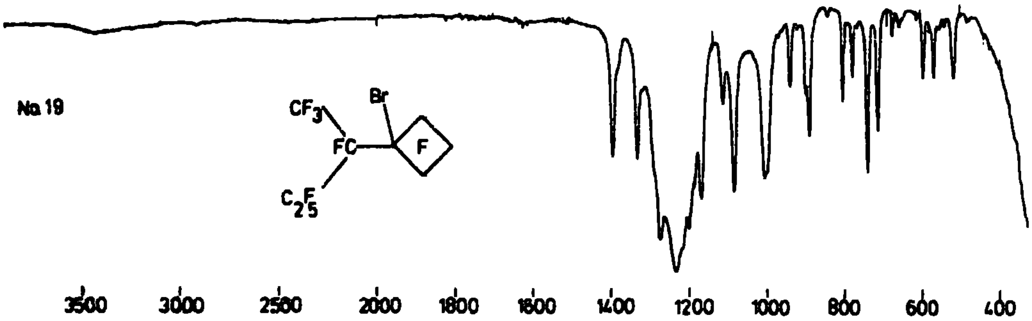

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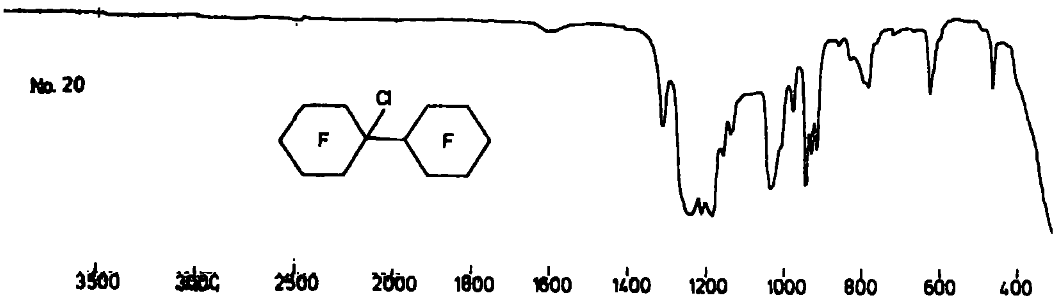

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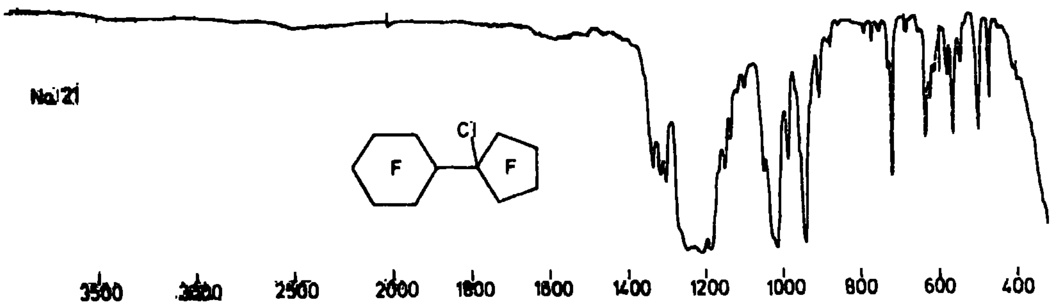

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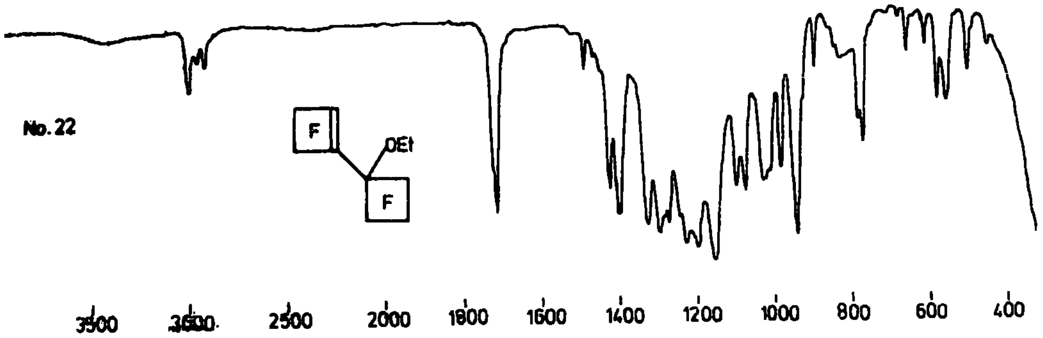

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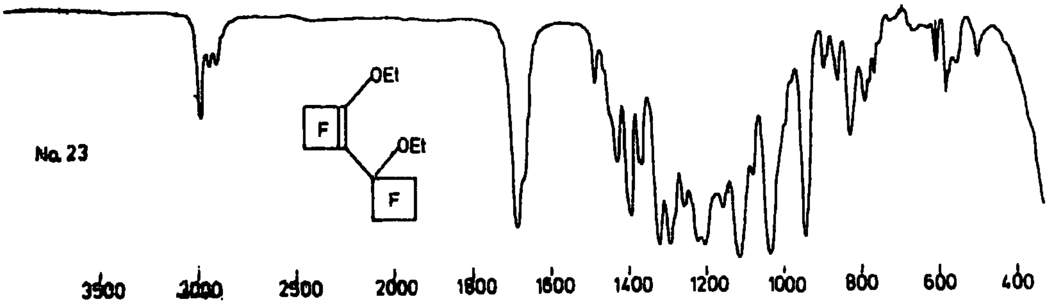

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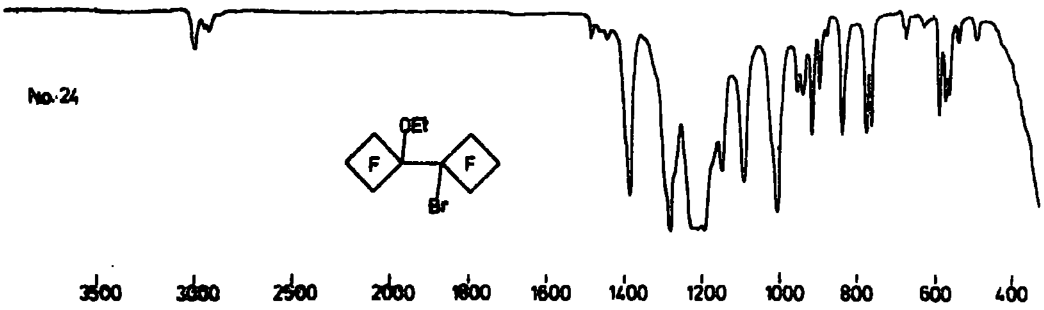

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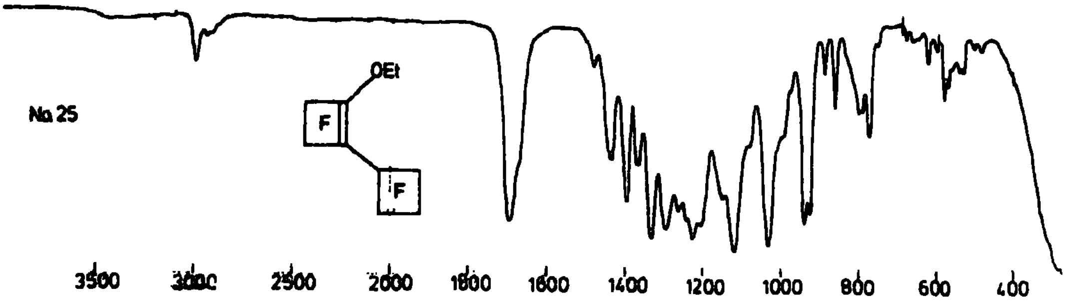

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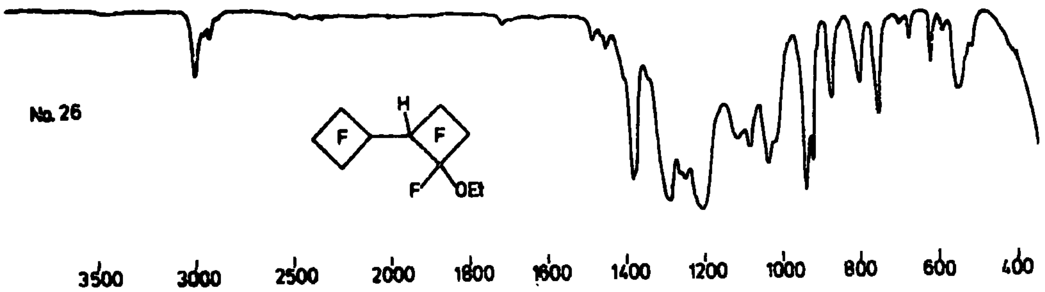

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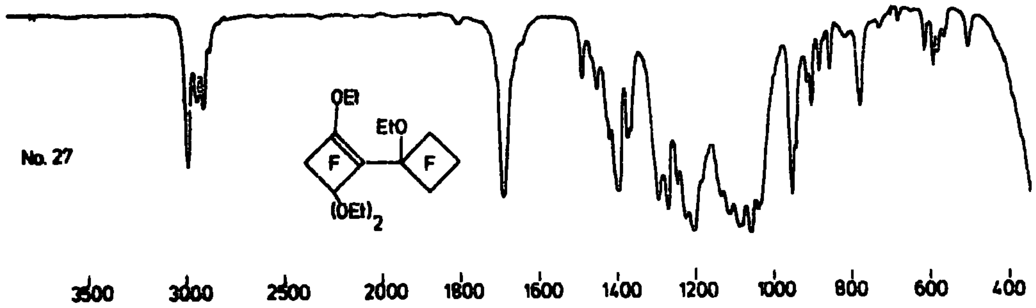

