I Halogenated derivatives of some polycycllc aromatic compounds II some polyfluorocycloalkene dimors

Pearce, Dennis

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UNIVERSITY OF DURHAM

A THESIS

entitled

I. Halogenated Derivatives of some Polycyclic Aromatic Compounds

II. Some Polyfluorocycloalkene Dimers

submitted by

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(Graduate Society)

A candidate for the degree of Doctor of Philosophy

1976

TO

Margaret and Vikki

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I also wish to record my appreciation of the valuable assistance given by the technical and laboratory staff of the Department of Chemistry, particularly to Dr. M. Jones for his many helpful discussions in the interpretation of some mass spectra.

Many thanks and a deep felt sympathy go to my wife, Margaret, for her endurance in the typing of this thesis.

Finally, thanks are due to the Science Research Council for a Maintenance Grant.

MEMORANDUM

The work described in this thesis was carried out at the University of Durham between April 1973 and May 1976. This work has not been submitted for any other degree and is the origional work of the author except where acknowledged by reference.

If the matter of this paper be certain,
you have mighty business in hand.

King Lear, Act 3, Scene V.

Summary

I Halogenated Derivatives of Some Polycyclic Aromatic Compounds

This work is concerned mainly with the preparation and attempted fluorination of some perchloropolycyclic compounds.

Decachlorobiphenyl, 1,2,3,4,5,6,7,8-octachlorofluorene, octachlorodibenzo(b,d)furan, octachlorodibenzo(b,d)thiophen, and octachlorothianthrene were synthesised by reaction of the corresponding parent compound with a chlorinating mixture containing sulphuryl chloride, sulphur monochloride, and aluminium chloride. Fluoren-9-one could only be partially chlorinated using this reagent, but decachlorofluorene was obtained by reaction of 1,2,3,4,5,6,7,8-octachlorofluorene with phosphorus pentachloride in an autoclave at 325°C. Oxidation of 1,2,3,4,5,6,7,8-octachlorofluorene with sodium dichromate in acetic acid, or hydrolysis of decachlorofluorene with 80%(^{v}/v) phosphoric acid yielded octachlorofluorene-9-one in low yield. Attempts to fluorinate these polychloro-systems, either in an autoclave, or in solution met only with limited success.

Both decachlorobiphenyl and octachlorodibenzo(b,d) thiophen reacted with sulphur in an autoclave at 325°C, to form 1,9-epidithio-2,3,4,6,7,8-hexachlorodibenzo(b,d)thiophen which was in turn reduced to 2,3,4,6,7,8-hexachlorodibenzo (b,d)thiophen with Raney-nickel catalyst.

Decafluorobiphenyl reacted with sulphur to give perfluoro- (bis-(p-phenyl phenylene) sulphide. When the

4,4'-positions of perfluorobiphenyl were blocked with perfluoroisopropyl groups, no reaction was observed. Perfluoro-(4,4'-bisisopropylbiphenyl) did react with methoxide ion to give a monomethoxy-derivative, the orientation of preferred nucleophilic attack being the 3-position.

II Some Polyfluorocycloalkene Dimers

Fluoride ion induced oligomerisation of octafluoro cyclopentene and decafluorocyclohexene gave perfluorobi-(cyclopentylidene) and perfluoro-(1-cyclohexylcyclohexene) respectively. Perfluorobi(cyclopentylidene) defluorinated to give perfluorobicyclopentenyl, when passed over iron at 500°C.

Perfluorobi(cyclopentylidene) was unchanged upon photolysis, neither did it react with bromine, concentrated sulphuric acid or sodium chlorodifluoroacetate. γ-irradiation in the presence of methanol gave a multicomponent product. Reactions with nucleophiles gave varying products, depending upon the nucleophile and reaction conditions used.

Neither perfluoro-(1-cyclohexylcyclohexene) nor perfluorobicyclopentenyl added bromine, but perfluorobicyclopentenyl reacted with concentrated sulphuric acid to give 1-(3-oxo-1H -hexafluorocyclopentyl)-3-oxopentafluorocyclopent-1-ene which formed an anion in solution.

Oxidation of perfluoro-(1-cyclohexylcyclohexene) gave octafluoroadipic acid, whereas perfluorobi(cyclopentylidene) underwent addition, giving 1,1'-dihydroxyhexadecafluorobicyclopentyl which could not be dehydrated with phosphorus pentoxide.

Perfluoro-(1-cyclohexylcyclohexene) underwent partial defluorination and decomposition when pyrolysed, whereas perfluorobi(cyclopentylidene) gave some defluorinated product along with rearranged isomers, the respective products being temperature dependent.

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PART I

HALOGENATED DERIVATIVES OF SOME POLYCYCLIC AROMATIC COMPOUNDS

INTRODUCTION

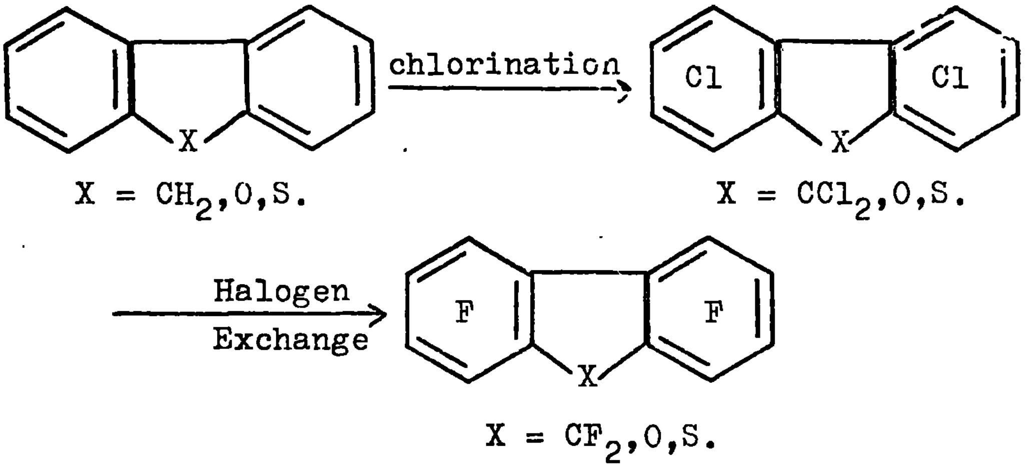
CHAPTER I

The Synthesis of Some Perchlorinated Aromatic Polycyclic Compounds

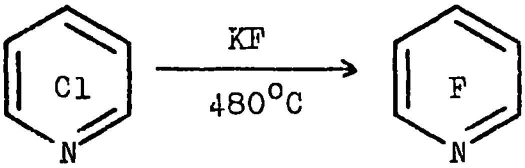
1. General Introduction

The initial aim of the work described in this thesis was to prepare the perfluoro-analogues of some polycyclic aromatic compounds. The desired synthetic route was the perchlorination of the parent compounds, followed by halogen exchange of chlorine with fluorine (see Scheme I).

Scheme I



The use of alkali metal fluorides as halogen exchange reagents has been investigated at Durham and has been applied to the preparation of the perfluoro-analogues of some monocyclic and bicyclic nitrogen containing aromatics. For example, pentafluoropyridine has been prepared by the reaction of pentachloropyridine with potassium fluoride in an autoclave at elevated temperatures.[1]



It will be seen in the later discussion, that although excellent synthetic routes to some perchloro polycyclic compounds have now been developed, the fluorination of these perchlorinated species met with limited success. The work described in the first part of this thesis deals mainly with the development of these chlorination procedures and also describes the many attempts of fluorinating the perchloro compounds.

The following review covers the preparation of some perchloro compounds and for convenience is split into two main sections, viz.: the preparation of some perchlorinated carbocyclic compounds, dealt with in order of increasing number of rings in the molecule, and secondly, the preparation of some perchlorinated heterocyclic compounds, again subdivided in a similar fashion (N.B. The preparation and properties of some chlorinated nitrogen containing heterocyclic compounds has been reviewed previously[2] and will be dealt with here only briefly).

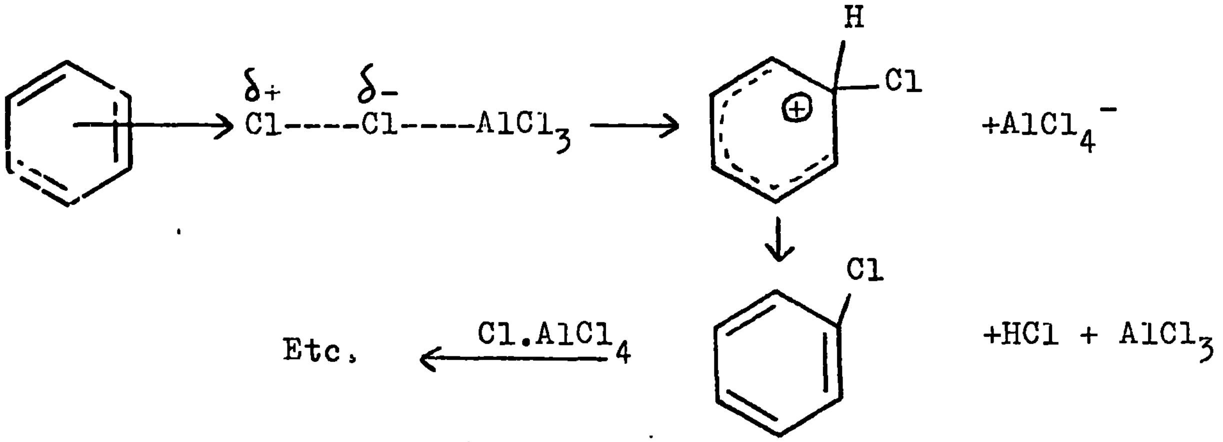
In describing the syntheses of some perchlorinated compounds, it is intended to cover a cross section of methods available for the preparation of perchlorinated species and, where applicable, discuss their relative merits.

2. Preparation of Some Perchlorinated Carbocyclic Compounds

Direct electrophilic substitution of chlorine into an aromatic carbocycle is usually carried out in the presence of a catalyst; e.g. a Lewis acid acceptor, which serves to increase the electrophilic character of the attacking chlorine species (i.e. a "positive halogen"). Examples of Lewis acid acceptors are $FeCl_3$, $AlCl_3$, $SnCl_4$, and a mechanism for their reaction is believed to be as follows:-

e.g. $$Cl_2 + AlCl_3 \longrightarrow \overset{\delta+}{Cl}------\overset{\delta-}{Cl}------AlCl_3$$

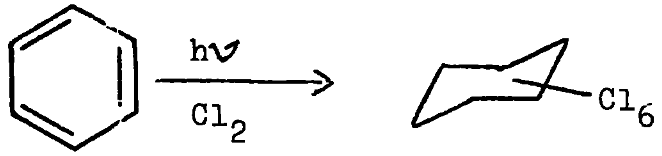
(or $Cl^{\oplus}$ $AlCl_4^{\ominus}$)



In some cases, by choice of catalyst and reaction conditions, perchlorinated species may be obtained using this method. If the substrate is activated towards electrophilic substitution; e.g. amines, phenols; the presence of a catalyst is not necessary and reaction proceeds smoothly in dilute solution at room temperature.

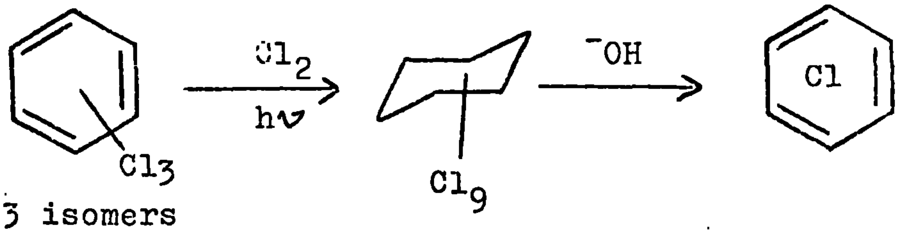
Free radical processes also serve to introduce chlorine into aromatic molecules, but these occur as addition reactions.

e.g.



Addition - elimination reactions may, in some cases, be used to obtain perchloro compounds.

e.g.



(Ref: 3)

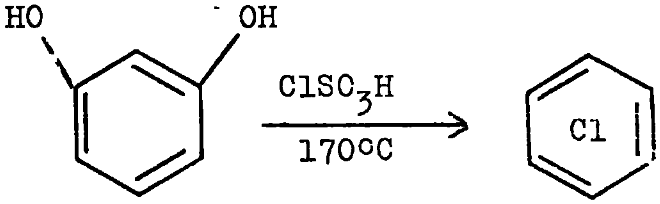
However, in general, more specialised synthetic routes are employed to achieve efficient perchlorination of substrates and the following review includes some of the methods available for obtaining perchloro-carbocyclic compounds.

2.1 Monocyclic Systems

2.1.1 Benzene

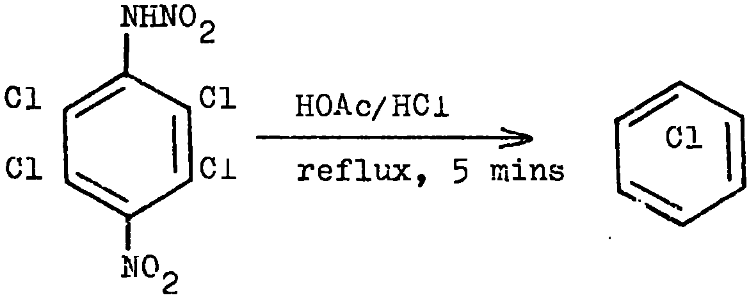
Many papers have been published which describe perchlorination of the benzene nucleus. Examples of these are the use of chlorine and a Lewis acid catalyst; Silberrad's reagent;[4] electrochemical chlorination;[5] vapour phase chlorination on alumina with iodine trichloride (180-300°C) or rhodium trichloride (300°C).[6]

Chlorosulphonic acid has been shown to induce nuclear halogenation of substituted benzenes, e.g. 1,2,4,5-tetrachlorobenzene,[7] and certain phenols, e.g. resorcinol.[8]



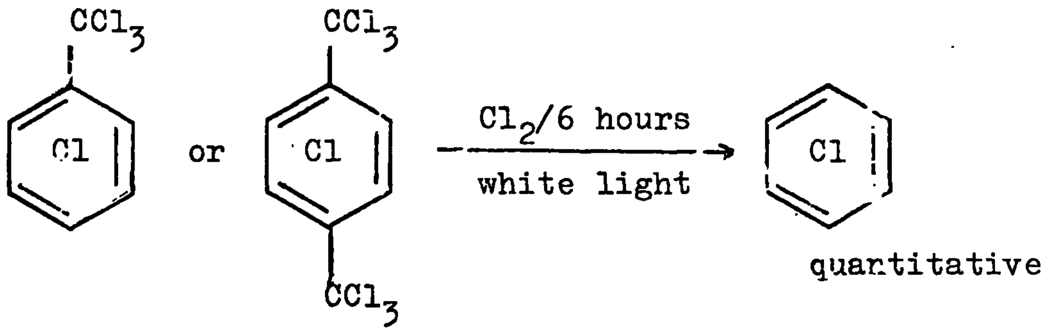
Some N-nitroaminobenzenes are sufficiently activated towards nucleophilic attack, that they yield hexachlorobenzene simply by refluxing with a mixture of hydrochloric and acetic acids.[9]

e.g.



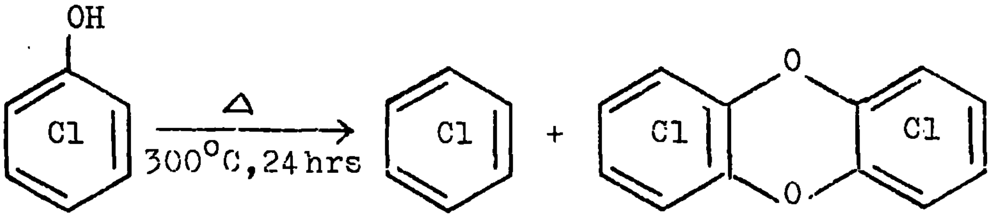
This reaction serves as an example of nucleophilic aromatic chlorination, opposed to the electrophilic reactions previously mentioned. Replacement of the p-NO_2 group by a proton increases the required reaction time by a factor of more than ten,[9] illustrating the efficiency of $-NO_2$ as an electron withdrawing group.

Chlorinolysis (i.e. fragmentation of the carbon framework) reactions may be used as a route to perchlorobenzene. Octachlorotoluene and decachloro-p-xylene undergo quantitative chlorinolysis with chlorine in the presence of white light.[10]

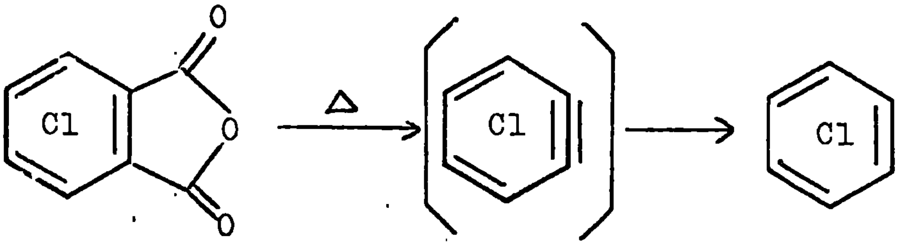


Fused polycyclic aromatic hydrocarbons may also undergo chlorinolysis.[11] Usually, compounds containing a built in biphenyl system yield perchlorobiphenyl as the ultimate product. Noteable exceptions to this generality are phenanthrene and benzidine, which both yield perchlorobenzene upon exhaustive chlorination.

An interesting pyrolysis reaction is that of heating pentachlorophenol at 300°C for 24 hours to yield hexachlorobenzene. Some perchlorodibenzo-p-dioxin is also formed in this reaction.[12] The mechanism presumably involves the intermolecular reaction of pentachlorophenoxy radicals.