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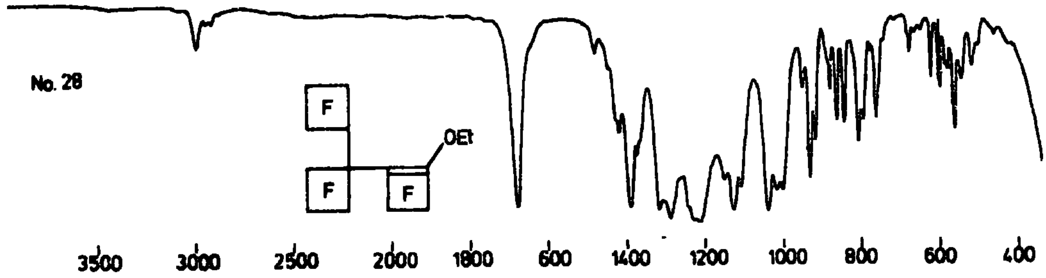

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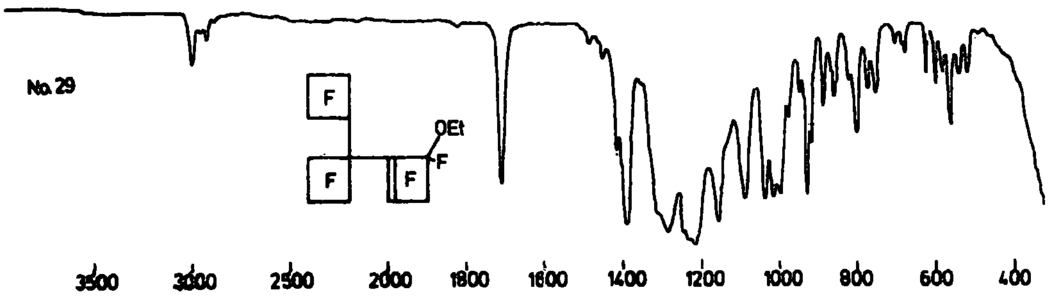

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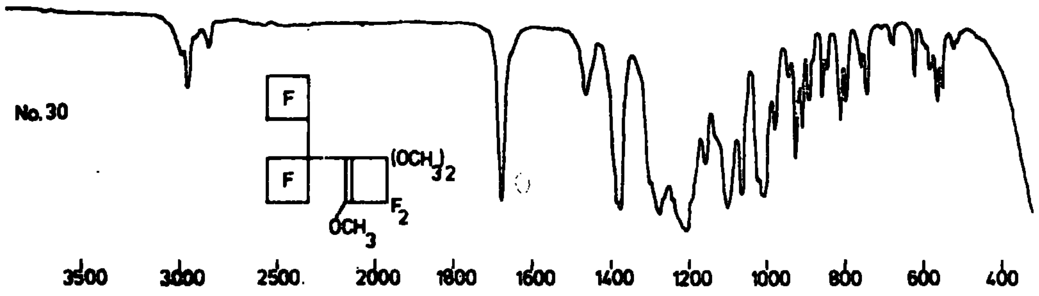

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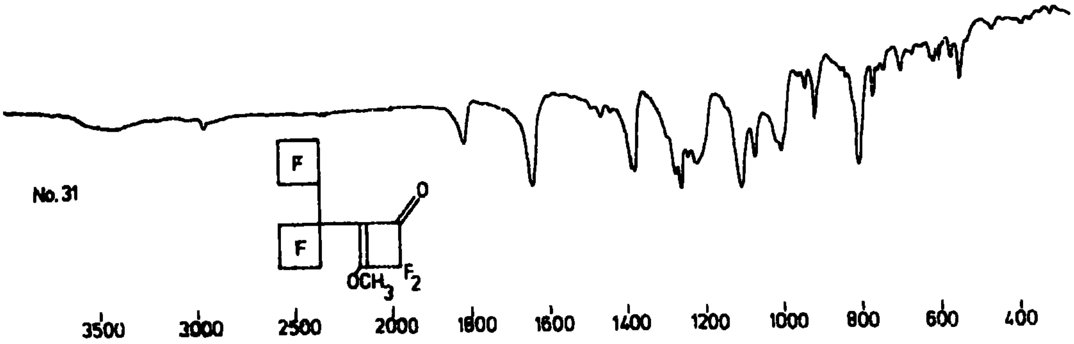

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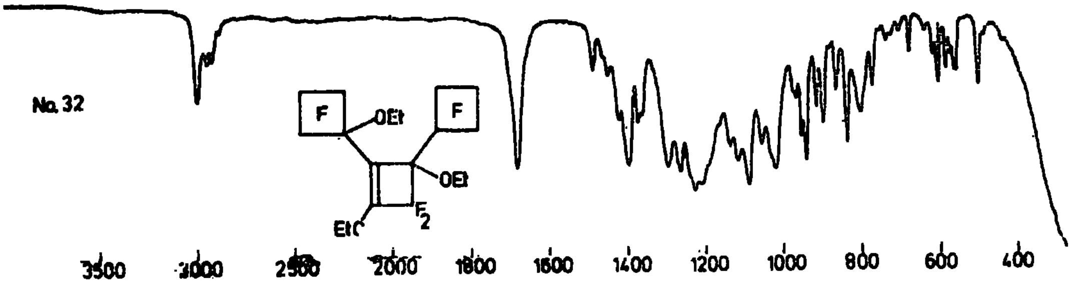

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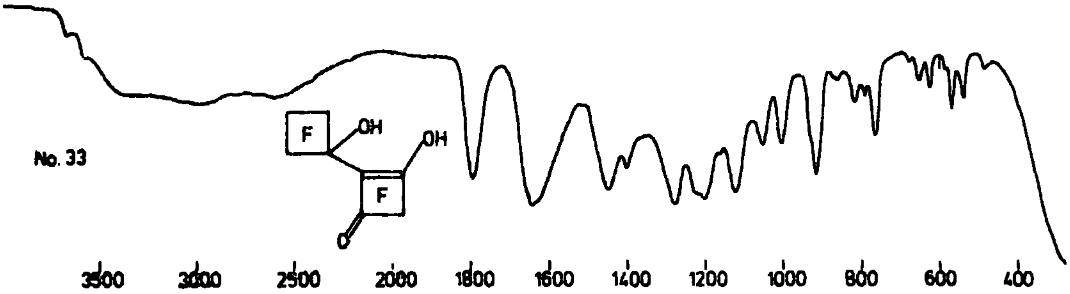

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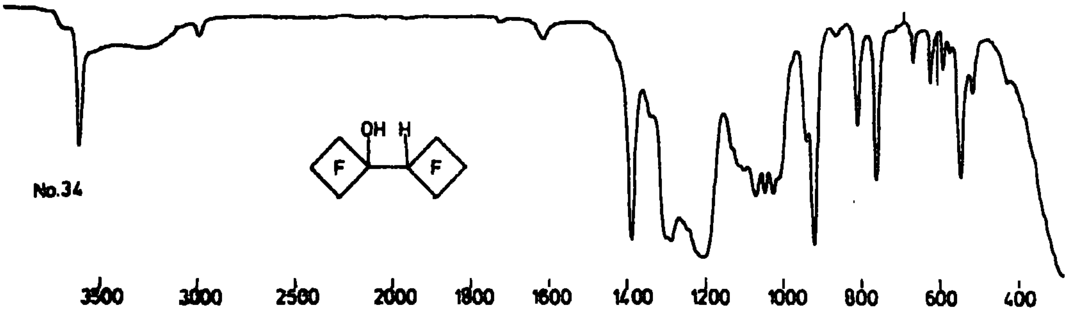

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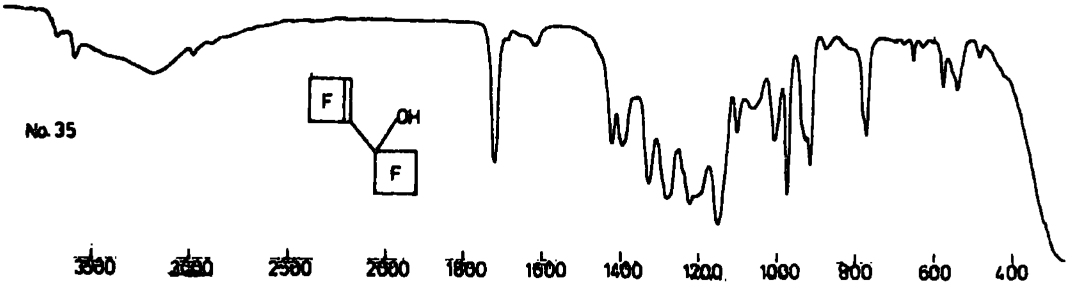

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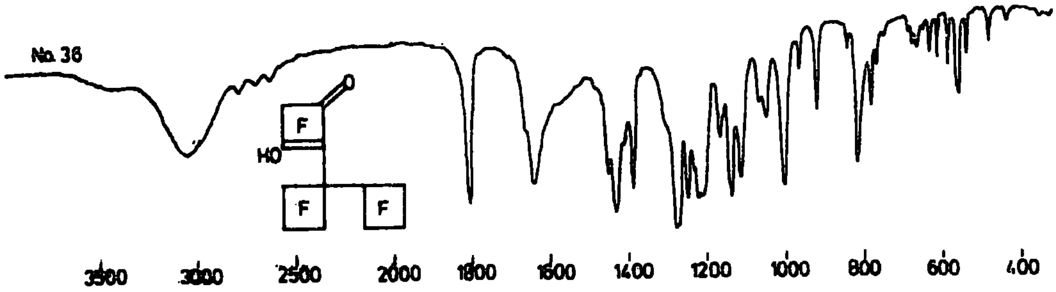