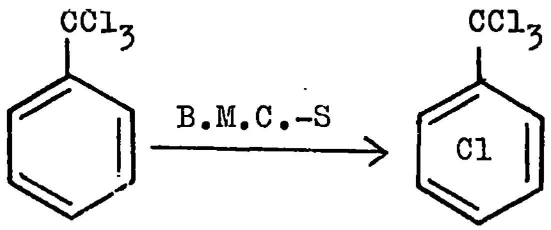
Finally, pyrolysis of perchloro phthalic anhydride at 800°C gives hexachlorobenzene in 34% yield.[13] The following mechanism involving a perchlorobenzyne intermediate has been suggested.[13]

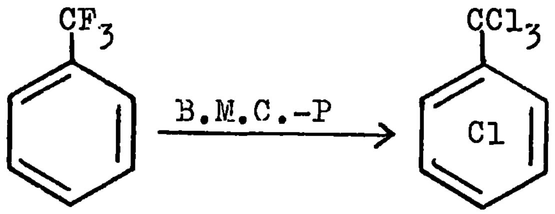


2.1.2 Substituted Benzenes

The substituted benzenes included in this section are arylalkanes, arylalkenes and arylalkynes. Aryl substituted benzenes; e.g. biphenyl, polyphenyls; will be dealt with under sections 2.2 and 2.3 respectively. It should be noted that in the following sections, (i.e. 2.1.2., 2.2., and 2.3.) frequent reference to reagent B.M.C. will be made. This extremely powerful nuclear chlorinating agent which comprises sulphuryl chloride, sulphur monochloride and aluminium chloride will be dealt with more fully at a later stage (See Discussion, Chapter II).

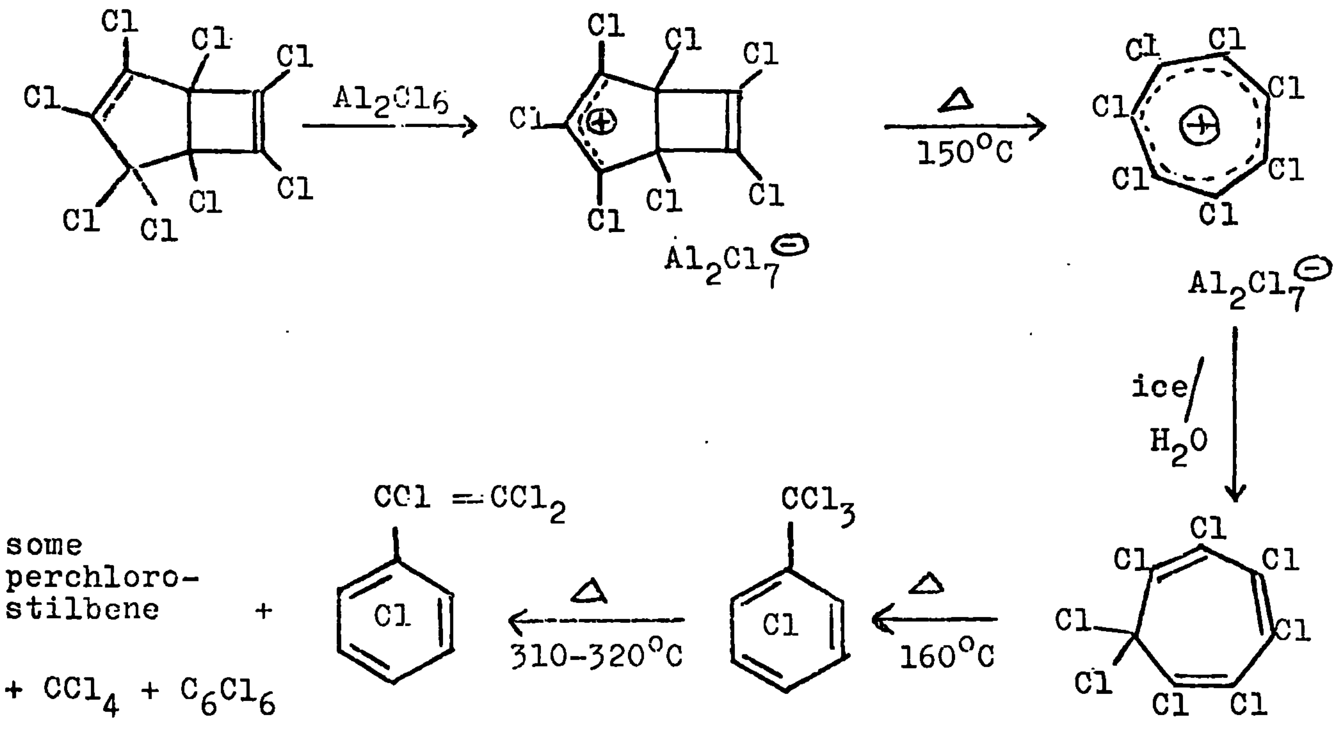
Early attempts to perchlorinate toluene[14] resulted in the formation of α-H-heptachlorotoluene or o-H-heptachlorotoluene as the ultimate products. Steric hinderance[15] and some electronic deactivation from chlorine (-I effect) were given as the reasons for incomplete chlorination. Too forcing reactions resulted in the formation of hexachlorobenzene. In 1954,[16] Ballester and Molinet succeeded in synthesising octachlorotoluene using a mixture which has become well known as B.M.C. reagent[10,17] More recently,[18] Ballester and his co-workers have employed reagents B.M.C.-S and B.M.C.-P to record high yield syntheses of octachlorotoluene from alkyl halogenated toluenes.





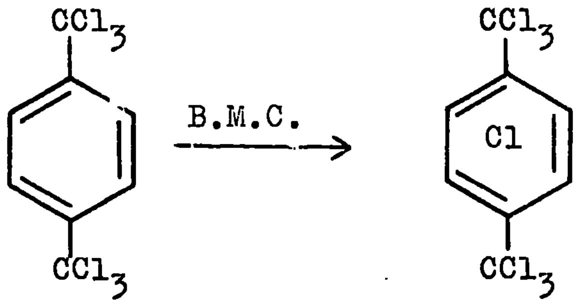
An interesting rearrangement has been described by West and his co-workers,[19,20] which involves the reaction of perchlorobicyclo (3.2.0.) hepta-2:6-diene with aluminium chloride. Initially, perchlorocycloheptatriene is isolated, pyrolysis of which may lead to perchlorotoluene, perchlorostyrene or hexachlorobenzene depending upon the conditions used. A reaction scheme involving a perchloroallyl carbonium ion has been suggested.[19] (see Scheme II)

Scheme II

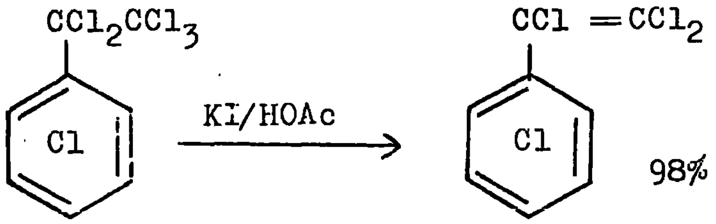


Perchloroethylbenzene has been prepared from the U.V. irradiation of octachlorotoluene in carbon tetrachloride.[21] The perchloroethylbenzene is said to result from the coupling of the two radicals $C_6Cl_5.\dot{C}Cl_2$ and $\dot{C}Cl_3$.

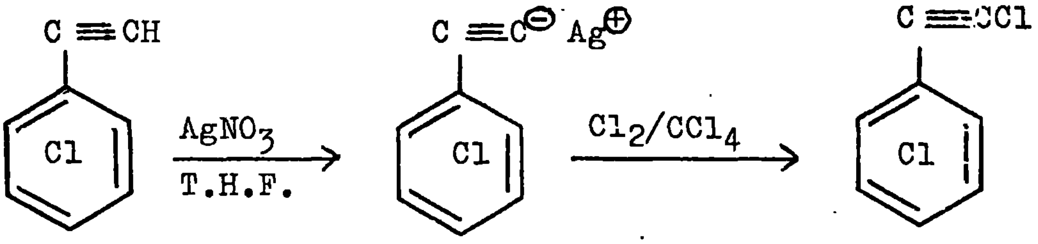
Attempts to chlorinate the xylenes have been recorded.[15] To date, perchloro-o-xylene and perchloro-m-xylene have not been synthesised. However perchloro-p-xylene has been reported by Ballester and co-workers,[16] prepared by the chlorination of p-bistrichloromethyl benzene with B.M.C. reagent. Their results were confirmed by Doorenbos.[22]



Perchlorostyrene has been prepared by the thermolysis of perchlorotoluene,[19] chlorination of β,β-dichloro styrene with reagents B.M.C.[10,17] and B.M.C.-P,[18] or by the action of warm KI/HOAc on perchloroethyl benzene.



ω-H-pentachlorophenylacetylene reacts with silver nitrate in anhydrous tetrahydrofuran to give a silver salt, which on treatment with chlorine in carbon tetrachloride at room temperature gives perchlorophenylacetylene in 91.7% yield.



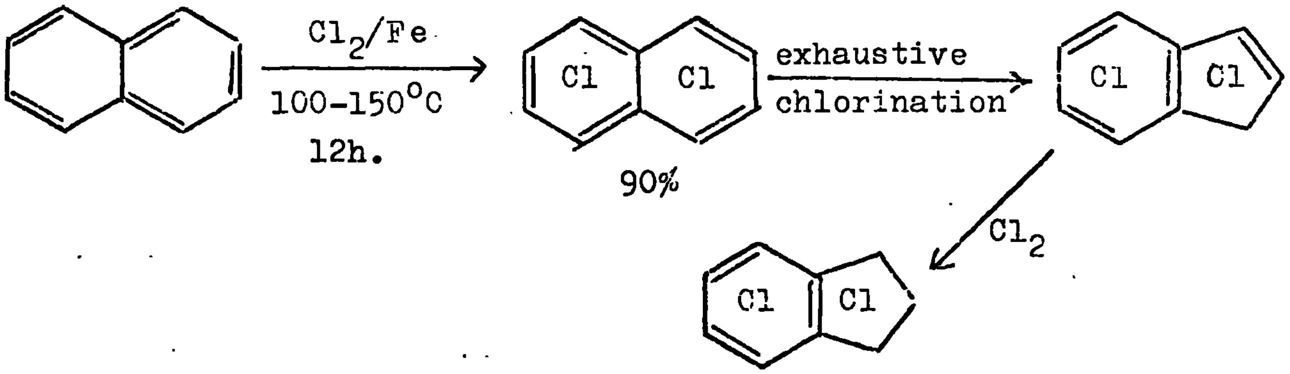
This acetylene has been found to undergo thermal oligomerisation, giving a mixture of perchloro-(1,2,3-triphenyl benzene), perchloro-(1,2,4-triphenyl benzene), and perchloro-(1-phenylnaphthalene). A mechanism involving a perchloro-diphenyltetrahedrane has been suggested.[18]

Many other polychlorobenzenes with unsaturated side chains have been prepared; e.g. trans-perchloropropenyl benzene,[23] perchloro-1-phenylbutadiene;[18] but will not be dealt with in this review.

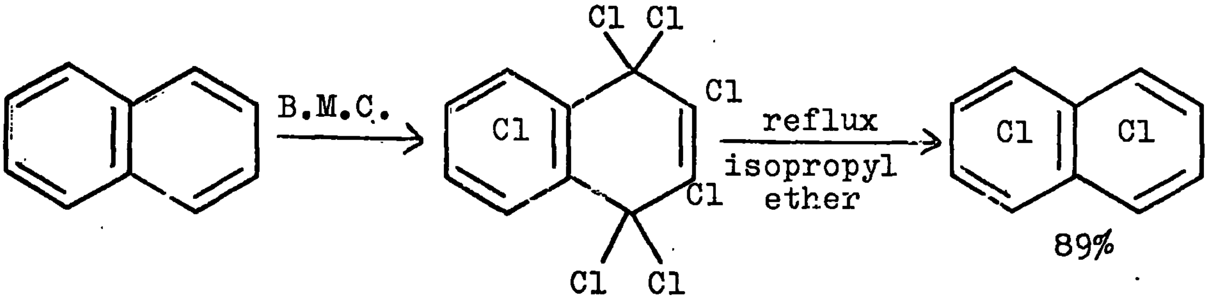
2.2 Bicyclic Systems

2.2.1 Naphthalene

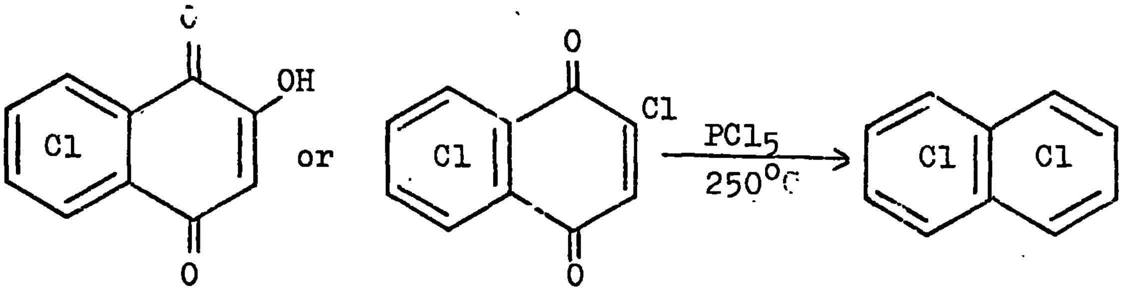
Perchloronaphthalene was prepared by Berthelot and Jungfleisch as early as 1868, by exhaustive chlorination of naphthalene with chlorine and antimony pentachloride to give a mixture of perchloronaphthalene and perchloro-1,4-dihydronaphthalene. Another Lewis acid catalysed reaction was realised by Schwemberger and Gordon,[11,24] who prepared perchloronaphthalene in 90% yield by direct chlorination of naphthalene in the presence of iron or iron and iodine at 100-150°C. Care had to be taken to avoid exhaustive chlorination, which eventually led to the formation of perchloroindane.[11]



Other workers have achieved this chlorination almost quantitatively in the vapour phase: over charcoal (400°C); over rhodium trichloride/silica (400-480°C); or over rhodium trichloride/alumina (400°C).[6] Ballester and co-workers[23,25] chlorinated naphthalene with reagent B.M.C. to give perchloro-1,4-dihydronaphthalene, which readily dechlorinated upon refluxing in isopropyl ether, to give an overall 89% yield of perchloronaphthalene.



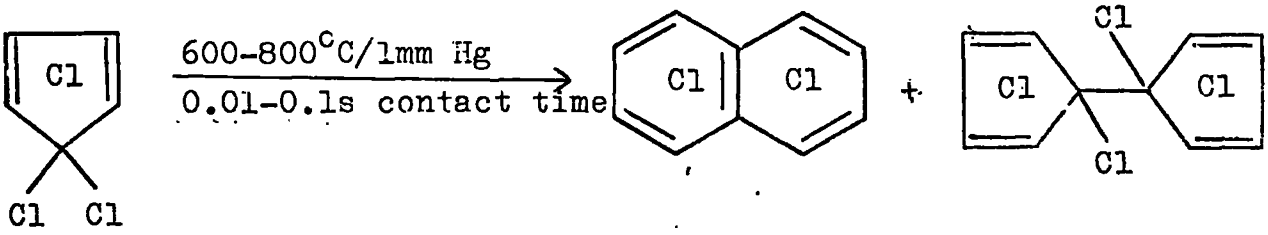
Reaction of phosphorus pentachloride with a variety of precursors yields perchloronaphthalene e.g. 2H,3-hydroxytetrachloro-1,4-naphthoquinone,[26] 2H-pentachloro-1,4-naphthoquinone[27] and 2,3,4-trichlorosulphonyl-α-naphthol[27] all react with PCl_5 at 250°C to give perchloronaphthalene.



Replacement of $>C=O$ or $>C-OH$ by chlorine probably involves nucleophilic substitution, with the formation of $>CCl_2$ and $POCl_3$ or $>C-Cl$, HCl and $POCl_3$ respectively. At high temperatures, the reaction mechanism may not necessarily be a straightforward nucleophilic displacement.

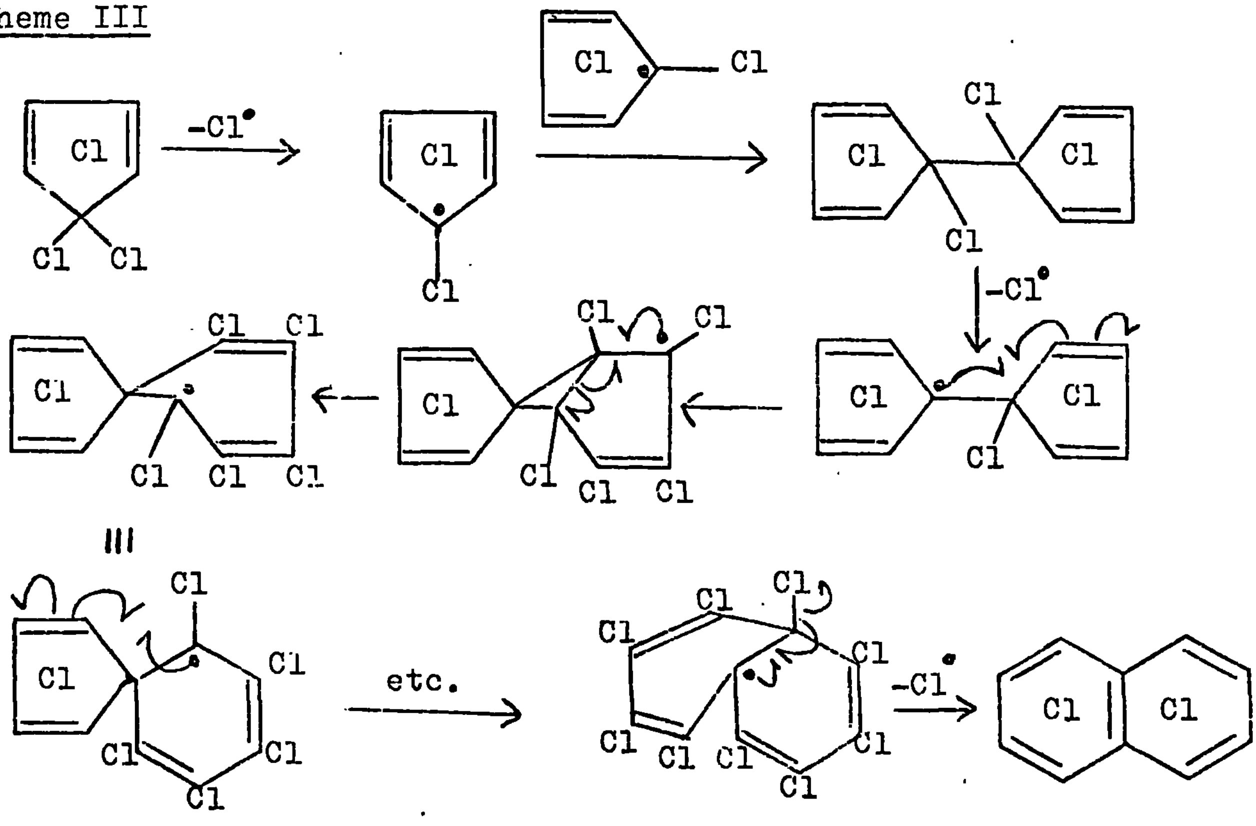
Farrar and Storms[28] obtained perchloronaphthalene by the exhaustive chlorination; i.e. a chlorinolysis reaction; of methyl-α-naphthoate with Fe/$FeCl_3$ at 110°C in perchloroethylene as solvent. Reaction of the methyl-β-naphthoate under similar conditions led to the formation of perchloro- 1,4-dihydronaphthalene.

A novel high yield synthesis of perchloronaphthalene has been described by Ginsberg and co-workers,[29] which consists of vapour phase pyrolysis of perchloro cyclopentadiene. Some perchlorobiscyclopentadienyl (approx. 5%) was also observed in the product.



A possible reaction mechanism for this process is outlined in Scheme III below.

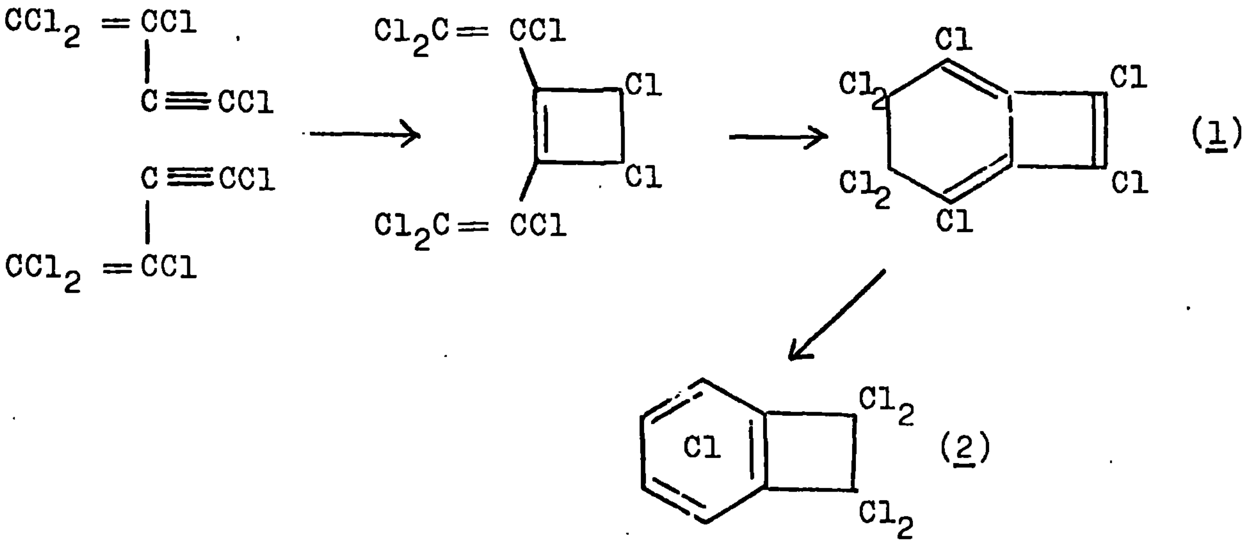
Scheme III



2.2.2 Benzocyclobutane

Roedig and Kohlhaupt observed that perchlorobutenyne dimerised at 160-180°C giving perchlorobenzocyclobutane(2).[30] The following mechanism (see Scheme IV) was suggested[31] to account for this unusual cycloaddition reaction.

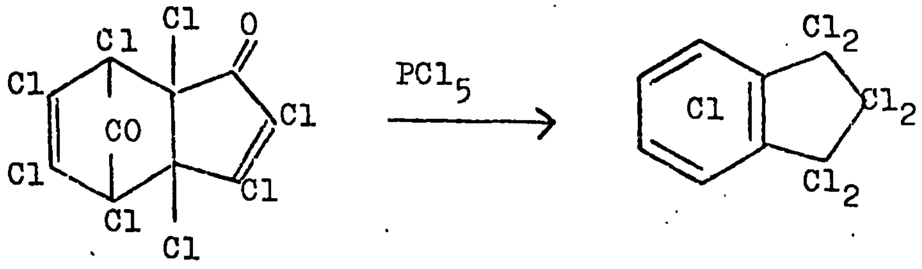
Scheme IV



The cyclohexadiene(1) is isolable at 80-100°C, but quantitative isomerisation to(2) takes place at room temperature in polar solvents such as D.M.F., D.M.S.O., and acetonitrile.

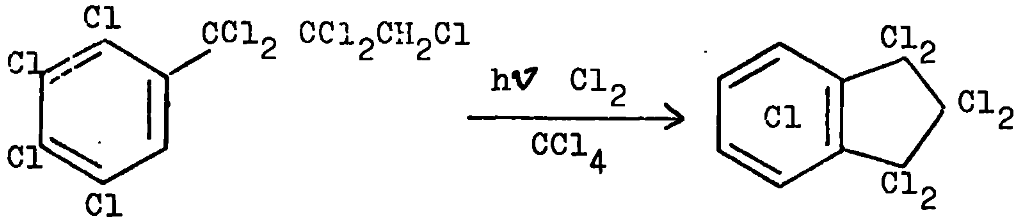
2.2.3 Indane

Zincke and Meyer have reported the synthesis of perchloroindane from the reaction of PCl_5 with either perchloroindanane or the chlorinated dimer, (3). More recently,[32] Eaton and co-workers have repeated this synthesis.



(3)

A photolytic cyclisation reaction giving some perchloroindane was observed by Ballester and Riera, when they irradiated a solution of γH γH - 2H-nonachloropropyl benzene in carbon tetrachloride.[33]

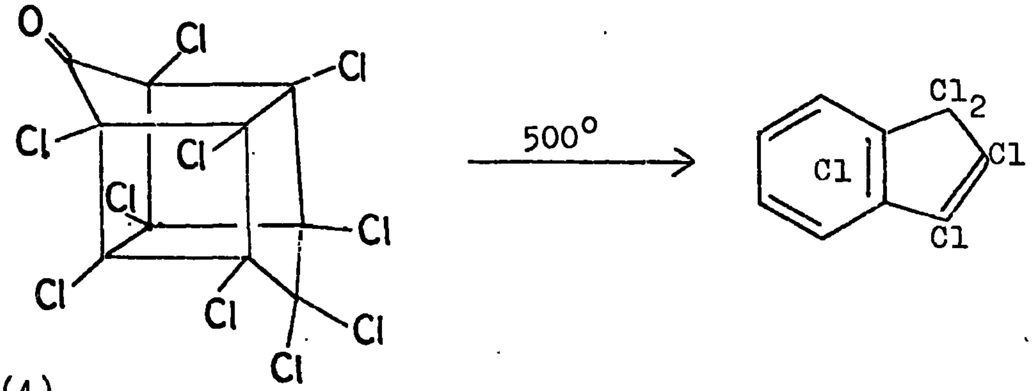


Other routes to perchloroindane include the action of heat on a perchloronaphthalene, $SbCl_5$, iodine mixture;[24] the destructive chlorination of perchloronaphthalene at 200-250°C;[11] or the destructive chlorination of hexachloronaphthalene with a chlorine, iron, iodine mixture at 160-180°C.[34]

2.2.4 Indene

Eaton and co-workers[32] synthesised perchloroindene by the action of PCl_5 on perchloroindenone. Some perchloroindane was also formed in this reaction. Mcbee and co-workers[35] observed the formation of some perchloroindene (approx. 9%) during the liquid phase pyrolysis of hexachlorocyclopentadiene.

A novel high yield synthesis (90-95%) of perchloroindene has been reported[32] when the cage ketone perchloropentacyclo-(5.3.0.0(2,6).0(4,10).0(5,9)) decan-3-one (4) is flash pyrolysed at 475-500°C.



(4)

2.2.5 Tetralin

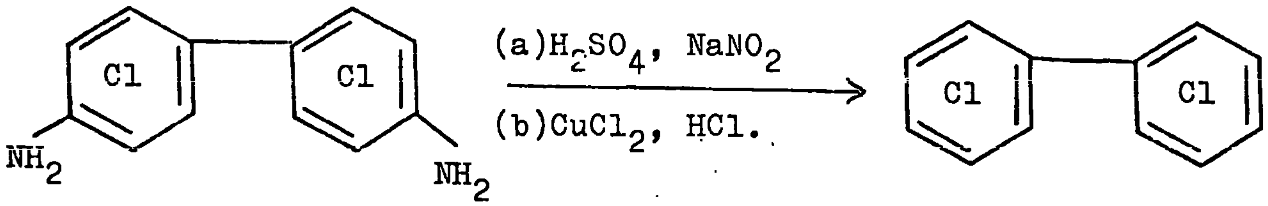
Attempts[15] have been made to synthesise perchlorotetralin but have met with limited success. The synthesis of this compound appears to be an unusually difficult process.

2.2.6 Biphenyl

In 1876, Ruoff chlorinated biphenyl with a chlorine/iodine mixture, eventually obtaining some decachlorobiphenyl. Other direct chlorinations of biphenyl giving the perchloro-compound have been reaction with antimony pentachloride at high temperatures (300°C) or reaction with chlorine over iron (100-200°C).

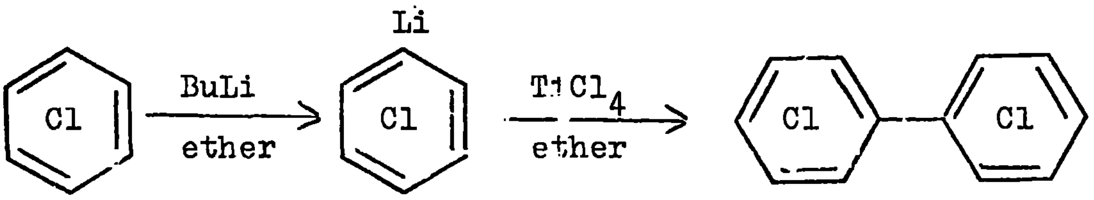
Wibaut and co-workers[36] synthesised decachlorobiphenyl in 75% yield by chlorination of commercially available pentachlorobiphenyl over ferric chloride/iodine (300°C). More recently, Ballester, Castaner and Riera[23] have claimed an almost quantitative yield of decachlorobiphenyl when biphenyl is treated with reagent B.M.C.

Substituted biphenyls have been used as precursors to decachlorobiphenyl. e.g. Van Roosmalen[37] has successfully employed a Sandmeyer type reaction on octachlorobenzidine, giving decachlorobiphenyl.



Attempts to form decachlorobiphenyl by reaction of 4,4'-dihydroxyoctachlorobiphenyl with phosphorus pentachloride up to temperatures of 230°C were unsuccessful.

Finally, oxidations of pentachlorophenyl lithium with compounds such as titanium tetrachloride in ether has given some decachlorobiphenyl in low yield.[38]



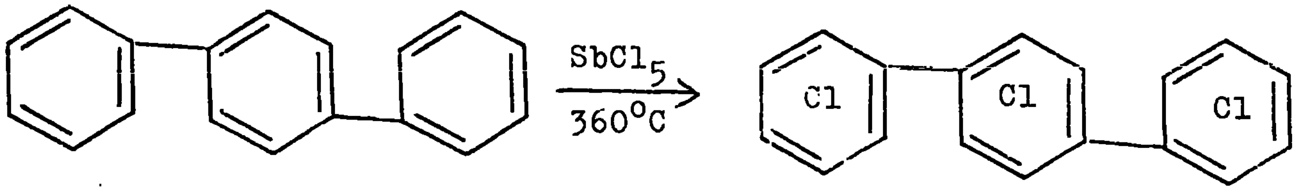
precipitated in low yield

2.3 Polycyclic Systems

Many perchloropolycyclic compounds have been described in the literature and a cross section of them is covered here. They are dealt with as follows: polyphenyls; fused aromatic systems (e.g. anthracene); and finally fused partially aromatic systems (e.g. acenaphthene). N.B. Perchlorofluorene will be covered more fully in the discussion section of this thesis and only a brief mention of it is made at this stage.

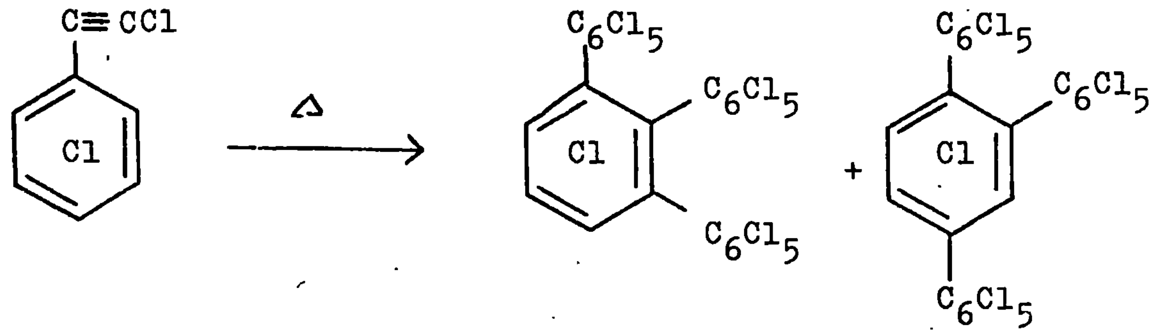
2.3.1 Polyphenyls

Perchloro-p-terphenyl was synthesised by Hutzinger and co-workers,[39] by the action of antimony pentachloride on the parent hydrocarbon at 360°C. Wibaut[36] extended this reaction to the preparation of perchloro-(4,4'-diphenyl biphenyl) from the corresponding hydrocarbon by reaction at 220-270°C.



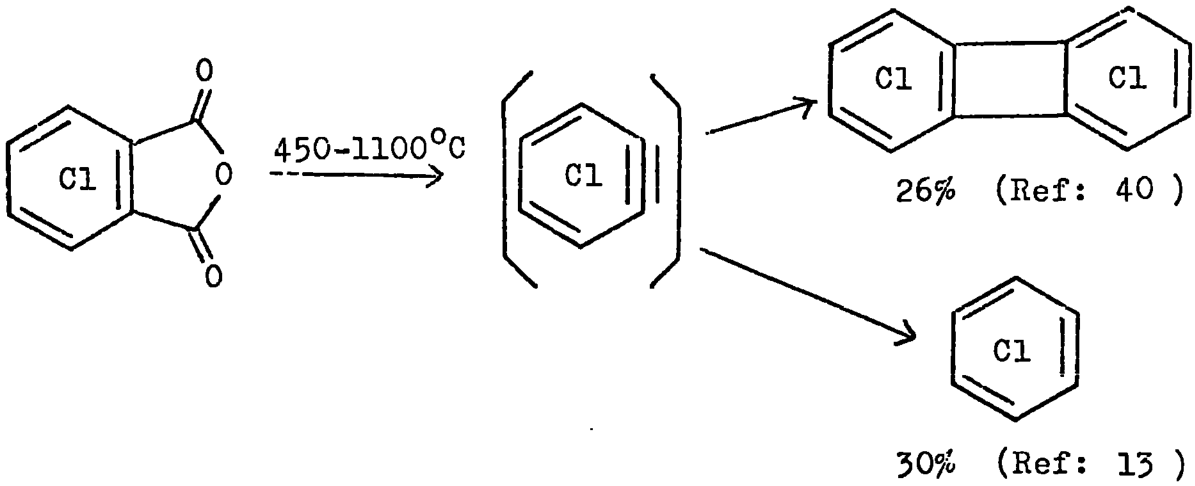
Ballester and co-workers[18] report the preparation of the three isomers of perchlorotriphenylbenzene, obtained by chlorination with reagent B.M.C., followed by reaction with antimony pentachloride at elevated temperatures. They also claim[18] that perchlorophenylacetylene undergoes some thermal oligomerisation giving the perchloro-1,2,3-and perchloro-1,2,4-triphenylbenzenes.

i.e.

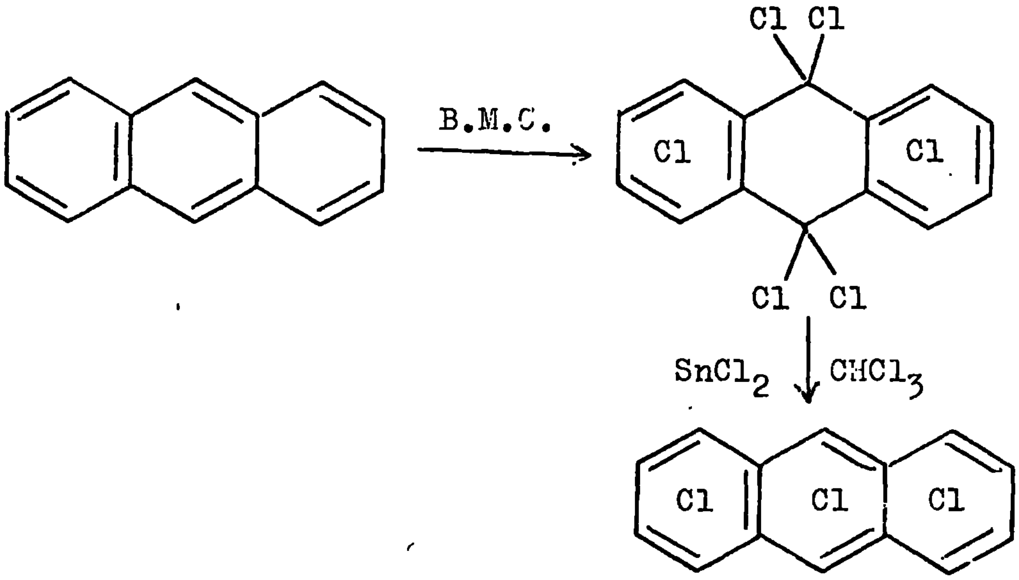


2.3.2 Fused Aromatic Systems

Perchlorobiphenylene was reported in 1967, both by Brown,[40] and by Cava and co-workers,[13] obtained from the vacuum pyrolysis of tetrachlorophthalic anhydride. According to Cava, some perchlorobenzene is formed in this reaction, and a perchloro-benzyne intermediate is involved.