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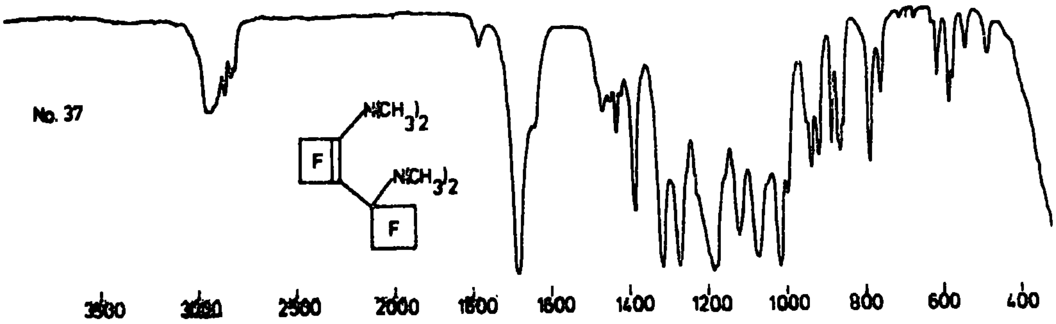

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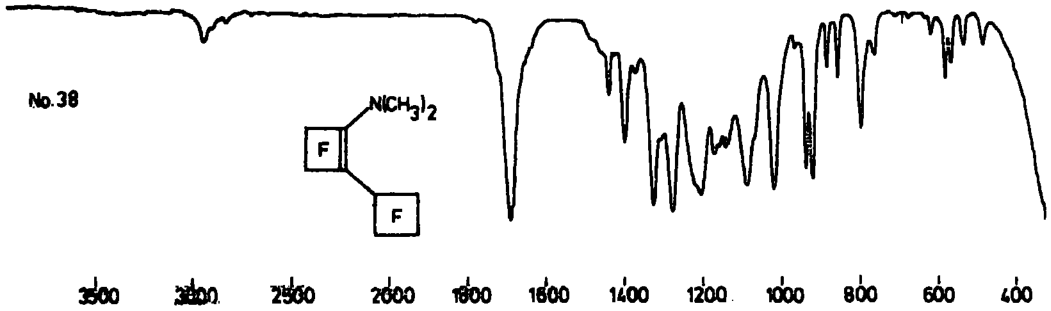

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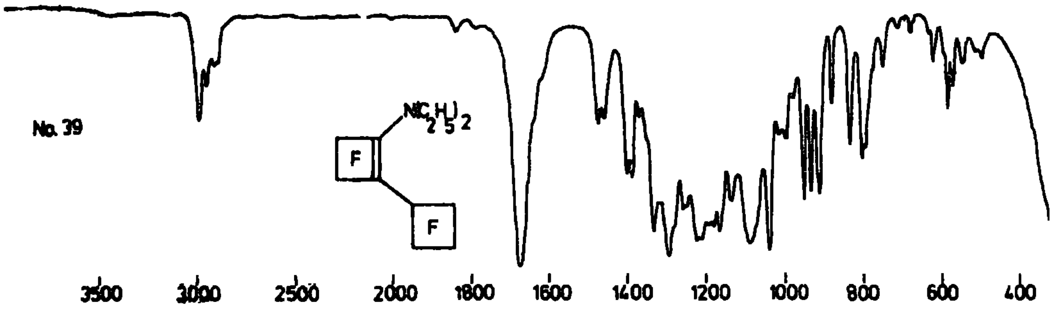

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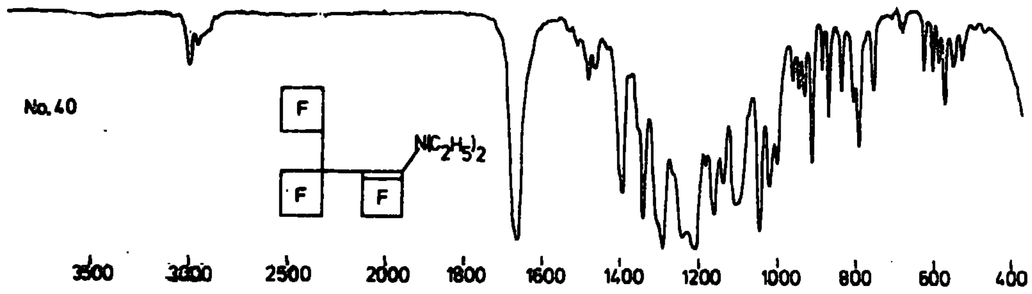

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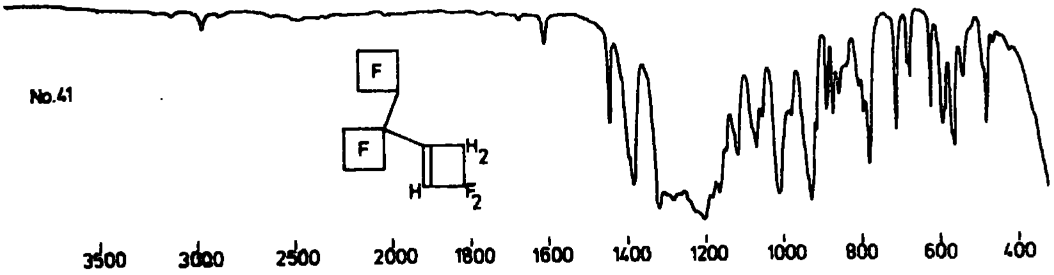

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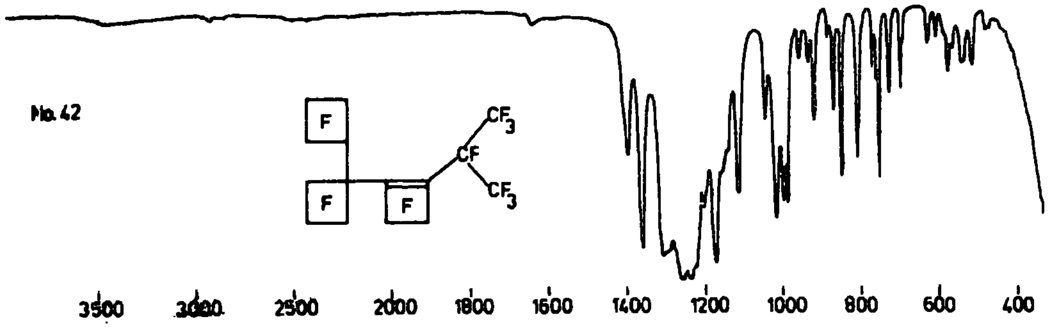

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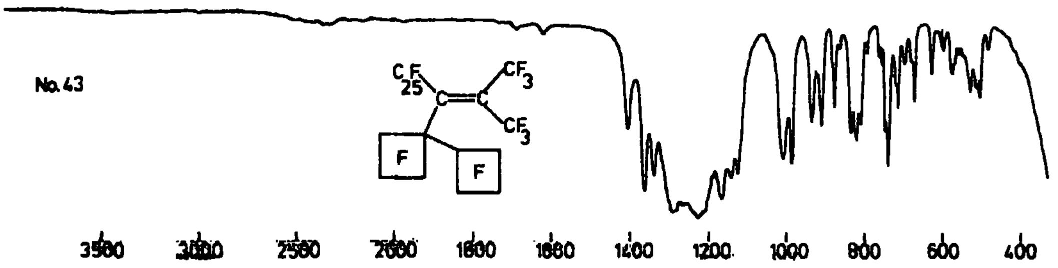

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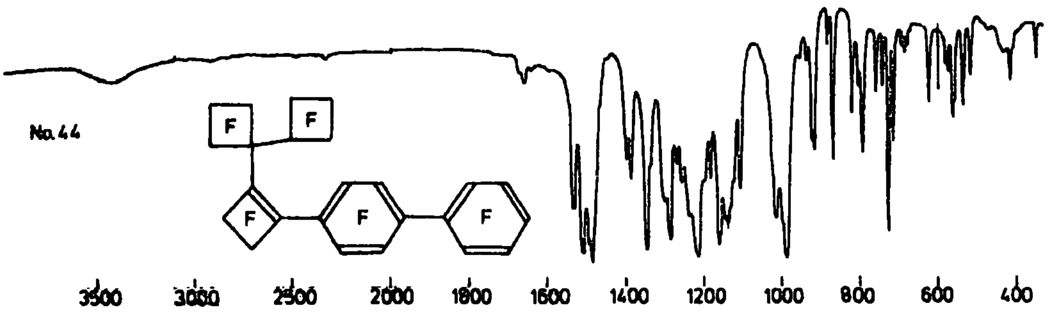

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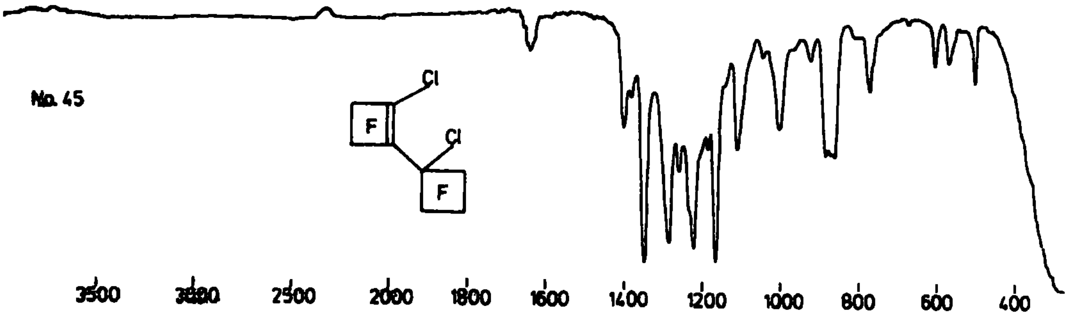