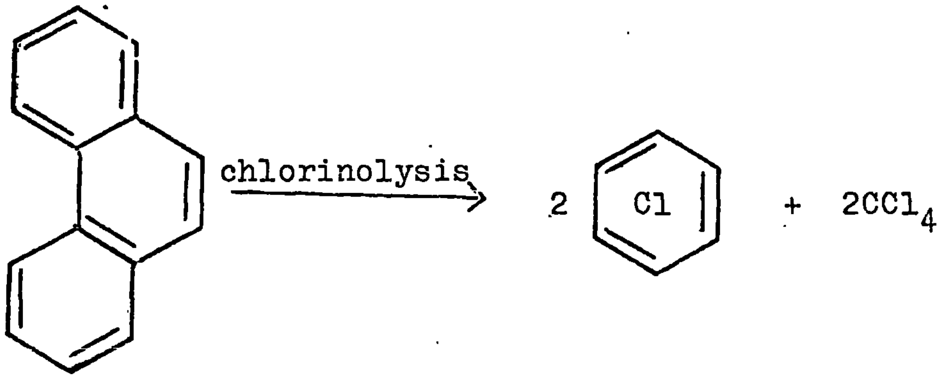


Perchloroanthracene has been prepared by Ballester and co-workers, by reaction of the parent hydrocarbon with reagent B.M.C.,[25] to form perchloro-9,10-dihydroanthracene, which then underwent reductive dechlorination by refluxing with stannous chloride in chloroform.

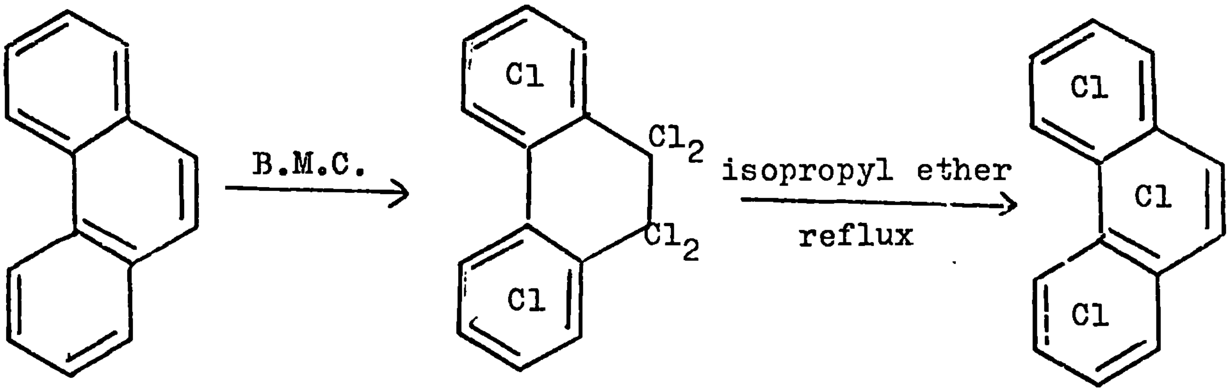


Perchloroanthracene has been observed to present thermochromy, being orange-yellow at room temperature, and orange-red at 100°C.

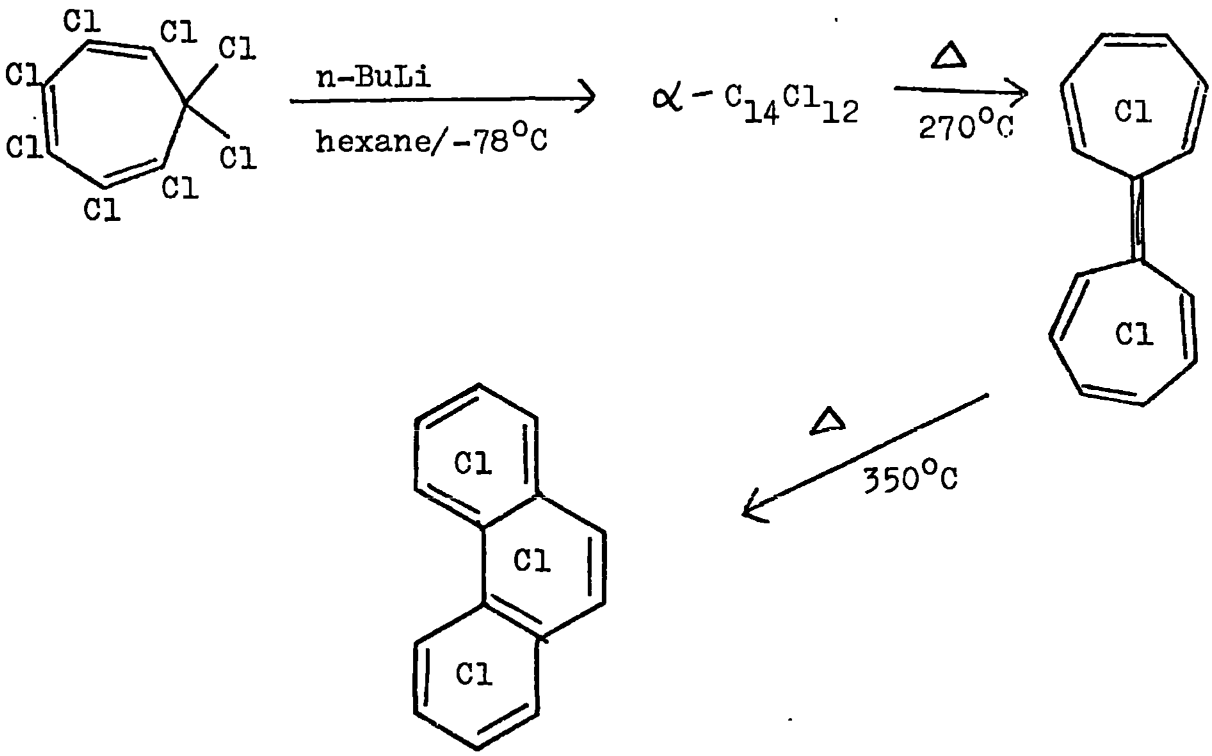
Early attempts to perchlorinate phenanthrene led to chlorinolysis occurring, giving ultimately hexachlorobenzene and carbon tetrachloride. In 1965, Ballester[23] succeeded in



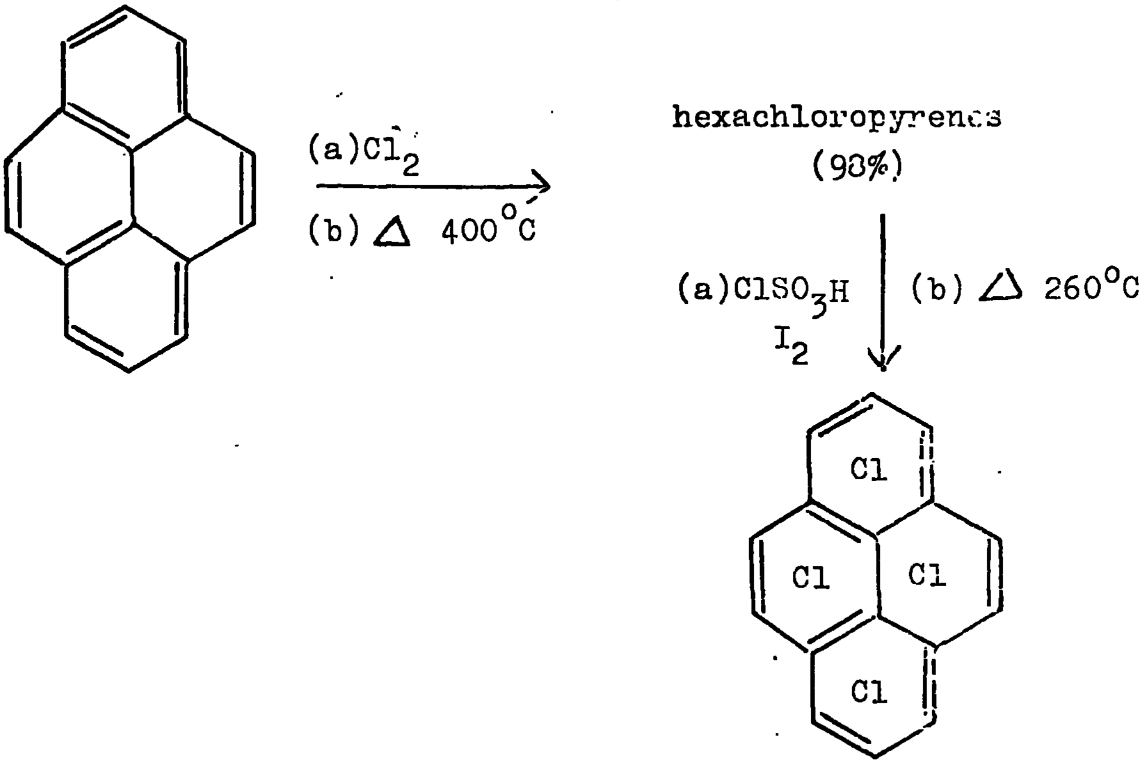
synthesising perchlorophenanthrene, by use of reagent B.M.C., followed by dechlorination of the product by refluxing with isopropyl ether.



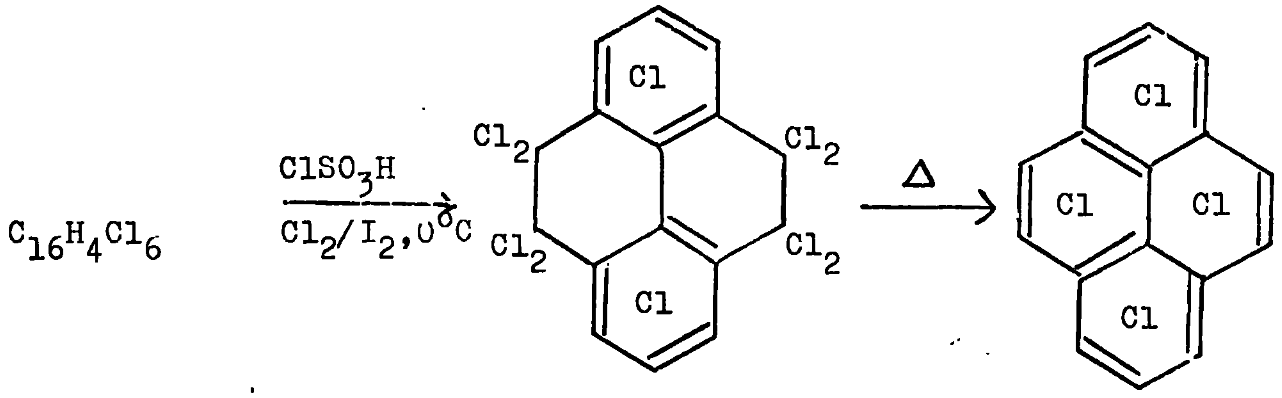
Brooks et al[41] reported a multi stage synthesis of perchlorophenanthrene, utilising chlorine and iodine; chlorosulphonic acid; followed by thermolysis at 330°C. An elegant synthesis of perchlorophenanthrene was recorded by West et al,[42] which involved the pyrolysis of dodecachloroheptafulvalene, this precursor being obtained from reaction of octachlorocycloheptatriene with n-butyllithium, followed by heating to 270°C.



The perchlorination of pyrene, involving a multistep procedure has been described by Vollmann[43] and co-workers. Initially, a mixture of hexachloropyrenes is isolated, obtained by the direct chlorination of pyrene, followed by thermolysis of the product at 400°C. A 98% yield is recorded for this stage of the synthesis. Further chlorination of this mixture with chlorosulphonic acid in the presence of iodine, again followed by pyrolysis, yields decachloropyrene.



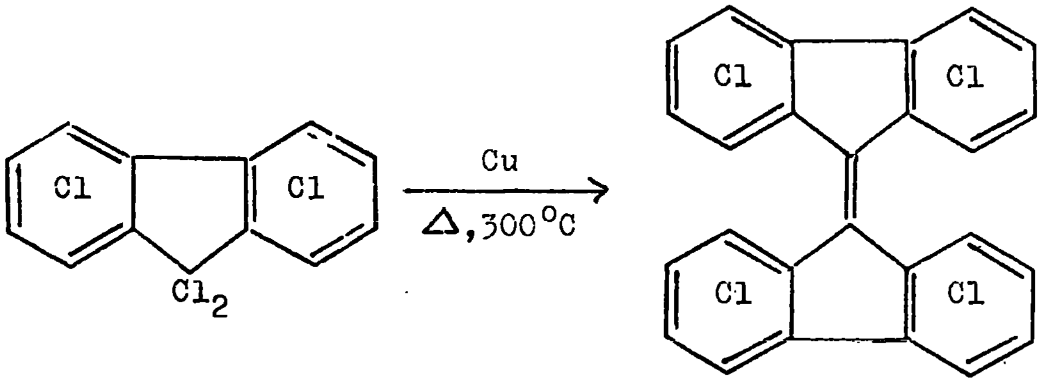
Reimlinger and King[44] repeated the chlorination of the mixture of hexachloropyrenes with chlorine, chlorosulphonic acid and iodine at 0°C, obtaining perchloro-4,5,9,10-tetrahydropyrene; which on heating above its melting point (312°C) eliminated chlorine to give perchloropyrene.



An unsuccessful attempt to synthesise perchlorochrysene has been recorded.[45]

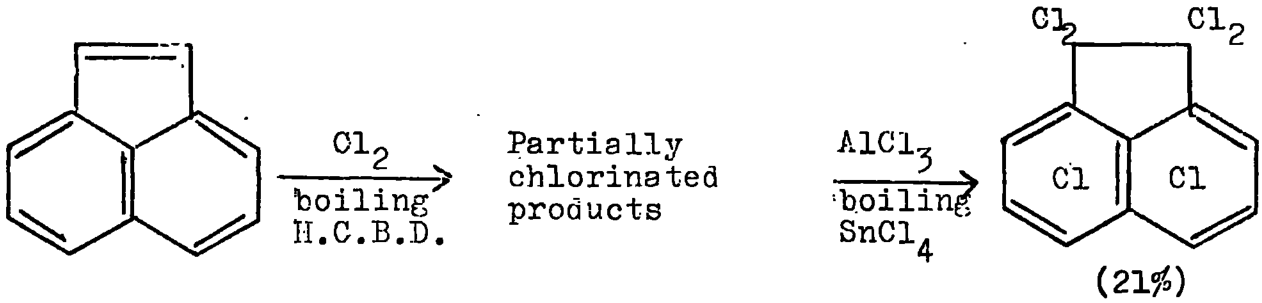
2.3.3 Fused Partially Aromatic Systems, Including Fluorene

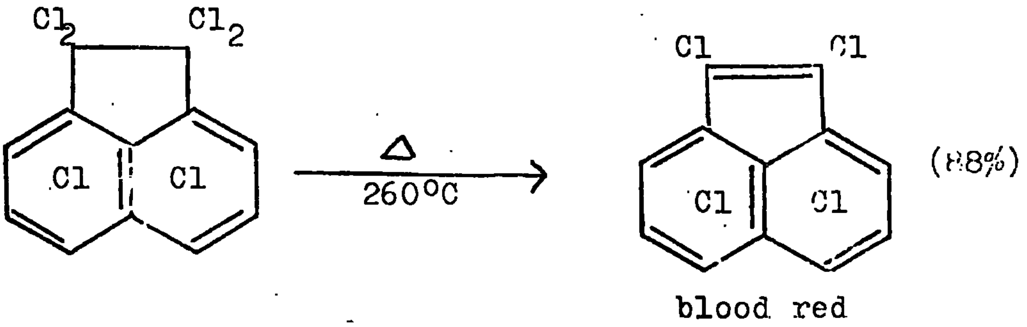
Perchlorofluorene was observed as a side product during the chlorination of dichlorodiphenylmethane with reagent B.M.C.[23,25,4] It has also been synthesised by the action of PCl_5 on octachloro-fluoren-9-one[23] or the reaction of 9,9-dichlorofluorene with reagent B.M.C.-P. When heated to 300°C in the presence of copper dust, the blue perchlorobifluorenylene is formed in 98% yield.[18]



Further consideration will be given tothe chlorination of fluorene and properties of chlorinated fluorene in the discussion section of this thesis.

Acenaphthylene undergoes partial chlorination with chlorine gas in boiling hexachlorobutadiene, further reaction of this chlorinated product with aluminium chloride in boiling stannic chloride gives perchloroacenaphthene in 21% yield, pyrolysis of which yields the blood red perchloroacenaphthylene.[47]





Dechlorination also occurs in 40% yield upon reaction with stannous chloride.[25,47,48]

Perchloroacenaphthene has also been prepared by Ballester and co-workers[25,48] by the action of reagent B.M.C. on the parent hydrocarbon.

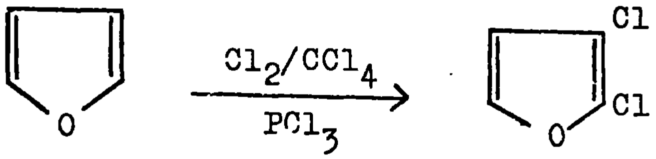
3. Preparation of Some Perchlorinated Heterocyclic Compounds

For convenience, this section will be sub-divided into four main parts, viz: oxygen containing heterocycles in order of increasing number of rings; sulphur containing heterocycles, dealt with in a similar fashion; a brief section concerned with nitrogen containing heterocycles; and finally a section devoted to miscellaneous polychloro heterocycles.

3.1 Oxygen Containing Compounds

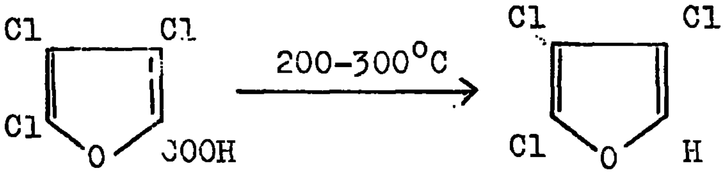
3.1.1 Furan

Direct chlorination of furan has been proven to be difficult; (a) because of its sensitivity to acid, and (b) because halogenation is frequently accompanied by violent polymerisation.[49] However, 2,3-dichlorofuran may be obtained by chlorination of furan in carbon tetrachloride solution, with a trace of phosphous trichloride as catalyst.[49]

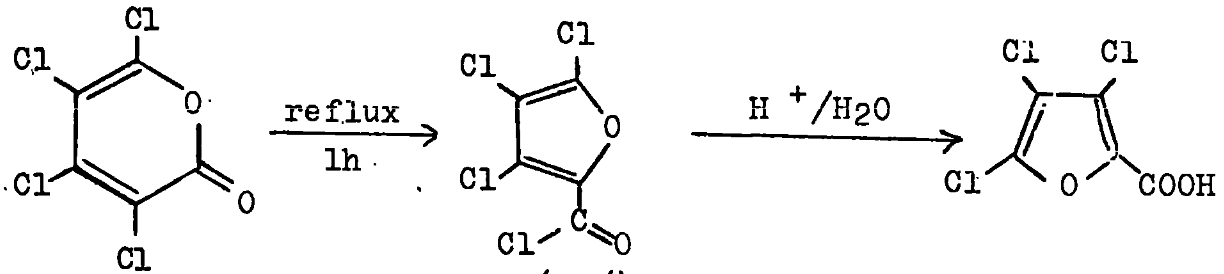


Other partially chlorinated furans may be obtained from decarboxylation of chlorofuroic acids. e.g. furoic acid may be chlorinated directly, the resulting 3-chlorofuroic acid being decarboxylated over copper/bronze or zinc at 300-400°C, to give 3-chlorofuran.[50] Dichloro- and trichlorofurans have been obtained in a similar fashion.[50]

e.g.

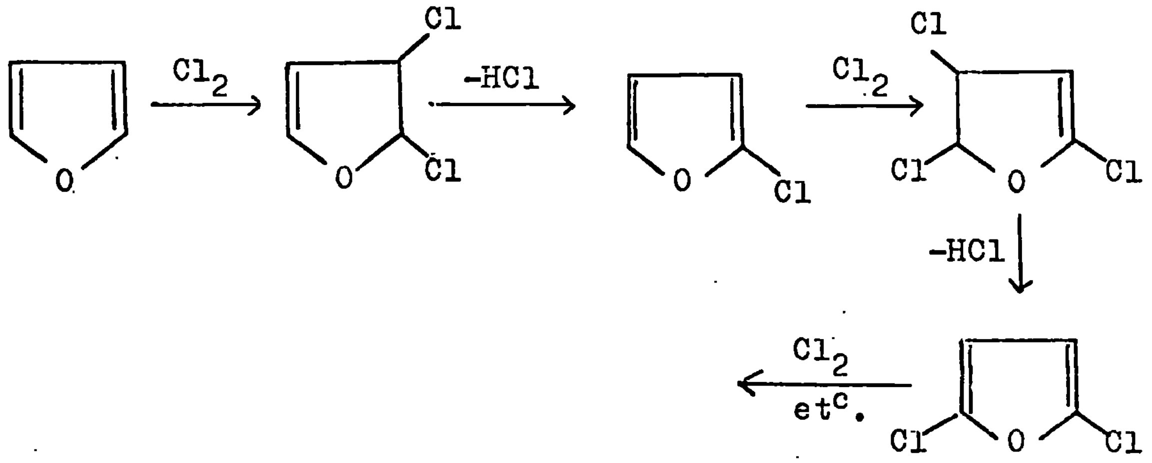


The trichlorofuroic acid may be obtained from the thermal rearrangement of tetrachloro-2H-pyran-2-one, followed by hydrolysis of the so formed trichloro-2-furoyl chloride. The intramolecular rearrangement is said to be favoured by the formation of the aromatic furan ring.[51]



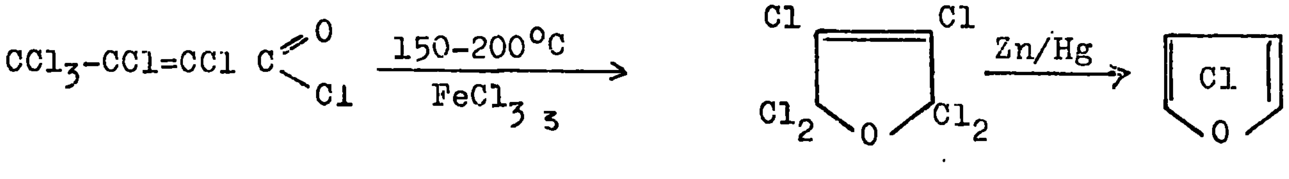
(82%)

A mixture of chlorinated species, viz: 2-chloro-; 2,5-dichloro-; 2,3,5-trichloro-; tetrachloro-; and hexachloro-2,5-dihydro- furans is obtained when furan is chlorinated at low temperatures (-20° to -40°C). Keeping the reaction mixture below 20°C allows the HCl formed during the reaction to gas off without causing any polymerisation of substrate. The reaction is throught to proceed via an addtion - elimination mechanism,[52,53] i.e.



Tetrachlorofuran may be conveniently prepared by the dechlorination of hexachloro-2,5-dihydrofuran,[54,55] this precursor being formed from the rearrangement and cyclisation of perchloro crotonyl chloride.[56,57]

$CCl_2{=}CCl.CCl.{=}CCl_2 \xrightarrow[EtOH]{NaOEt} CCl_2 = CCl.CCl = CClOC_2H_5 \xrightarrow{Cl_2}$



(85 - 95%)

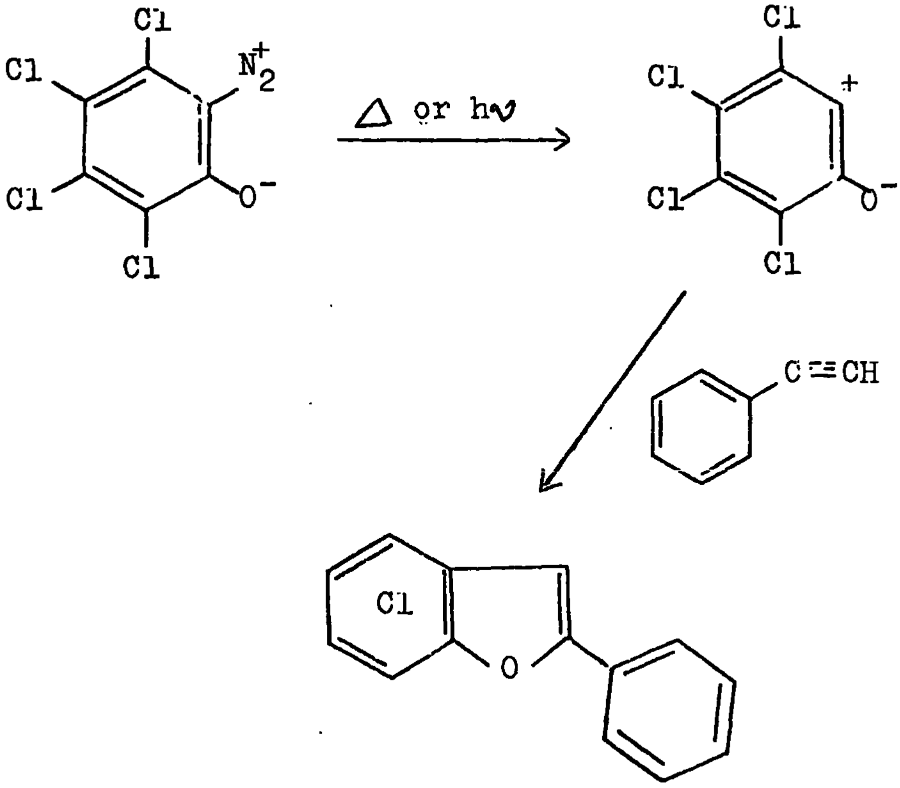
Many other chlorinated derivatives of furan have been synthesised e.g. trichlorofuran-2-carboxylic acid provides a convenient precursor to amides, ethyl esters, nitriles etc. Some of these derivatives have proven useful as herbicidal and pesticidal agents.[58]

3.1.2 Benzofurans

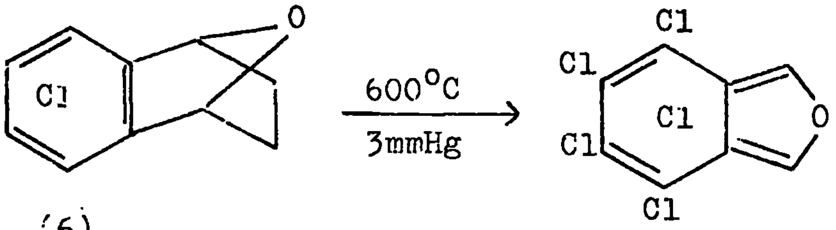
Hexachlorobenzo(b)furan and pentachloro-benzo(b)furan appear to be unknown.[59]

The direct chlorination of benzofuran has been reported to give a mixture of tri- and tetra-chlorobenzo(b)furans.[60]

A wide range of derivatives of 1,2,3,4-tetrachlorobenzo(b)furan is recorded in the literature. These derivatives may be readily obtained via cyclo addition reactions, e.g. thermolysis or photolysis of tetrachloro-o-benzoquinone dioxide gives the polar oxide,[61,62] which readily undergoes 1,3-dipolar cyclo addition reactions, forming tetrachlorobenzo(b)furans in good yields.



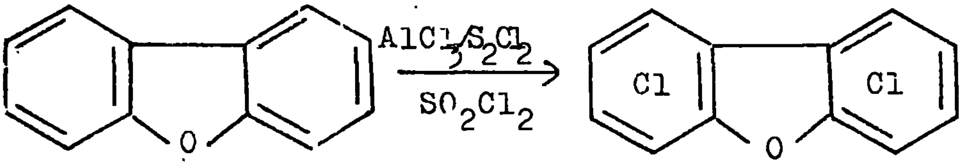
When the polycyclic compound(6) below is subjected to flow pyrolysis at c600°C/3mm Hg under nitrogen, it gives quantitative yields of tetrachlorobenzo(c)furan.[63]



(6)

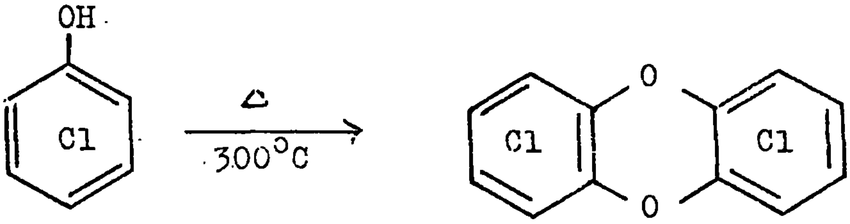
3.1.3 Dibenzo(b,d)furan

The fully chlorinated title compound has been prepared,[64] and will be dealt with more fully in the discussion section of this thesis.

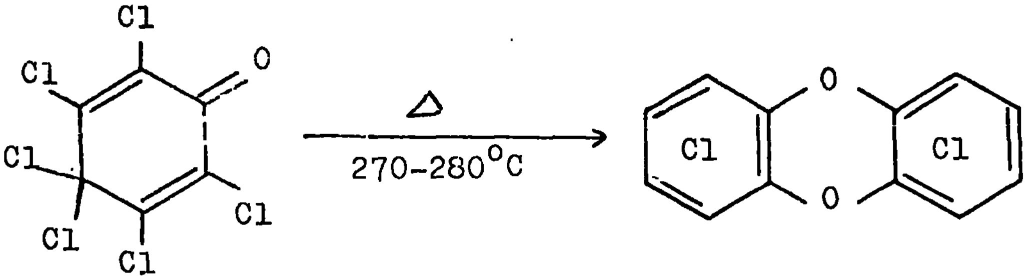


3.1.4 Dibenzo-p-dioxin

Both Sandermann and co-workers,[12] and Denivelle and co-workers[65] report the formation of 1,2,3,4,6,7,8,9-octachlorodibenzo-p-dioxin during the pyrolysis of pentachlorophenol.



Other methods for its formation include the direct chlorination of 2,6-dichlorodibenzo-p-dioxin with chlorine and antimony pentachloride,[65] or the pyrolysis of 2,3,4,4,5,6-hexachloro-2,5-cyclohexadienone.[66] A pentachlorophenoxy radical has been suggested as an intermediate in the above reaction.[66]

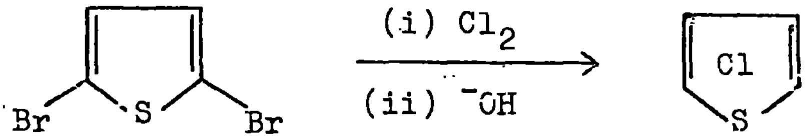


3.2 Sulphur Containing Compounds

3.2.1 Thiophens

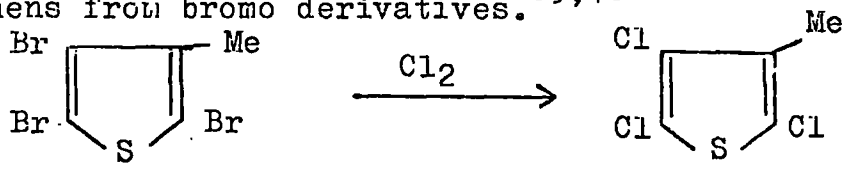
The chlorination of thiophen is well documented, and depending upon the reaction conditions used, almost any degree of chlorination may be achieved. Exhaustive chlorinations to give thiolenes and thiolanes, and inter conversion of these back to thiophenes may also be readily accomplished.

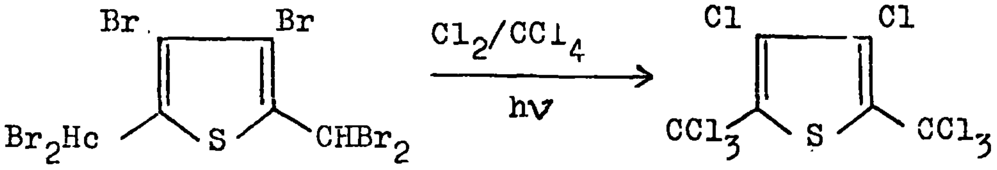
Tetrachlorothiophene was first recorded by Weitz, from the chlorination of 2,5-dibromothiophene.[67,68]



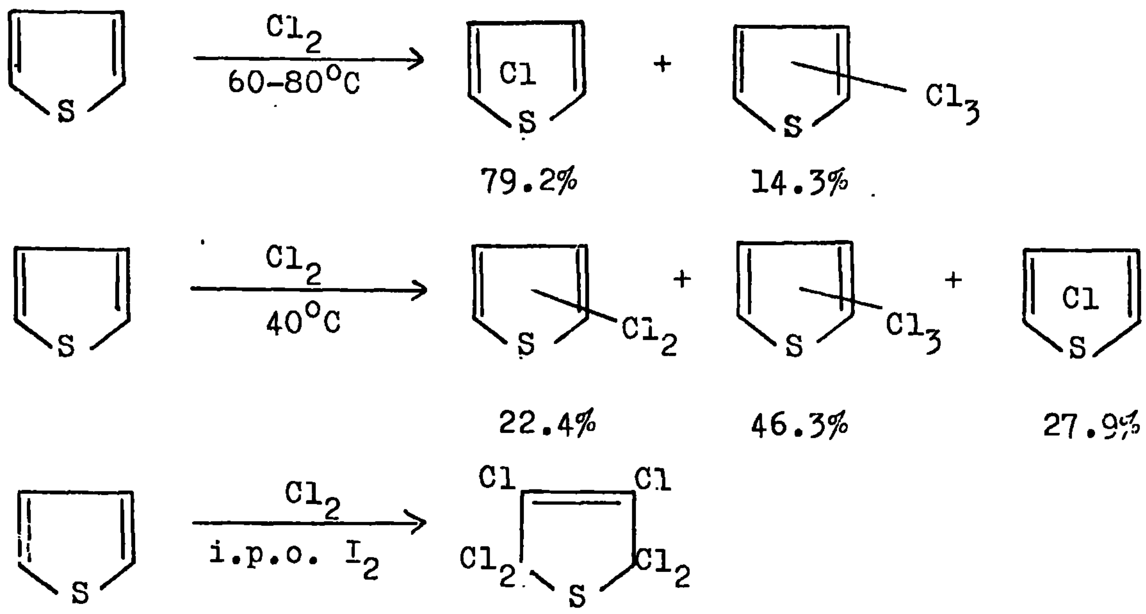
The ready exchange of chlorine for bromine has also been demonstrated in the synthesis of certain chloroalkyl thiophens from bromo derivatives.[69,70]

e.g.

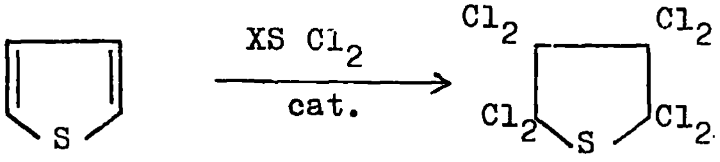


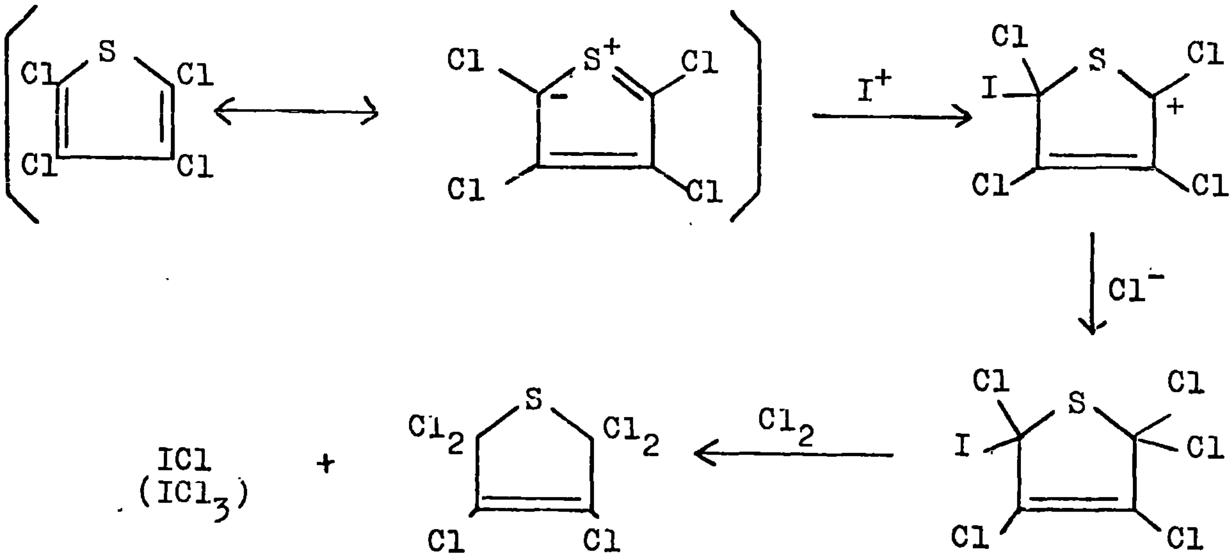


Direct chlorination of thiophen has been shown to yield different mixtures of chlorinated derivatives, depending upon the conditions used. e.g. Coonradt and co-workers have varied the chlorination conditions of thiophen; giving at 70°C mainly tetrachlorothiophen;[71] at 40°C a mixture of di-, tri-, and tetra-chlorothiophens;[72] and in the presence of iodine as a catalyst, the formation of hexachlorothiolene.[73]

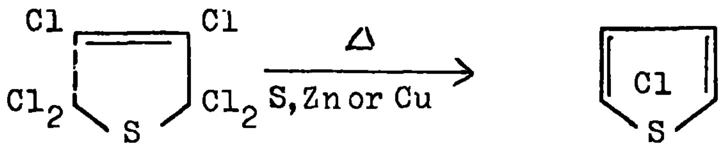


Chlorinations over elongated reaction times, and in the presence of catalysts have yielded octachloro-thiolane[74,75] A mechanism for the iodine catalysed chlorination of thiophen has been suggested,[73] i.e.