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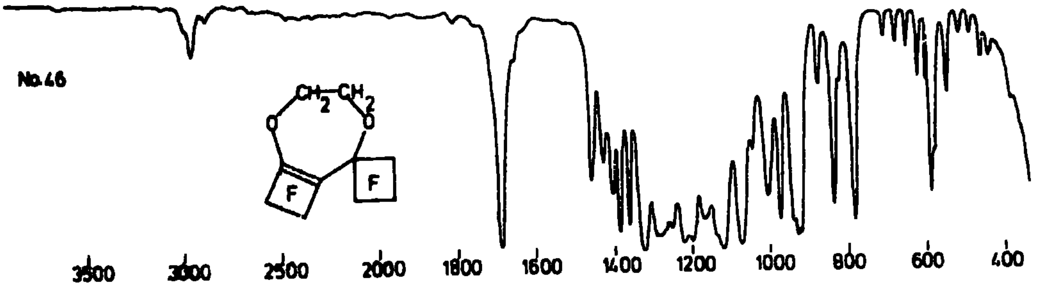

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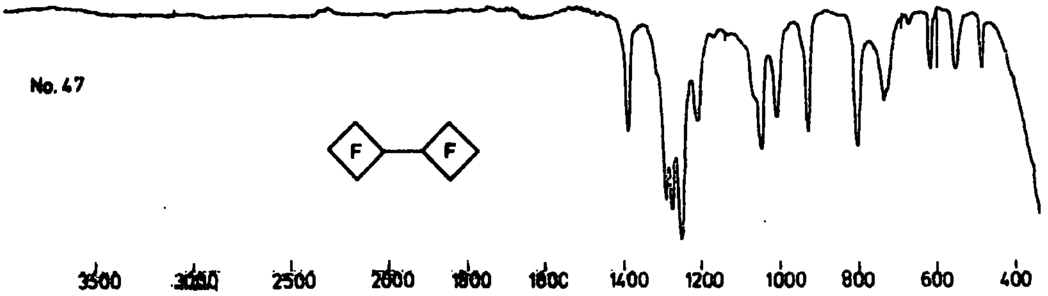

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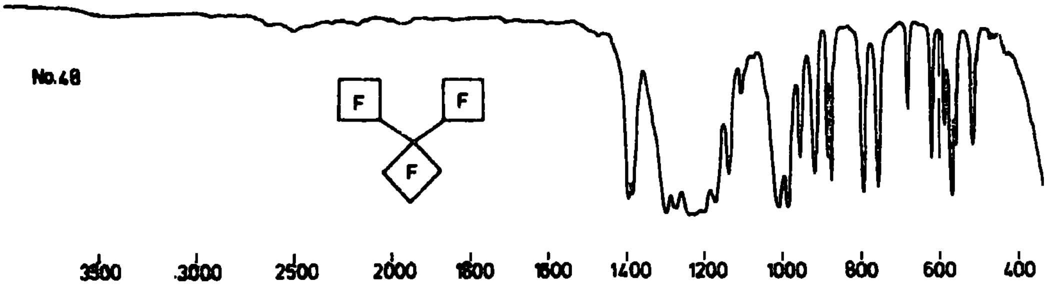

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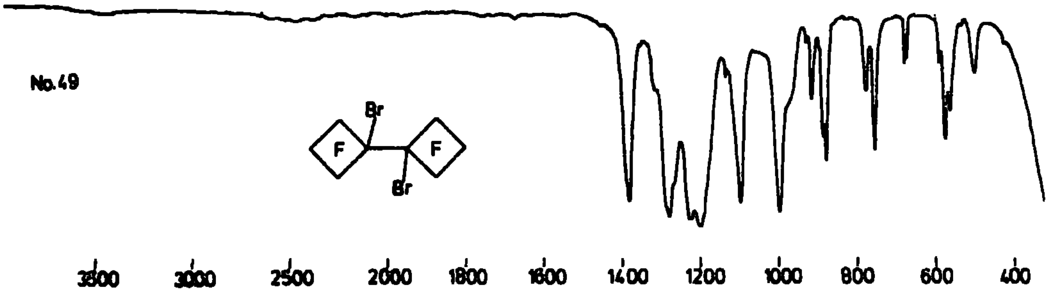

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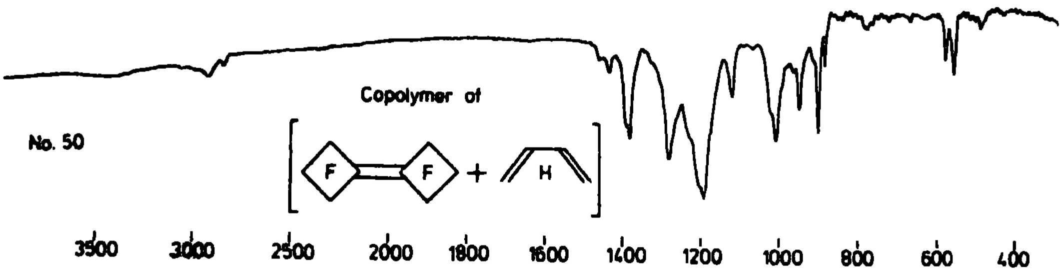

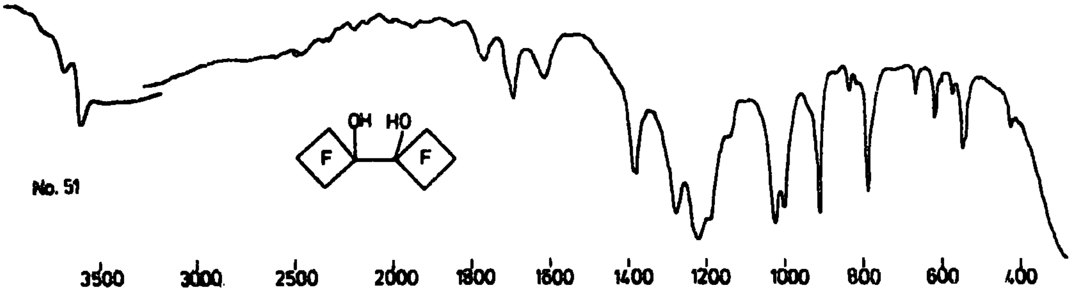

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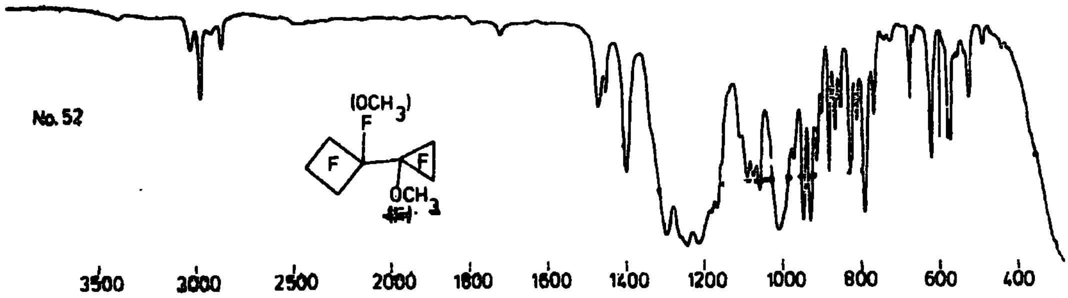

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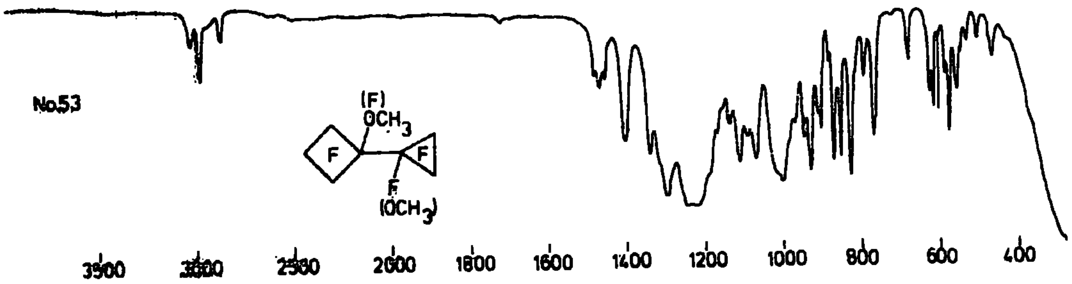

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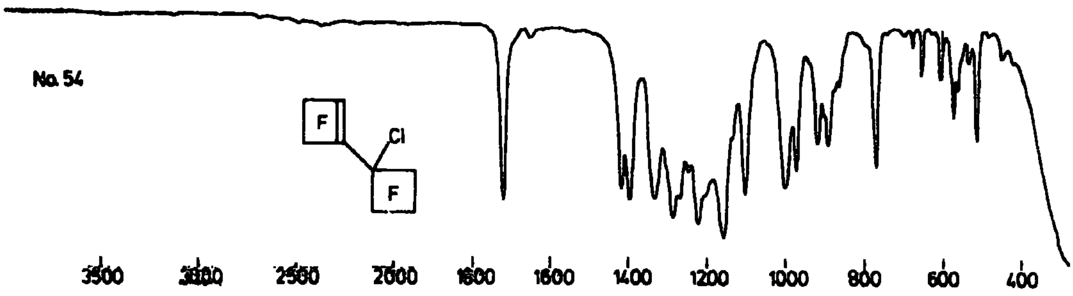

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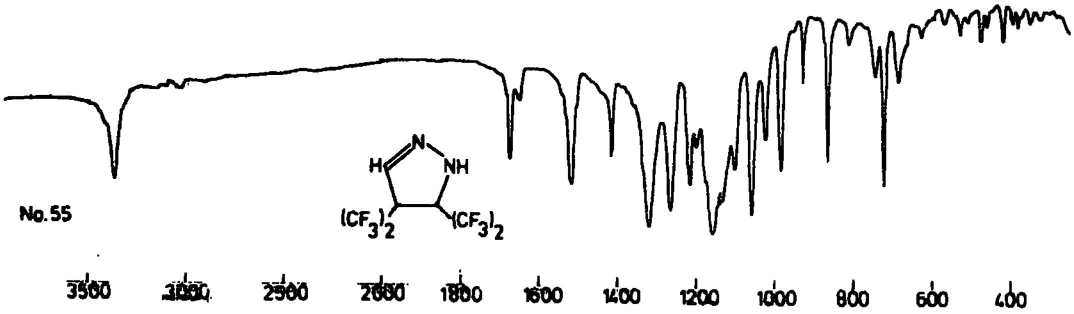

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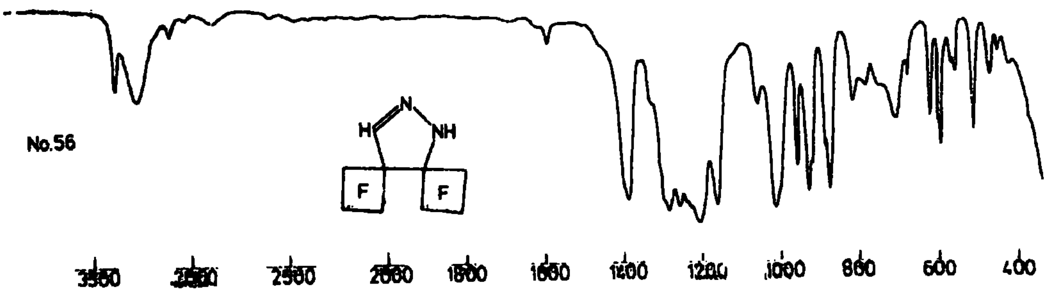

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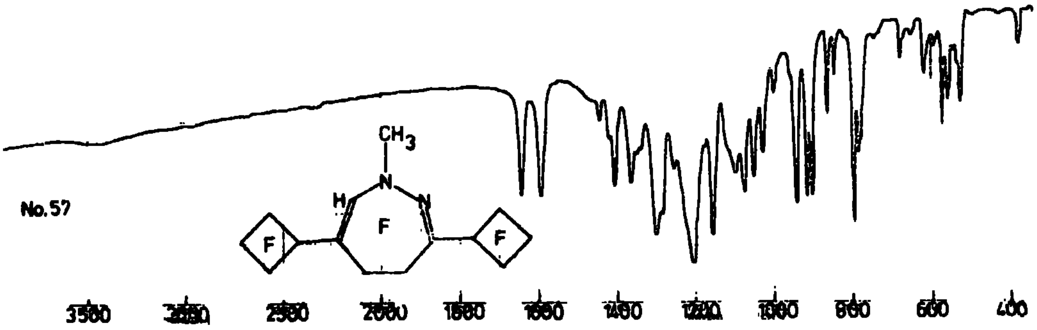

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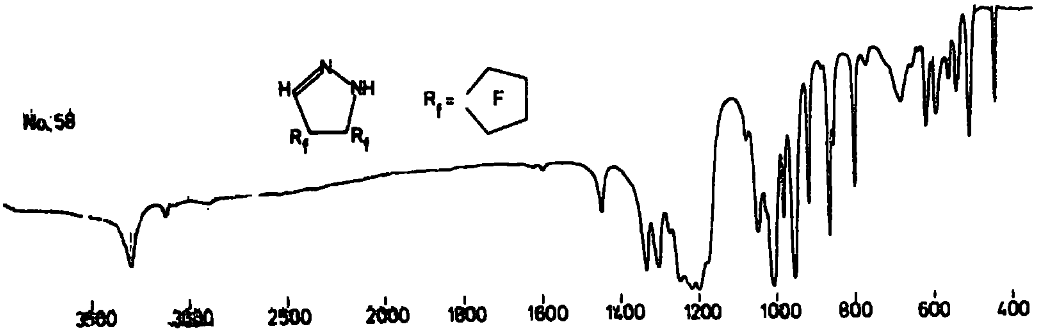

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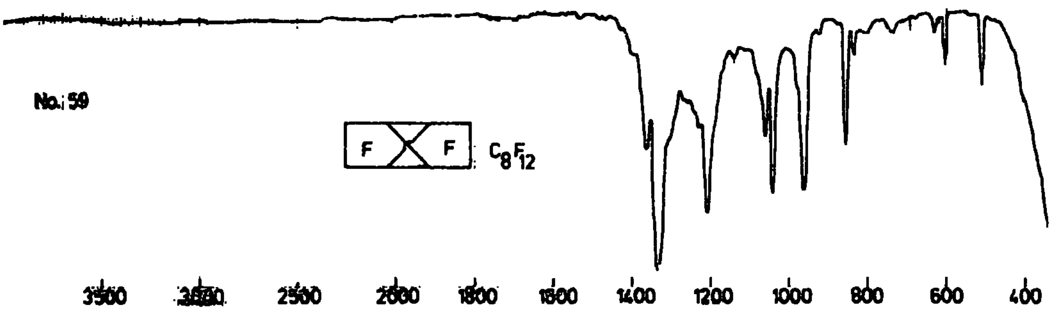

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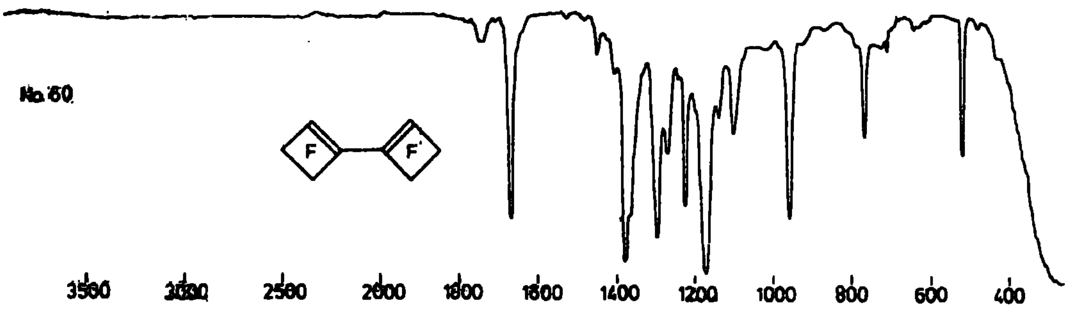

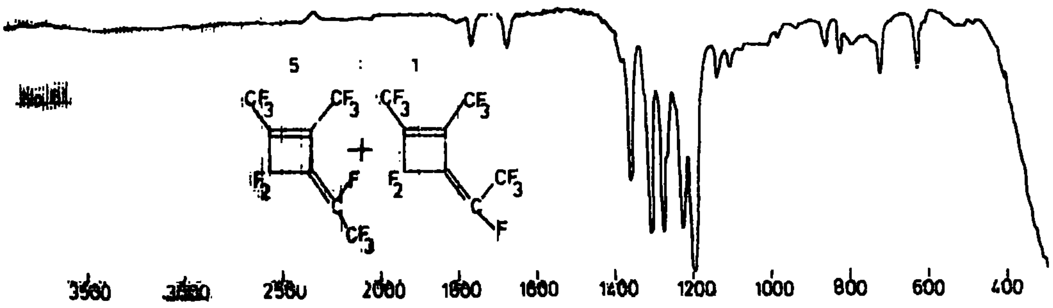
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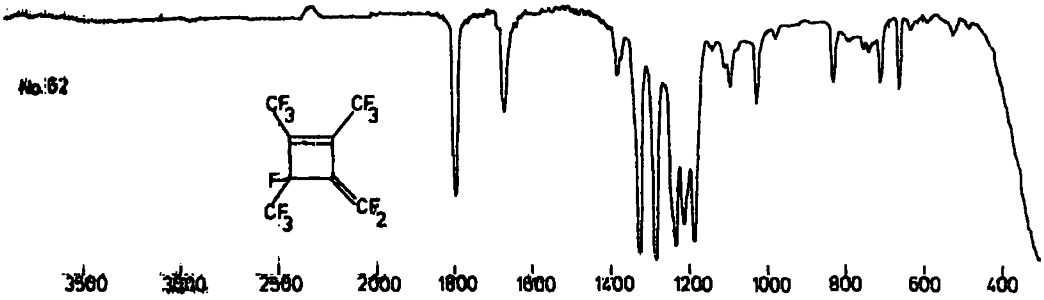
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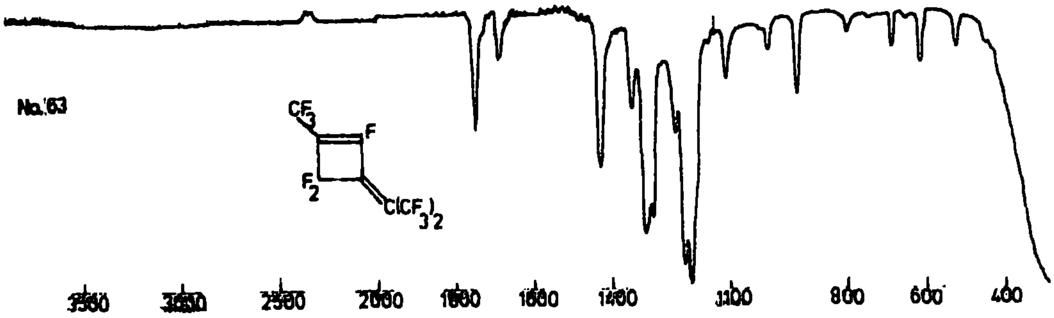
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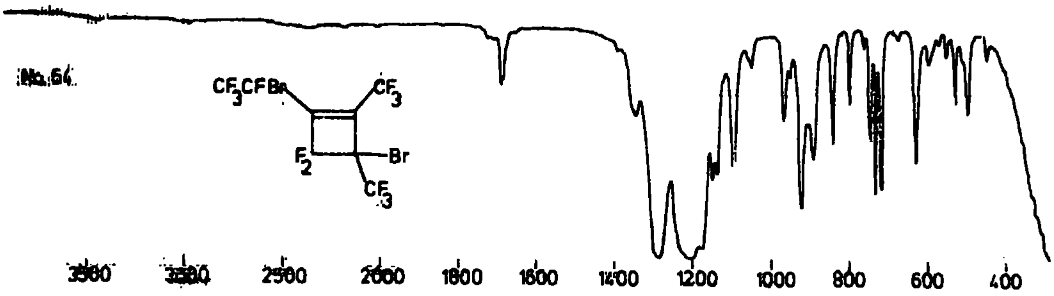
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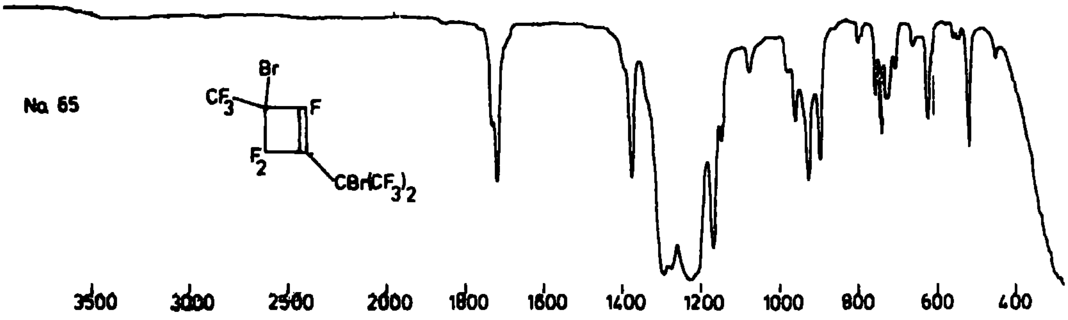
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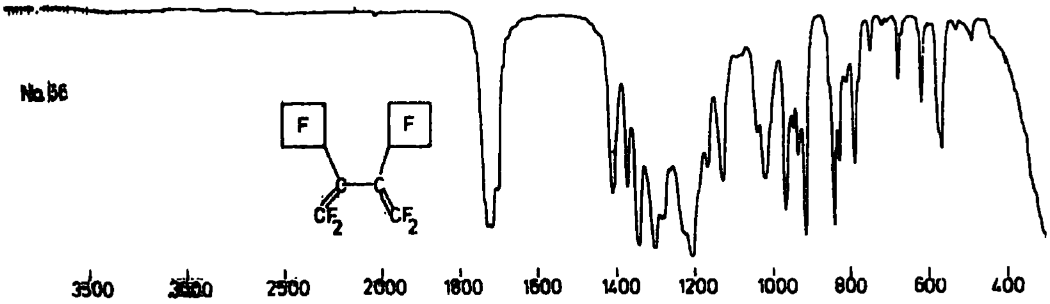