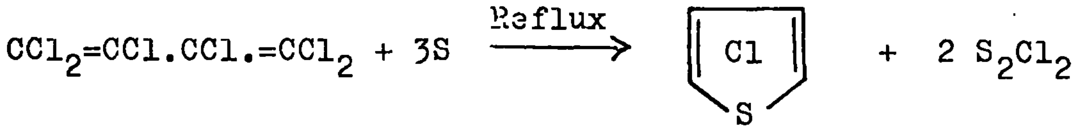




The semi saturated thiolenes and thiolanes may be readily converted back to thiophenes, simply by heating alone,[76] or by heating in the presence of a dechlorinating agent such as sulphur,[77] zinc,[78] or copper.[74]



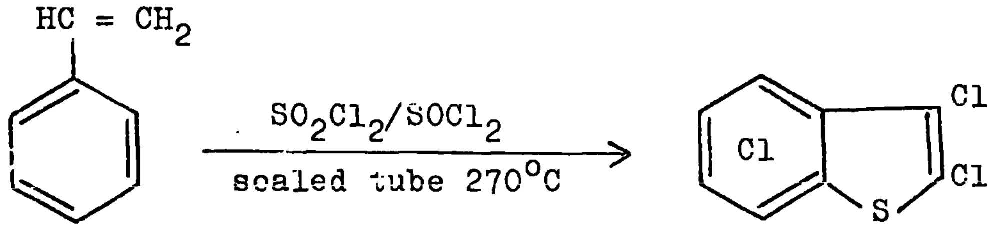
A cyclisation reaction giving tetrachlorothiophen in quantitative yield has been described by several workers.[79,80,81] Hexachlorobutadiene is refluxed with sulphur, and sulphur monochloride formed during the reaction is removed in situ.



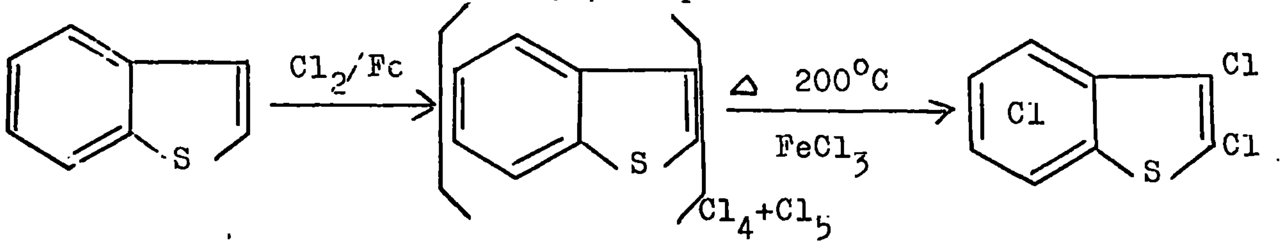
quantitative

3.2.2 Benzothiophens

Treatment of styrene or α,β- dibromostyrene with thionyl chloride and sulphuryl chloride at elevated temperatures has been shown to yield hexachlorobenzo(b)thiophen in low yield.[82,83]



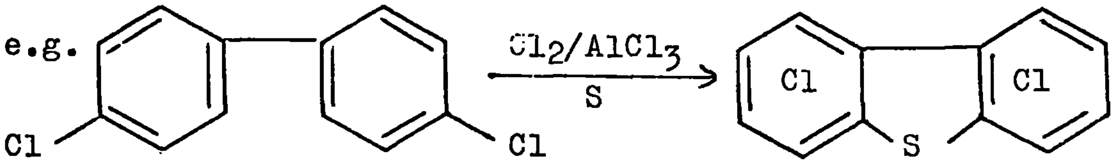
Direct chlorination of benzo(b)thiophen in carbon tetrachloride solution yields a mixture of mono- and di-chloro derivatives,[84] whereas chlorination over iron has been shown to yield a mixture of tetra- and penta-chlorobenzo(b)thiophens, the positions of substitution being undetermined.[84] Hudson and Iddon[83] claim that raising the temperature to 200°C and adding $FeCl_3$ during the latter stages of the chlorination over iron enables hexachlorobenzo(b)thiophen to be made.



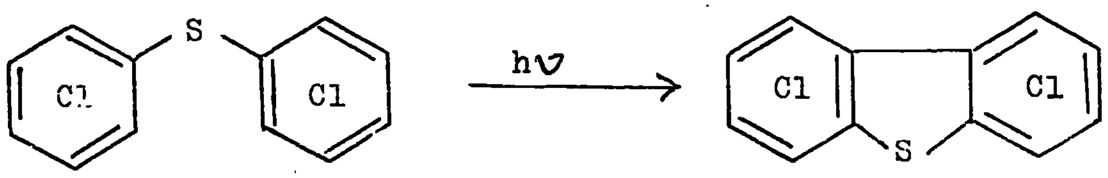
3.2.3 Dibenzo(b,d)thiophen

The fully chlorinated title compound has been prepared,[85,86] and will be dealt with more fully in the discussion section of this thesis.

e.g.



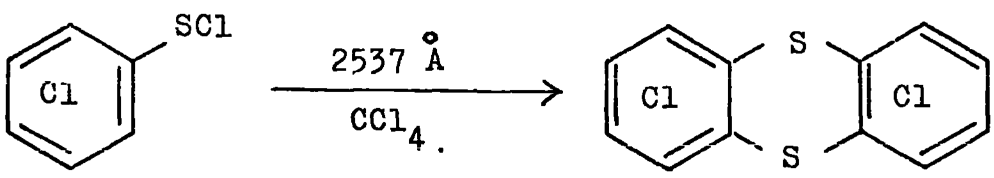
(Ref.85)



(Ref.86)

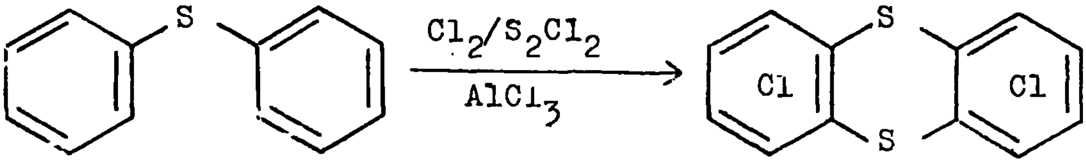
3.2.4 Dibenzo-1,4-dithiin (Thianthrene)

Octachlorodibenzo-1,4-dithiin may be obtained from the irradiation of a solution of pentachlorobenzenesulphenyl chloride in carbon tetrachloride.[86]



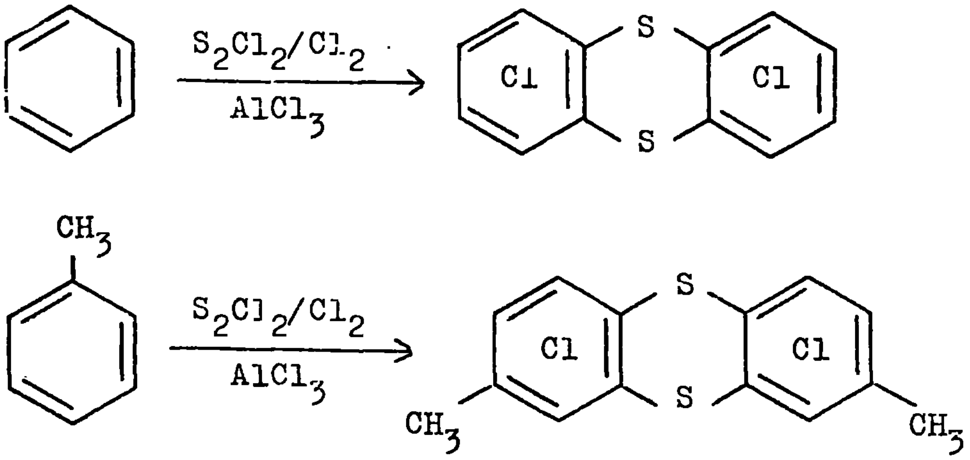
Cyclisation reactions may also be used in the synthesis of this compound, e.g. the chlorination and cyclisation of diphenylsulphide in the presence of sulphur or sulphur monochloride and a Friedel-Craft catalyst.[85]

e.g.



If benzene or toluene are reacted under similar conditions, octachlorothianthrene and 2,8-dimethylhexachlorothianthrene are the respective products.[87]

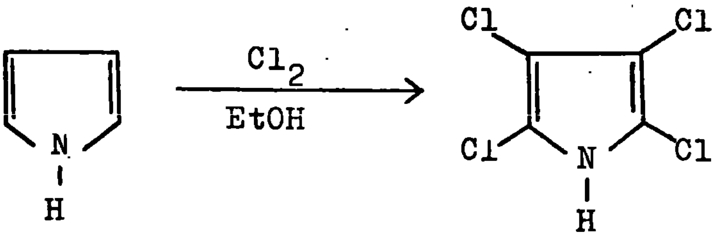
i.e.



3.3 Nitrogen Containing Compounds

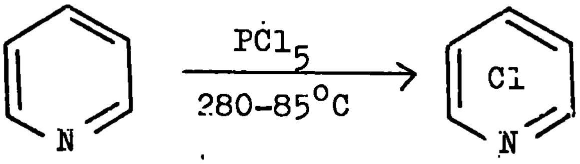
3.3.1 Monocyclic Systems

Many polychloronitrogen containing systems have been prepared, examples of which include tetrachloropyrrole, pentachloropyridine, tetrachloropyrazine, tetrachloropyridazine and cyanuric chloride. Their methods of preparation are varied, ranging from direct chlorination, as in the case of pyrrole,[88] to reaction with phosphorus pentachloride in an autoclave at elevated temperatures. This latter technique has been successfully developed at Durham, and applied to the synthesis of compounds such as pentachloropyridine,[1] tetra-

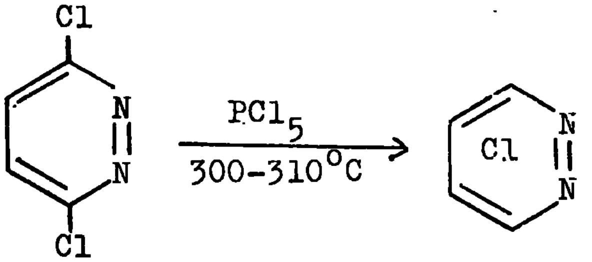


(Ref:88)

chloropyridazine[89] and tetrachloropyrazine.[90]



+ less chlorinated species (recycled) (Ref:1)



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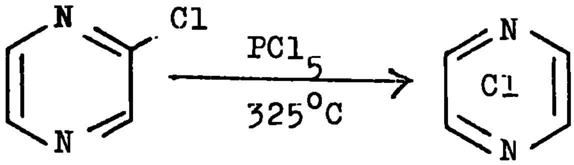
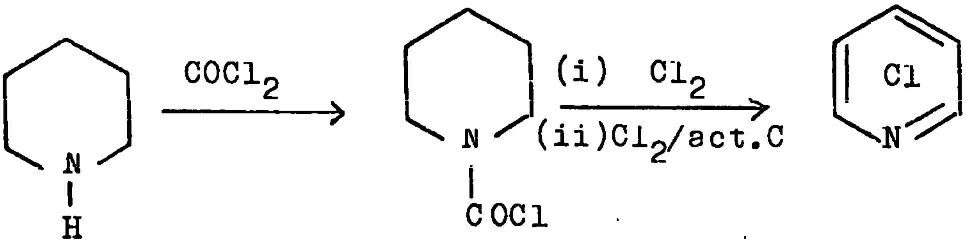
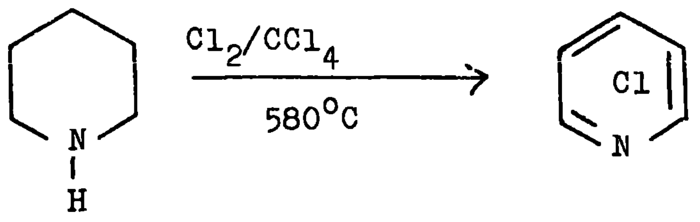


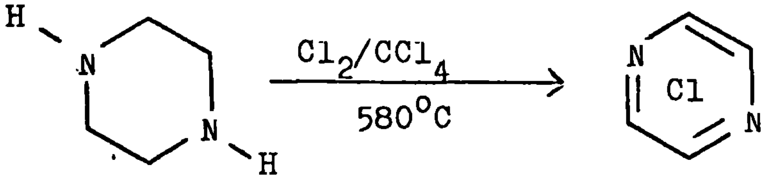
(Ref:90)

Vapour phase chlorination of carbonyl chlorides is a useful synthetic route to some perchlorinated N- containing heterocycles;[93] e.g. piperidine is treated with $COCl_2$ to give piperidine-N-carbonyl chloride, which is then converted to pentachloropyridine by pre-chlorination at 50-150°C, followed by chlorination at 150-500°C in the presence of activated carbon.

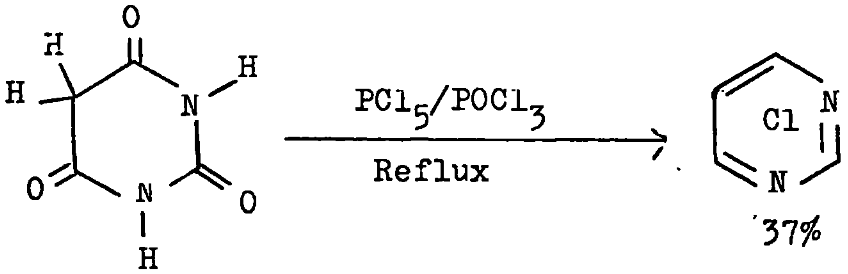


Pentachloropyridine and tetrachloropyrazine have been prepared by passage of their saturated hydrocarbon analogues down a hot tube with chlorine gas and carbon tetrachloride as diluent.[94]





Other methods of obtaining perchlorinated species include the reaction with chlorine in the presence of a Lewis acid catalyst; solvent reactions with phosphorus pentachloride in phosphorus oxychloride,[91] and photochemically induced processes.[92]



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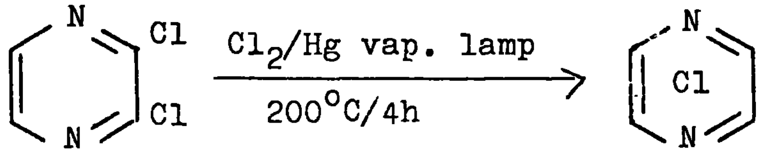

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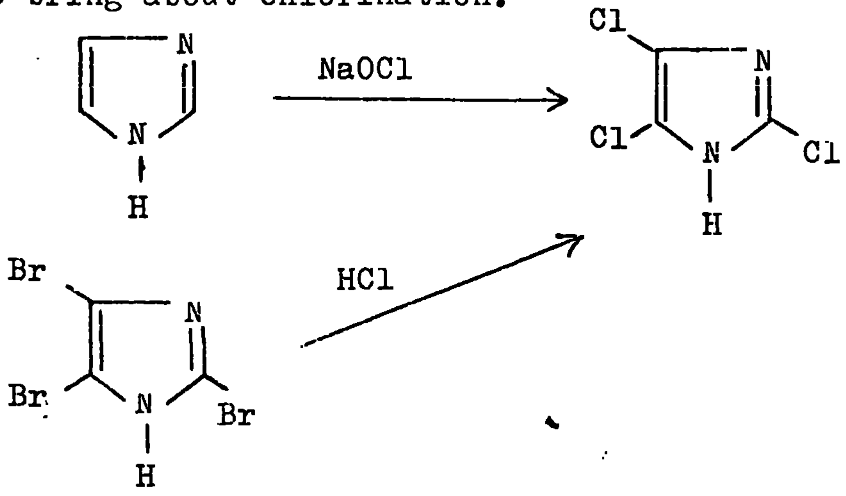
In some cases, e.g. imidazoles, refluxing the heterocycle in sodium hypochlorite,[95] or reaction of a brominated derivative with hydrochloric acid[96] is sufficient to bring about chlorination.

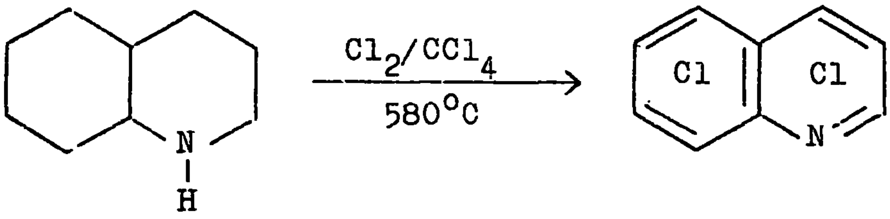


It is worth noting that neither trichloro- nor tetrachloro-pyrazole is reported.[97,98]

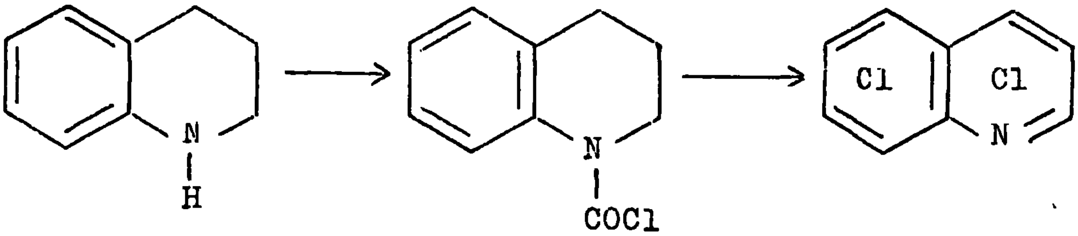
3.3.2 Bicyclic Systems

Many of the procedures applied to the chlorination of monocyclic nitrogen containing systems may be extended to the preparation of perchlorobicyclic compounds. e.g. Autoclave chlorinations with phosphorus pentachloride have been widely used by Chambers and co-workers to effect the perchlorination of several bicyclic systems. Some of the conversions they have reported are heptachloroindole from a mixture of trichloroindoles;[99] hexachlorocinnoline from 3,4,7,8-tetrachlorocinnoline;[100] and hexachloroquinazoline from 2,4-dichloroquinazoline.[101] Taplin achieved the vapour phase perchlorination of the quinolines, by reaction of the respective heterocycles with chlorine and carbon tetrachloride at 600°C.[102]

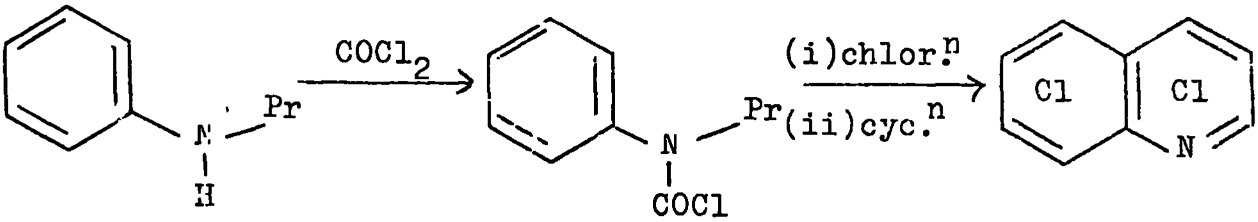
Johnston and Ruetman[94] describe a similar process, where heptachloroquinoline is prepared by the chlorination of the fully saturated hydrocarbon analogue with chlorine and carbon tetrachloride diluent at 580°C.



Heptachloroquinoline may also be prepared by the chlorination of the N-carbonyl chloride derivative of 1,2,3,4-tetrahydroquinoline in the presence of activated charcoal.



Tarnow and co-workers describe a cyclisation process which yields heptachloroquinoline.[103] Initially, phenyl propylamine is reacted with carbonyl chloride to give the N-carbonyl derivative, which is then chlorinated by a multistep procedure and cyclised giving heptachloroquinoline.



3.3.3 Polycyclic Systems

The perchloro analogues of acridine, phenanthridine and 7,8-benzoquinoline have been prepared at Durham by direct chlorination of the appropriate ring systems.[2]

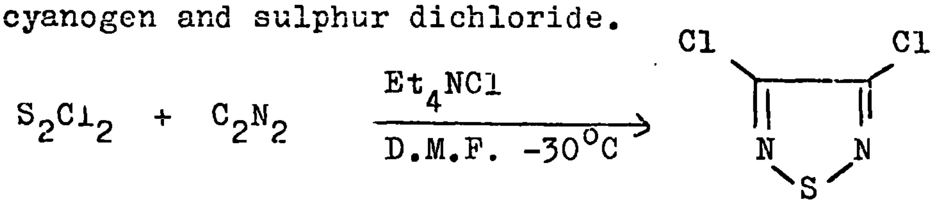
A more comprehensive review of the preparation of nitrogen containing heterocycles is to be found in reference 2.

3.4 Miscellaneous Heterocyclic Systems

3.4.1 Monocyclic Systems (oxazoles, thiazoles etc.)

Very little seems to be known about monocyclic polychloro systems containing two or more heteroatoms. Dichloro thiazole has been reported,[104] but the trichloro compound appears to be unknown, as are the perchloro analogues of oxazole, isoxazole and isothiazole.

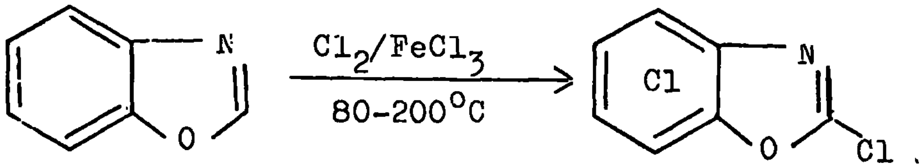
Vest[105] has reported the synthesis of 3,4-dichloro-1,2,5- thiadiazole from a cyclisation reaction involving cyanogen and sulphur dichloride.



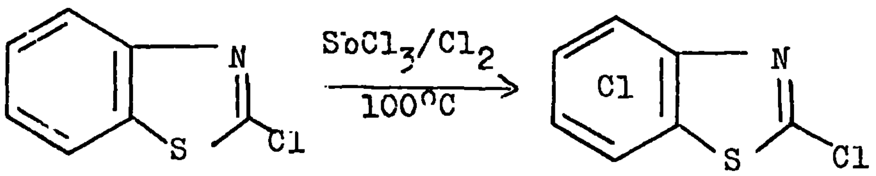
(88%)

3.4.2 Bicyclic Systems (Benzoxazoles, benzothiazoles etc.)

Again, very little appears to be known about these perchloro systems. Pentachlorobenzoxazole is obtained when the parent heterocycle is chlorinated in the presence of ferric chloride.[106]



High yields of pentachlorobenzothiazole are obtained when the parent heterocycle or one of its 2-substituted derivatives are exhaustively chlorinated in the presence of antimony trichloride.[107] The action of heat on pentachlorophenylisothiocyanate also gives pentachlorobenzothiazole in good yield.[108]

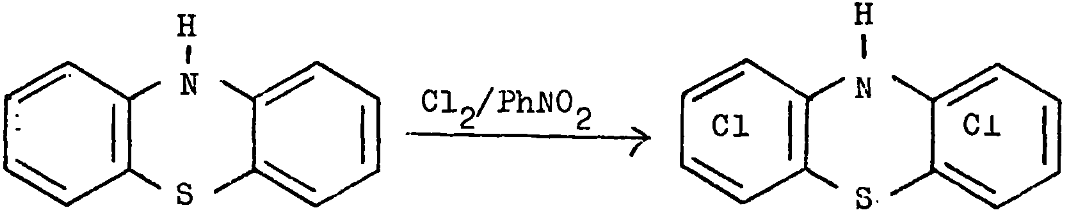


(Ref:107)

The perchloroanalogues of benzisoxazole and benzoisothiazole appear to be unknown.

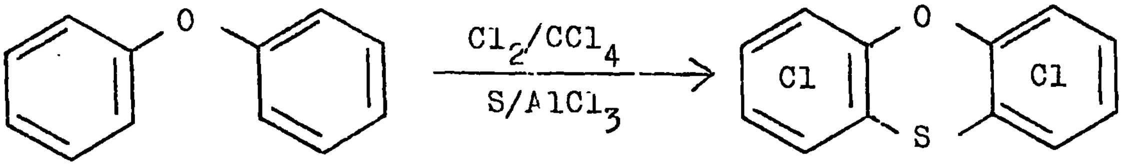
3.4.3 Polycyclic Systems

The preparation of octachlorophenothiazine has been reported by several workers. This may be achieved by direct chlorination of the parent heterocycle,[109] or by reaction with sulphuryl chloride.[110]

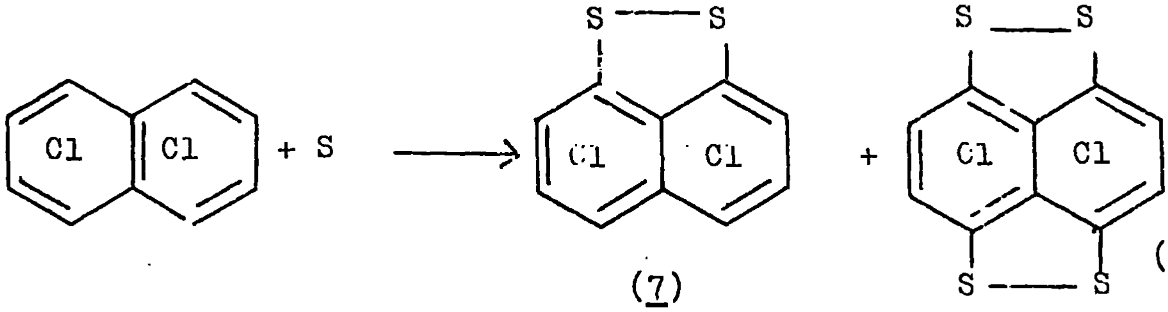


(Ref:109)

The synthesis of perchlorodibenzo-1,4-oxathiins by reaction of diphenyl ethers with sulphur in the presence of aluminium chloride has been described by Klug.[87]



Klingsberg[111] has reported an unusual reaction between octachloronaphthalene and sulphur, giving the systems (7) and (8) below. He suggested that simultaneous bidentate attack of



(7)

(8)

S_2^{2-} at the peri positions, the favourable geometry, and the activating influence of chlorine are responsible for the production of these products. Selenium is also said to give similar products.

DISCUSSION

CHAPTER II

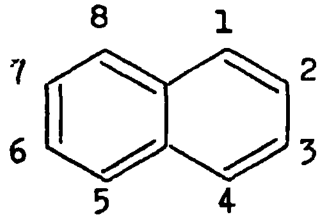
The Synthesis of Some Perchloropolycyclic Compounds

1. Introduction

As mentioned earlier, routes to some perchloropolycyclic compounds have been developed and this chapter traces the techniques used to achieve this perchlorination. Incorporated with this is a summary of previous attempts and established methods of chlorination of these systems.

1.1 Ring Systems, Numbering and Nomenclature

Seven ring systems were investigated, two of which were bicyclic, and the remainder tricyclic. The bicyclic systems were naphthalene (9) and biphenyl (10). Their structure and numbering system are as shown below:-



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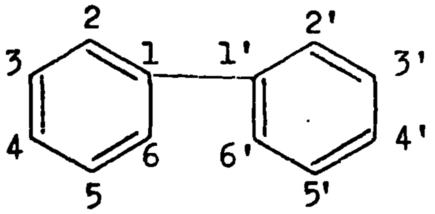
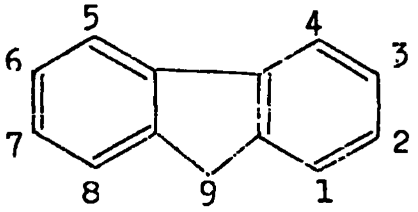
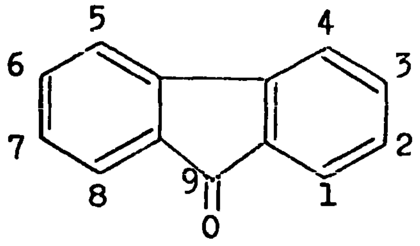


(10)

Of the remaining five systems, fluorene (11) and fluoren-9-one (12) have the structures and numbering systems shown here:-

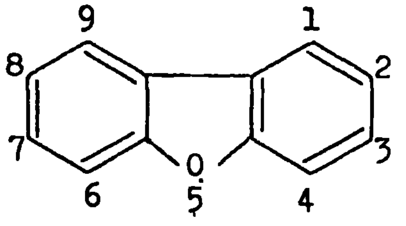


(11)

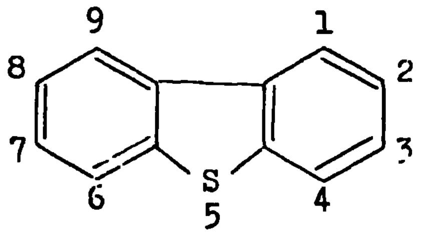


(12)

In the case of the two heterocycles dibenzo(b,d)furan (13) and dibenzo(b,d)thiophen (14), numbering is started at the top right as written, proceeding in a clockwise manner, round the system, the bridgehead atom now occupying the 5-position. The (b,d) in this nomenclature refers to the respective side of

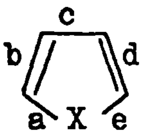


(13)



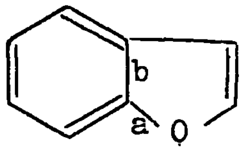
(14)

the parent heterocycle to which the "benzo-substituents" are attached, i.e.

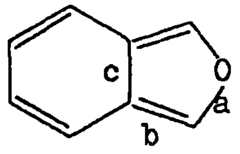


X = S,O

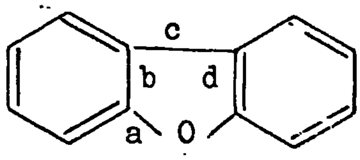
Thus: (15) becomes benzo(b)furan; (16) becomes benzo(c)furan; and (17) becomes dibenzo(b,d)furan.



(15)

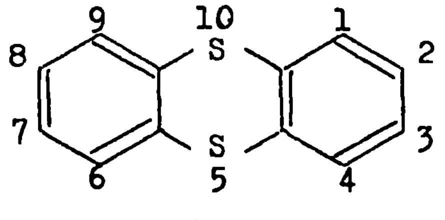


(16)



(17)

The final heterocycle, thianthrene (18) has the bridgehead atoms occupying the 5 and 10 positions:-



(18)

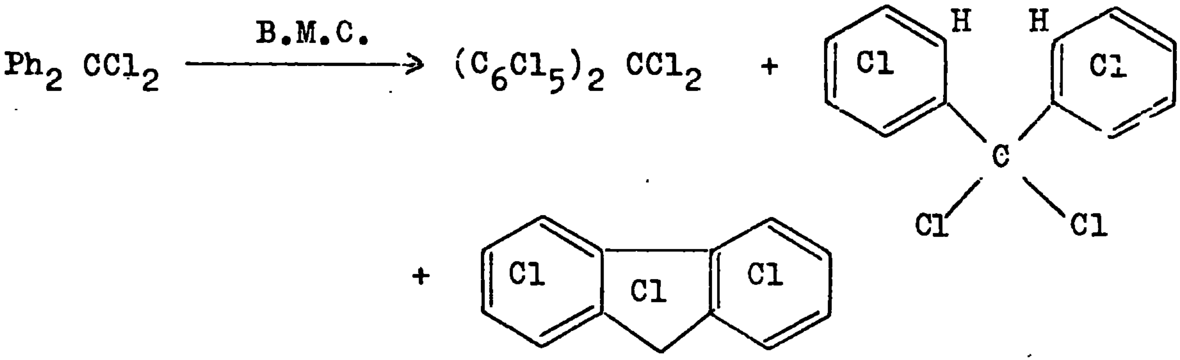
Thianthrene is often also found under the title of dibenzo-1,4-dithiin (c.f. dibenzo-1,4-dioxin).

1.2 Earlier Work on the Perchlorination of the Systems Being Studied

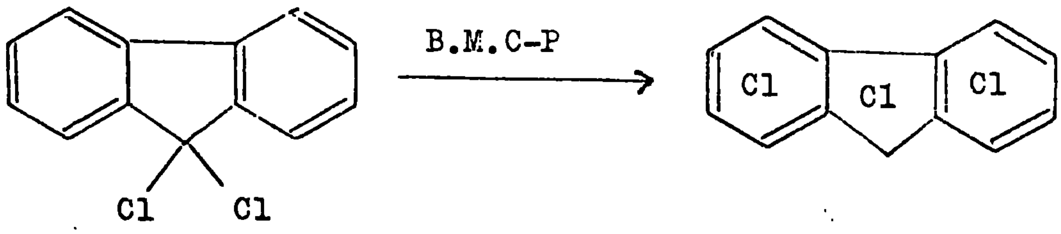
1.2.1 Naphthalene, Biphenyl, Fluorene, and Fluoren-9-one

The preparations of octachloronaphthalene and of decachlorobiphenyl have been dealt with earlier in the introduction (see Chapter I, Sections 2.2.1 and 2.2.6 respectively).

Ballester and co-workers have described the syntheses of decachlorofluorene and octachlorofluoren-9-one,[46] the former being observed as a by-product (approx. 7% yield) when dichlorodiphenylmethane was chlorinated with reagent B.M.C. (The development of reagent B.M.C. and its use in the laboratories at Durham will be dealt with in Sections 2.1 to 2.3 of this Chapter).



More recently,[18] they have reported the reaction of 9,9-dichlorofluorene with reagent B.M.C.-P to give an overall 72% yield of decachlorofluorene.

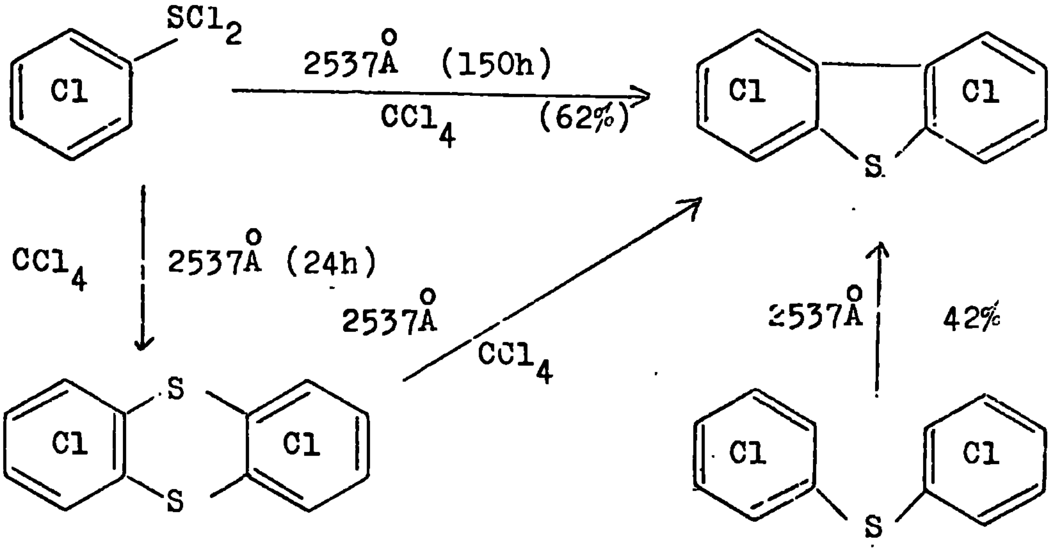


Perchlorofluorene may also be obtained by the reaction of octachlorofluoren-9-one with phosphorus pentachloride.[25] The reverse reaction may be achieved by reaction of decachlorofluorene with oleum,[46] or by photooxidation in carbon tetrachloride solution in the air,[18] giving octachlorofluoren-9-one.