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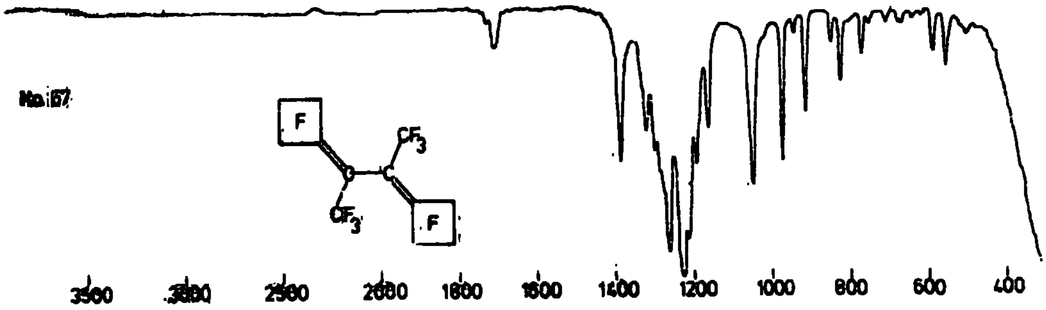

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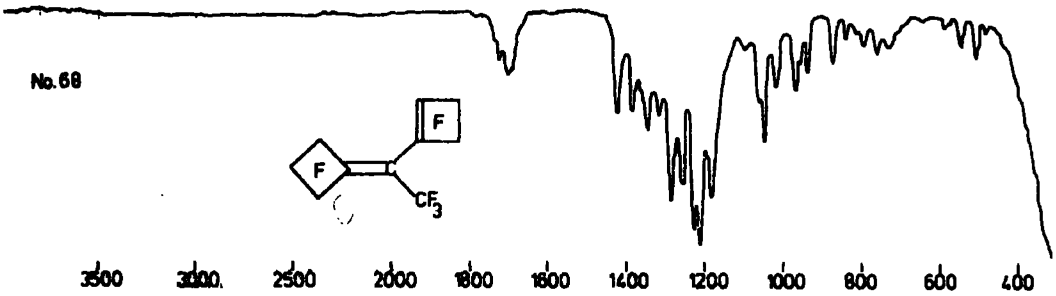

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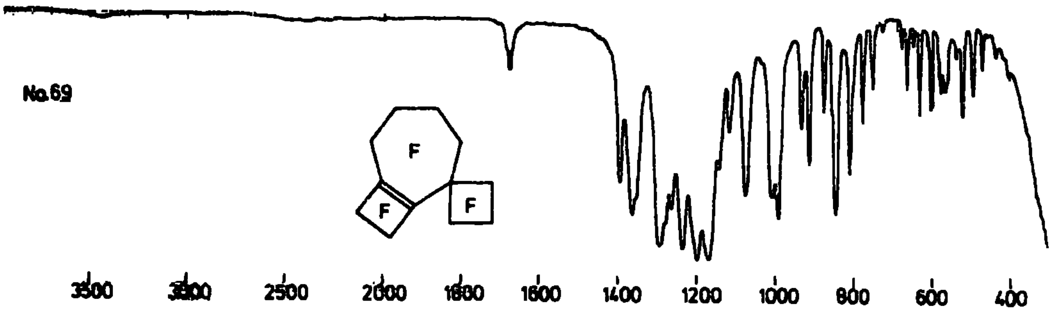

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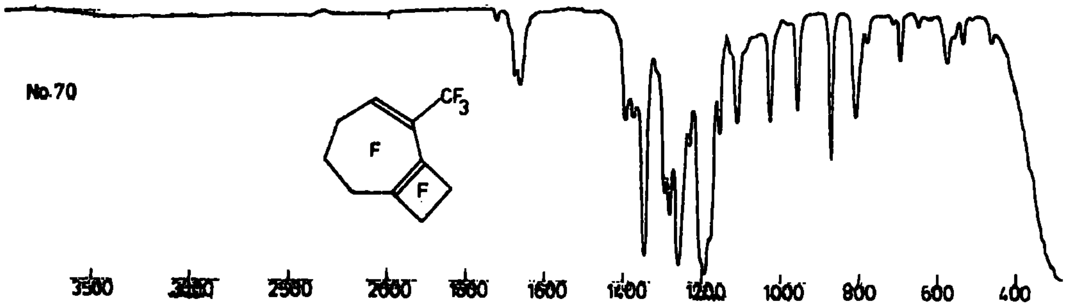

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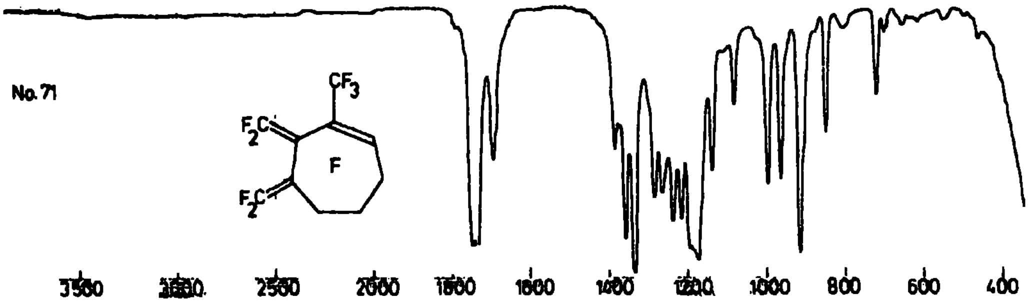

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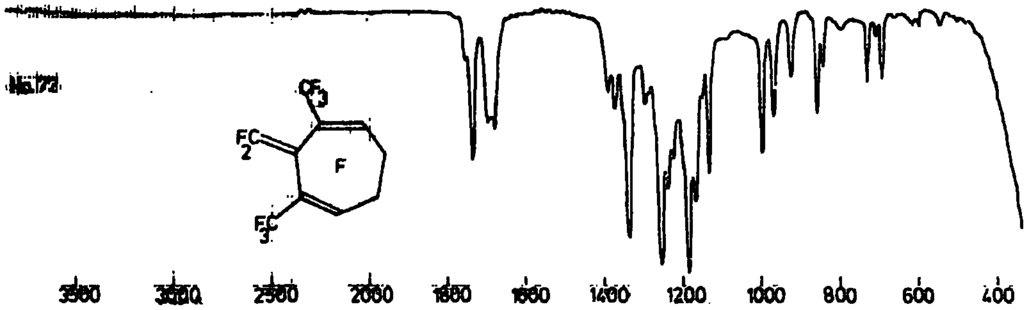

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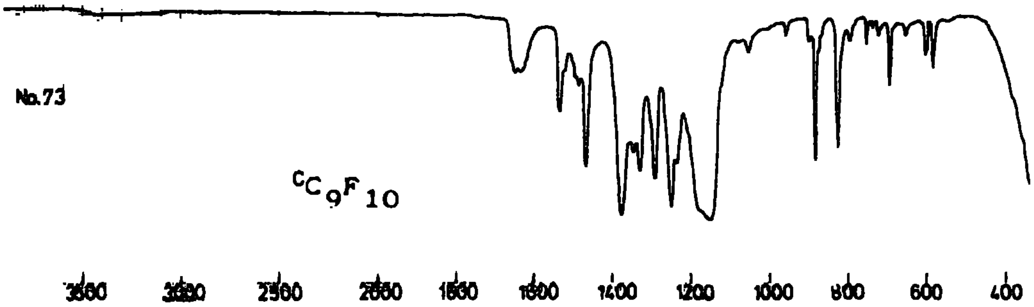

$^{c}C_{9}F_{10}$

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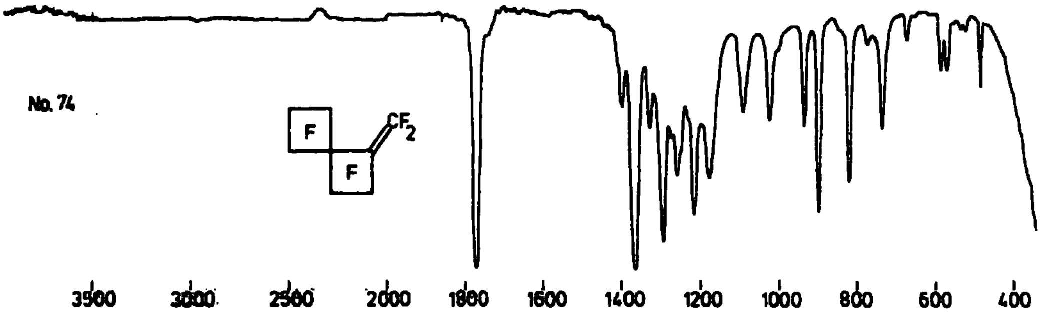

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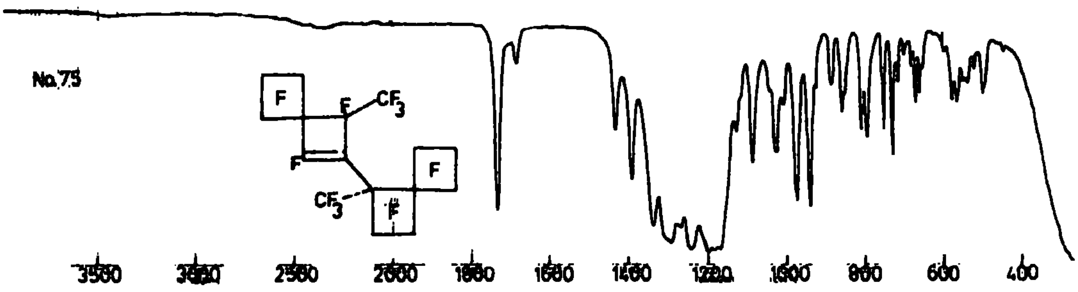

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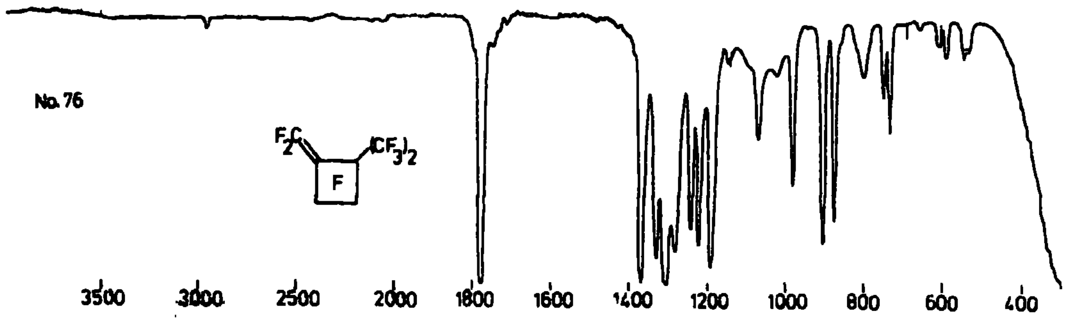

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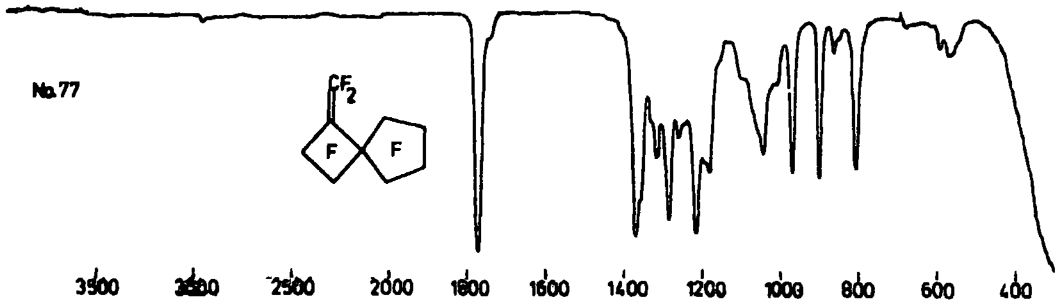

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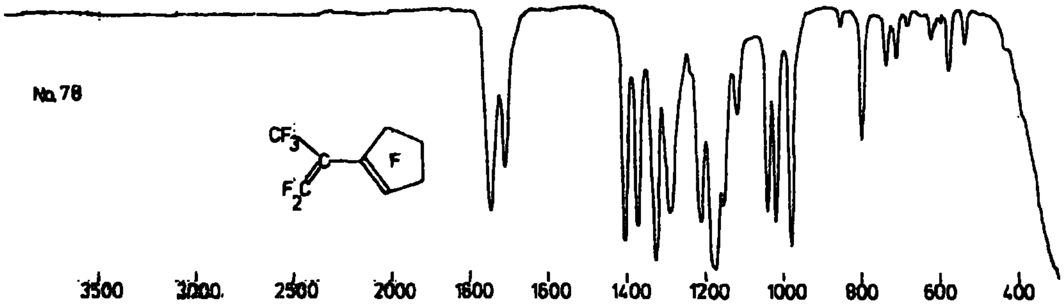

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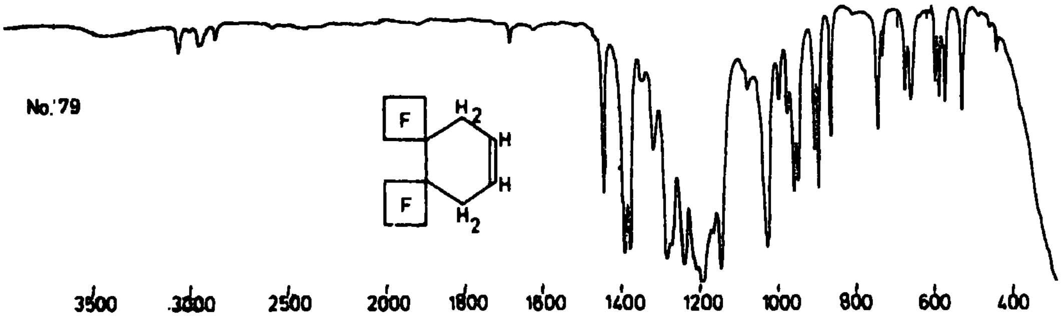

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APPENDIX III

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing

(a) all research colloquia, research seminars and lectures (by external speakers) arranged by the Department of Chemistry since 1 October 1976,

and (b) all research conferences attended and papers read out by the author of the thesis, during the period when the research was carried out.

Research Colloquia, Seminars and Lectures

1. University of Durham Chemistry Colloquia

1976-77

* 20th Oct. Professor J.B. Hyne (University of Calgary), "New Research on an Old Element - Sulphur".

* 10th Nov. Dr. J.S. Ogden (Southampton University), "The Characterisation of High Temperature Species by Matrix Isolation".

* 17th Nov. Dr. B.E.F. Fender (University of Oxford), "Familiar but Remarkable Inorganic Solids".

* 24th Nov. Dr. M.I. Page (Huddersfield Polytechnic), "Large and Small Rate Enhancements of Intramolecular Catalysed Reactions".

* 8th Dec. Professor A.J. Leadbetter (University of Exeter), "Liquid Crystals".

26th Jan. Dr. A. Davis (ERDR), "The Weathering of Polymeric Materials".

2nd Feb. Dr. A.M. Falk (NRC Canada), "Structural Deductions from the Vibrational Spectrum of Water in Condensed Phases".

* 9th Feb. Professor R.O.C. Norman (U. of York) "Radical Cations in Organic Reactions".

23rd Feb. Dr. G. Harris (U of St. Andrews),"Halogen Adducts of Phosphines and Arsines".

25th Feb. Professor H.T. Dieck (Frankfurt U), "Diazadienes-New Powerful Low-Valent Metal Ligands".

* 2nd Mar. Dr. F. Hibbert (Birkbeck Coll., London), "Fast Reaction Studies of Slow Proton Transfers Involving Nitrogen and Oxygen Acids".

4th Mar. Dr. G. Brink (Rhodes U, R.S.A.), "Dielectric Studies of Hydrogen Bonding in Alcohols".

* 9th Mar. Dr. I.O. Sutherland (Sheffield U), "The Stevens Rearrangement: Orbital Symmetry and Radical Pairs".

18th Mar. Professor H. Bock (Frankfurt U), "Photoelectron Spectra and Molecular Properties: A Vademecum of the Chemist".

30th Mar. Dr. J.R. McCallum (U of St. Andrews), "Photooxidation of Polymers".

20th Apr. Dr. D.M.J. Lilley (G.D. Searle, Research Div.), Tails of Chromatin Structure - Progress Towards a Working Model".

27th Apr. Dr. G.C. Tabisz (U of Manitoba), "Collision Induced Light Scattering by Compressed Molecular Gases".

* 11th May Dr. R.E. Banks (UMIST), "The Reaction of Hexafluoropropene with Heterocyclic N-Oxides".

18th May Dr. J. Atwood (U of Alabama), "Novel Solution Behaviour of Anionic Organoaluminium Compounds: the Formation of Liquid Clathrates".

25th May Professor M.M. Kreevoy (U of Minnesota), "The Dynamics of Proton Transfer in Solution".

1st Jun Dr. J. McCleverty (U of Sheffield), "Consequences of Deprivation and Overcrowding on the Chemistry of Molybdenum and Tungsten".

6th Jul. Professor J. Passmore (U of Brunswick), "Adducts Between Group 5 Pentahalides and a Postscript on S_7I^+".

1977-78

27th Sep. Dr. T.J. Broxton (La Trobe U, Australia), "Interaction of Aryldiazonium Salts and Arylazoalkyl Ethers in Basic Alcoholic Solvents".

19th Oct. Dr. B. Heyn (U of Jena, D.D.R.), "Sigma-organo Molybdenum Complexes as Alkene Polymerisation Catalysts".

* 27th Oct. Professor R.A. Filler (Illinois Institute of Technology, U.S.A.) "Reactions of Organic Compounds with Xenon Fluorides".

2nd Nov. Dr. N. Boden (U of Leeds), "NMR Spin-Echo Experiments for Studying Structure and Dynamical Properties of Materials Containing Interacting Spin-½ Pairs".

9th Nov. Dr. A.R. Butler (U of St. Andrews), "Why I Lost Faith in Linear Free Energy Relationships".

7th Dec. Dr. P.A. Madden (U of Cambridge), Raman Studies of Molecular Motions in Liquids".

14th Dec. Dr. R.O. Gould (U of Edinburgh), "Crystallography to the Rescue in Ruthenium Chemistry".

25th Jan. Dr. G. Richards (U of Oxford), "Quantum Pharmacology".

* 1st Feb. Professor K.J. Irvin (Queens U, Belfast), "The Olefin Metathesis Reaction: Mechanism of Ring Opening Polymerisation of Cycloalkenes".

3rd Feb. Dr. A. Hartog (Free U, Amsterdam), "Suprising Recent Studies in Organo-magnesium Chemistry".

* 22nd Feb. Professor J.D. Birchall (Mond Division, I.C.I.), "Silicon in the Biosphere".

1st Mar. Dr. A. Williams (U of Kent), "Acyl Group Transfer Reactions".

3rd Mar. Dr. G. van Koten (U of Amsterdam), "Structure and Reactivity of Arylcopper Cluster Compounds".

15th Mar. Professor G. Scott (U of Aston), "Fashioning Plastics to Match the Environment".

22nd Mar. Professor H. Vahrenkamp (U of Frieburg, Germany), "Metal-Metal Bonds in Organometallic Complexes".

19th Apr. Dr. M. Barber (UMIST), "Secondary Ion Mass Spectra of Surfaces and Absorbed Species".

16th May Dr. P. Ferguson (C.N.R.S., Grenoble), "Surface Plasma Waves and Adsorbed Species on Metals".

18th May Professor M. Gordon (U of Essex), "Three Critical Points in Polymer Chemistry".

22nd May Professor D. Duck (University of Windsor, Ontario), "Electrochemical Synthesis of Inorganic and Organometallic Compounds".

24 & 25th May Professor P. von R. Schleyer (U of Erlangen, Nurnberg)

* I "Planar Tetra-coordinate Methanes, Perpendicular Ethenes and Planar Allenes".

* II "Aromaticity in Three Dimensions".

*III "Non-classical Carbocations".

21st Jun. Dr. S.K. Tyrlik (Acad. of Sci., Warsaw), "Dimethyl-glyoxime-cobalt Complexes - Catalytic Black Boxes".

23rd Jun. Professor W.B. Pearson (U of Florida), "Diode Laser Spectroscopy at 16um".

30th Jun. Professor G. Mteescu (Cape Western Reserve U), "A Concerted Spectroscopy Approach to the Characterisation of Ions and Ion-pairs: Facts, Plans and Dreams".

1978-79

8th Sep. Dr. A. Diaz (I.B.M., San Jose, California), "Chemical Behaviour of Electrode Surface Bonded Molecules".

15th Sep. Professor W. Siebert (Marburg, W. Germany), "Boron Heterocycles as Ligands in Transition Metal Chemistry".

22nd Sep. Professor T. Fehlner (Notre Dame, U.S.A.), "Ferraboranes: Synthesis and Photochemistry".

* 12th Dec. Professor C.J.M. Stirling (U of Bangor), "Parting is such Sweet Sorrow - the Leaving Group in Organic Chemistry".

31st Jan. Professor P.D.B. de la Mare (U of Auckland, New Zealand), "Some Pathways Leading to Electrophilic Substitution".

14th Feb. Professor B. Dunnell (U of British Columbia), "The Application of NMR to the Study of Motions of Molecules in Solids".

14th Mar. Dr. J.C. Walton (U of St. Andrews), "Pentadienyl Radicals".

28th Mar. Dr. A. Reiser (Kodak Ltd.), "Polymer Photography and the Mechanism of Cross-link Formation in Solid Polymer Matrices".

25th Apr. Dr. C.R. Patrick (U of Birmingham), "Chlorofluoro-carbons and Stratospheric Ozone: an Appraisal of the Environmental Problem".

1st May Dr. G. Wyman (European Reseach Office, U.S. Army), "Excited State Chemistry of Indigoid Dyes".

2nd May Dr. J.D. Hobson (U of Birmingham), "Nitrogen-centred Reactive Intermediates".

8th May Professor A. Schmidpeter (Inst. of Inorg. Chem., Munich U), "Five-membered Phosphorus Heterocycles Containing Dicoordinate Phosphorus".

* 9th May Professor G. Maier (Lahn Giessen U), "Tetra-tert-butyltetrahedrane".

9th May Dr. A.J. Kirby (U of Cambridge),"Structure and Reactivity in Intramolecular and Enzymic Catalysis".

16th May Dr. J.F. Nixon (U of Sussex), "Some Recent Developments in Platinum-metal Phosphine Complexes".

23rd May Dr. B. Wakefield (U of Salford), "Electron Transfer in Reaction of Metals and Organometallic Compounds with Polychloropyridine Derivatives".

* 13th Jun. Dr. G. Heath (U of Edinburgh), "Putting Electrochemistry in Mothballs".

2. Durham University Chemical Society

1976-77

* 19th Oct. Dr. J.A. Salthouse (U of Manchester), "Chemistry and Energy".

* 26th Oct. Dr. R.E. Richards (U of Oxford), "NMR Measurements on Intact Biological Tissue".

* 2nd Nov. Dr. B. Sutcliffe (U of York), "The Chemical Bond as a figment of the Imagination."

* 16th Nov. Mr. R. Ficken (Rohm & Haas) "The Graduate in Industry".

* 30th Nov. Dr. R.J. Donovan (U of Edinburgh), "The Chemistry of the Atmosphere".

* 18th Jan. Professor I. Fells (U of Newcastle), "Energy Storage: the Chemist's Contributuion to the Problem".

* 8th Feb. Dr. M.J. Cleare (Johnson Matthey Reseach Centre), "Platinum Group Metals as Anti-Cancer Agents".

* 1st Mar. Professor J.A.S. Smith (Q.E. Coll., London), "Double Resonance".

* 8th Mar. Professor C. Eaborn (U of Sussex), "Structure and Reactivity".

1977-78

* 13th Oct. Dr. J.C. Young & Mr. A.J.S. Williams (U of Aberystwyth), "Experiments and Considerations Touching Colour".

* 20th Oct. Dr. R.L. Williams (Metropolitan Police Forensic Science Dept.), "Science and Crime".

* 3rd Nov. Dr. G.W. Gray (U of Hull), "Liquid Crystals - Their Origins and Applications".

* 24th Nov. Mr. G. Russell (Alcan), "Designing for Social Acceptability".

* 1st Dec. Dr. B.F.G. Johnson (U of Cambrigde), "Chemistry of Binary Metal Carbonyls".

* 2nd Feb. Professor R.A. Raphael (U of Cambridge), "Bizarre Reactions of Acetylenic Compounds".

* 16th Feb. Professor G.W.A. Fowles (U of Reading), "Home Winemaking".

* 2nd Mar. Professor M.W. Roberts (U of Bradford), "The Discovery of Molecular Events at Solid Surfaces".

* 9th Mar. Professor H. Suschitsky (U of Salford), "Fruitful Fissions of Benzofuroxans".

* 4th May Professor J. Chatt (U of Sussex), "Reactions of Coordinated Dinitrogen".

* 9th May Professor G.A. Olah (Case Western Reserve U, Ohio), "Electrophilic Reactions of Hydrocarbons".

1978-79

* 10th Oct. Professor H.C. Brown (Purdue U), "The Tool of Increasing Electron Demand in the Study of Cationic Processes".

* 19th Oct. Mr. F.C. Shenton (Public Analyst, Co. Durham), "There is Death in the Pot".

26th Oct. Professor W.J. Albery (Imperial Coll., London), "Photogalvanic Cells for Solar Energy Conversion".

* 9th Nov. Professor A.R. Katritsky (U of E. Anglia), "Some Adventures in Heterocyclics".

16th Nov. Dr. H.C. Fielding (I.C.I. Ltd., Mond), "Fluoro-

-chemical Surfactants & Textile Finishes".

23rd Nov. Dr. C. White (Sheffield U), "The Magic of Chemistry".

18th Jan. Professor J.C. Robb (Birmingham U), "The Plastics Revelution".

8th Feb. Mr. C.G. Dennis (Vaux Ltd.), "The Art & Science of Brewing".

1st Mar. Professor R. Mason (Govt. Scientific Advisor), "The Scientist in Defence Policy".

10th May Professor G. Allan (Chairman SRC), "Neutron Scattering for Polymer Structures".