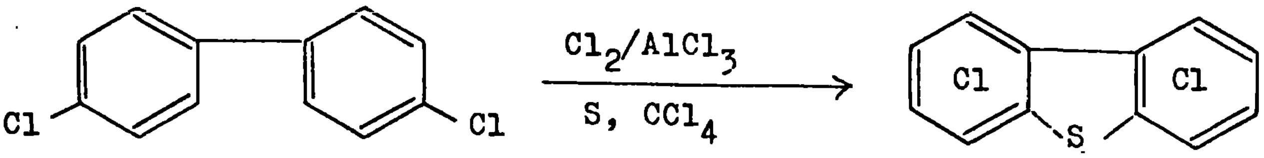
1.2.2 Dibenzothiophen, Dibenzofuran and Thianthrene

Photolysis of perchlorothiophenol has been shown to produce octachlorodibenzo(b,d)thiophen and octachlorothianthrene.[86] Octachlorodibenzo(b,d)thiophen is also obtained in 42% yield when bispentachlorophenyl sulphide is photolysed. Scheme V illustrates these reactions.

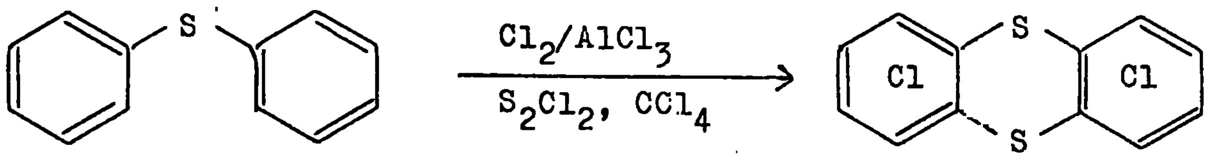
Scheme V



Klug[85,87] has also reported the preparation of these two compounds and some related derivatives. e.g. The chlorination of 4,4'-dichlorobiphenyl with gaseous chlorine in the presence of sulphur and aluminium chloride gives octachlorodibenzo(b,d)thiophen, along with tars. Similarly,

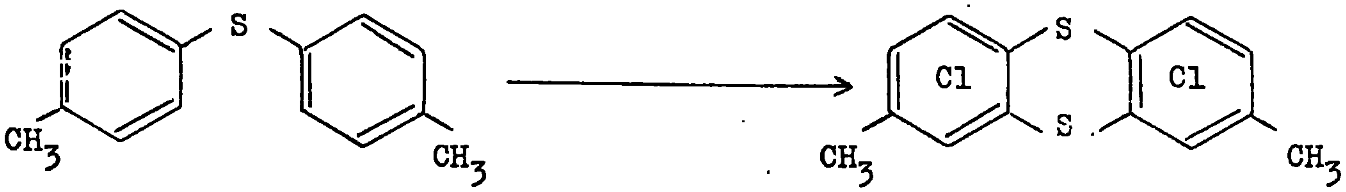


diphenyl sulphide may be used to obtain octachlorothianthrene.



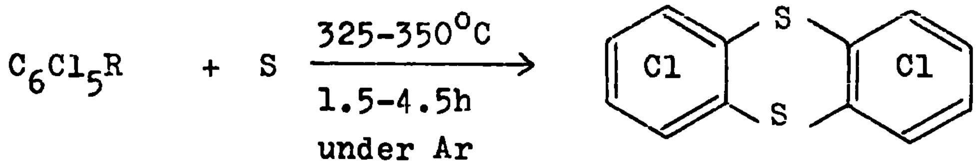
Methyl substituted polychloro compounds may be obtained by reaction of a suitable precursor, the methyl group remaining unchanged during the chlorination and cyclisation.

e.g.



Beck and Holtschmidt[112] describe a cyclisation reaction which leads to octachlorothianthrene, or substituted derivatives thereof.

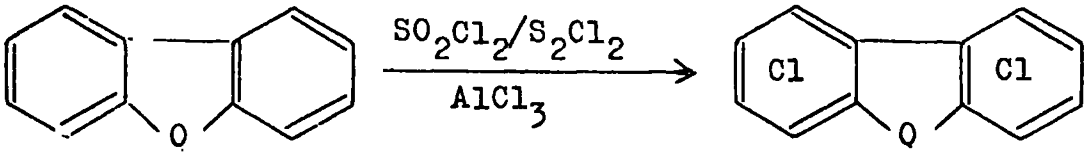
e.g.



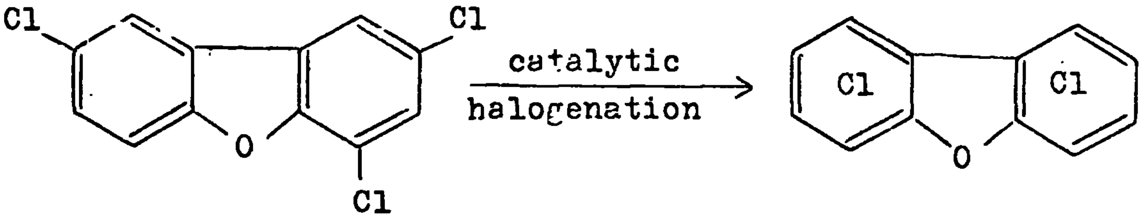
(R = Cl,CN,NCO)

Some oligomeric species were also observed as by-products of this reaction.

Octachlorodibenzo(b,d)furan is obtained from the chlorination of the parent heterocycle with a mixture of reagents similar to the "B.M.C. reagent".[64]



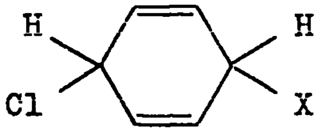
Dazzi and co-workers[113] achieved this synthesis by catalytic halogenation of 2,4,8-trichlorodibenzofuran.



2. The Use of $SO_2Cl_2/S_2Cl_2/AlCl_3$ as a Chlorinating Agent

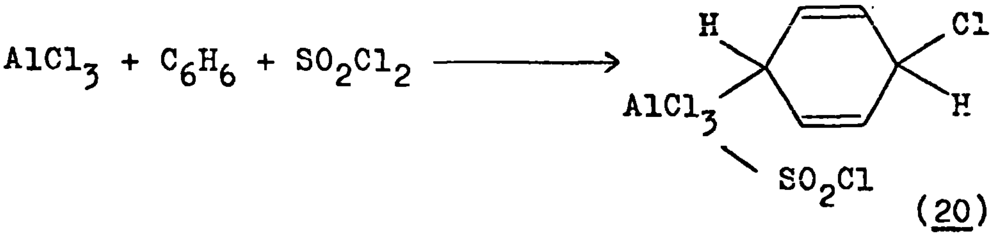
2.1 Silberrad's Reagent

In 1921, Silberrad[114] investigated the chlorination of benzene with sulphuryl chloride and various catalysts. (N.B. when benzene is refluxed in sulphuryl chloride alone, no chlorination is observed). During these experiments, he observed the formation of some highly coloured intermediate species of the type (19).



(19)

The following route was postulated[114] to account for the reaction when aluminium chloride is the catalyst.

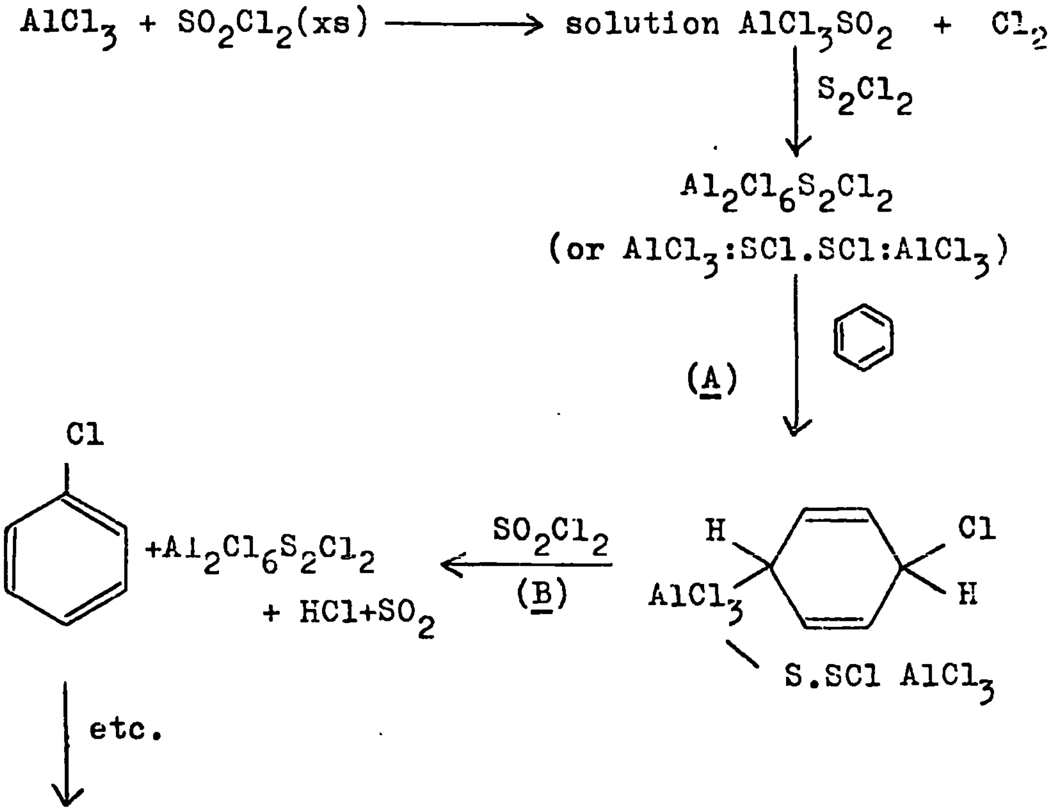


(20)

(20) $\longrightarrow$ $AlCl_3{:}SO_2$ + C_6H_5Cl + HCl + some p-dichlorobenzene.

Addition of thionyl chloride to the chlorinating agent ($SO_2Cl_2/AlCl_3$) reduced the temperature required to bring about chlorination, and the presence of sulphur or sulphur monochloride brought about chlorination in the cold. Hence, a mixture of $SO_2Cl_2/S_2Cl_2/AlCl_3$ was used as the chlorinating agent and depending upon the amount of sulphuryl chloride added, di-, tetra-, or hexa-chlorobenzene could be obtained.[4] A complete reaction mechanism was postulated and is shown in Scheme VI.

Scheme VI



Reactions (A) and (B) appeared to proceed continuously until either the sulphuryl chloride was expended, or the hydrocarbon was fully chlorinated.

More recently, Doorenbos and co-workers[22,115] have postulated that the reactive species is $SCl_3^+AlCl_4^-$ formed via the following reaction sequence:-

(a) $S_2Cl_2 + SO_2Cl_2 \longrightarrow 2SCl_2 + SO_2$

(b) $SCl_2 + SO_2Cl_2 \longrightarrow SCl_4 + SO_2$

(c) $SCl_4 + AlCl_3 \longrightarrow AlSCl_7$ or $(SCl_3^+ AlCl_4^-)$.

2.2 The Development of Reagent B.M.C.

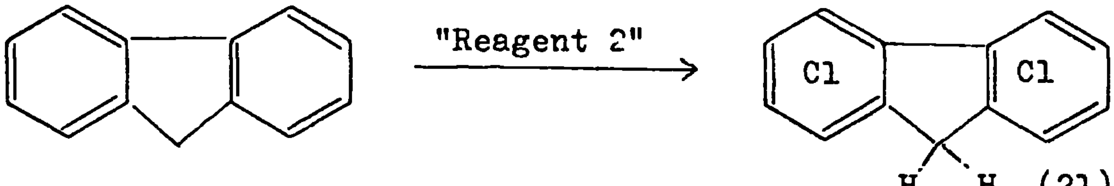
In 1960, Ballester, Molinet, and Castaner[10] reported the chlorination of highly strained aromatic chlorocarbons (e.g. perchloro-p-xylene) using an extremely powerful, yet selective, nuclear chlorinating agent. Its composition was similar to that described by Silberrad[4,114] (i.e. a mixture of $SO_2Cl_2/S_2Cl_2/AlCl_3$), the only difference being a variation in the relative proportions of reagents. This reagent became known as reagent B.M.C., after the authors, and many perchlorinated aromatic and alkaromatic carbocycles have been described since its development.

More recently, Ballester[18] has reported the use of reagents B.M.C.-P and B.M.C.-S. However, these reagents still comprise the same constituents, but the relative concentrations are again altered.

2.3 The Development of Chlorinating Agents Comprising $SO_2Cl_2/S_2Cl_2/AlCl_3$ in the Laboratories at Durham

Initially, the reagent as described by Ballester and co-workers[10] was used in an attempt to perchlorinate fluorene. The attempt was unsuccessful, and the reagent also had the disadvantage of utilising a large volume of sulphuryl chloride to chlorinate a relatively small amount of substrate ($100cm^3$ SO_2Cl_2 per 1g substrate). A new reagent was employed (Reagent 1 - See experimental) which used only one third the volume of sulphuryl chloride (approx. $35cm^3$ SO_2Cl_2 per 1g substrate). This reagent resulted in the formation of the same product as that obtained using B.M.C. reagent, when fluorene was the substrate. However the reagent proved to be as effective a nuclear chlorinating agent as reagent B.M.C. when biphenyl, naphthalene, and toluene were used as substrates.

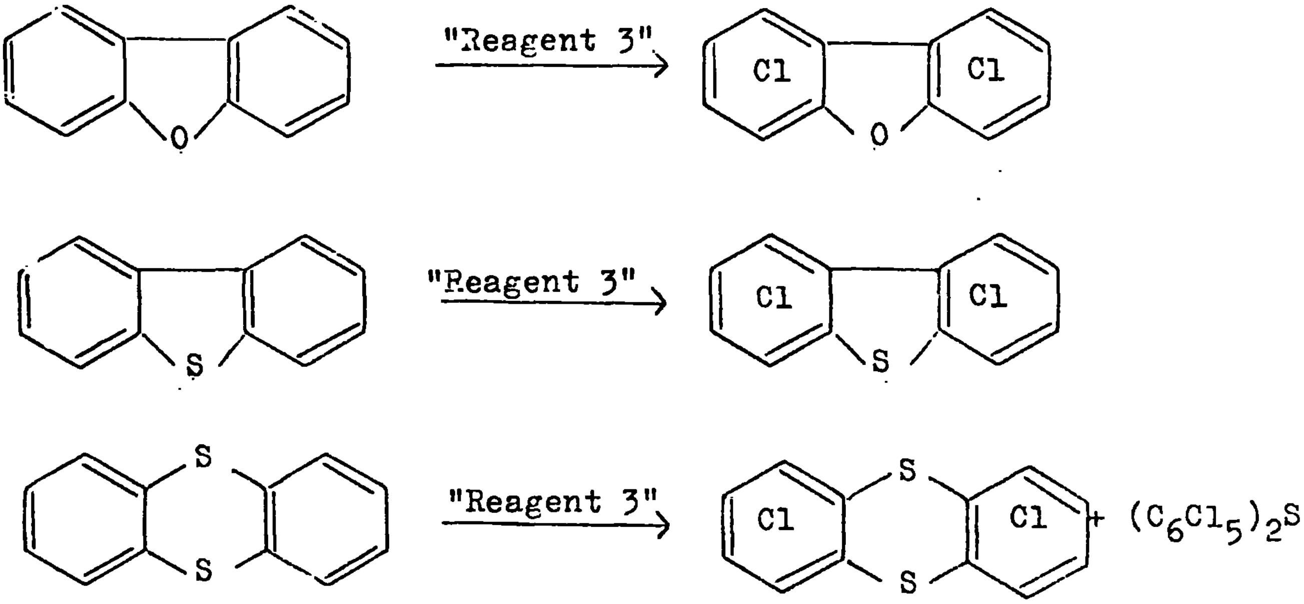
A second new combination of these reagents was investigated (Reagent 2 - See experimental) and was successful in achieving nuclear chlorination of fluorene, giving 1,2,3,4,5,6,7,8-octachlorofluorene (21) quantitatively.



(21)

This reagent again used less sulphuryl chloride per weight of substrate ($10cm^3$ SO_2Cl_2 per 1g substrate) and the reaction conditions were also slightly altered: a concentration step was not necessary as with reagents 1 and B.M.C.; and the reflux stage was omitted. This had the effect of leaving the fluorene skeleton intact and also achieving nuclear chlorination. N.B. Fluorene was the only substrate chlorinated utilising reagent 2.

Finally, reagent 3 (see experimental) was developed, which, as well as using a relatively small amount of sulphuryl chloride (25cm^3 SO_2Cl_2 per 1g substrate), had a proportionately larger quantity of aluminium chloride present. i.e. an increase from 0.25g $AlCl_3$ to 1g $AlCl_3$ per 1g of substrate. This change was introduced to cater for the chlorination of compounds containing a hetero atom, which would normally complex to some degree with the aluminium chloride, thus rendering it ineffective as a catalyst. Using reagent 3, octachlorodibenzo(b,d)furan, octachlorodibenzo(b,d)thiophen and octachlorothianthrene could all be prepared directly from their parent heterocycles.

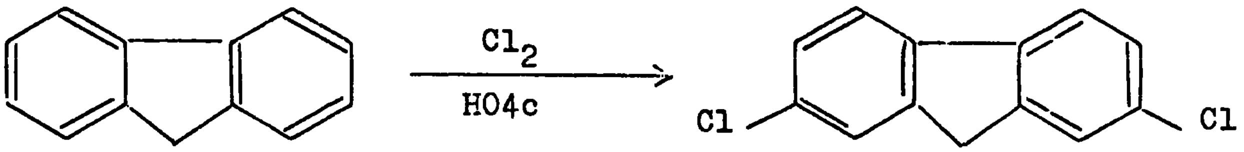


3. Chlorination Reactions

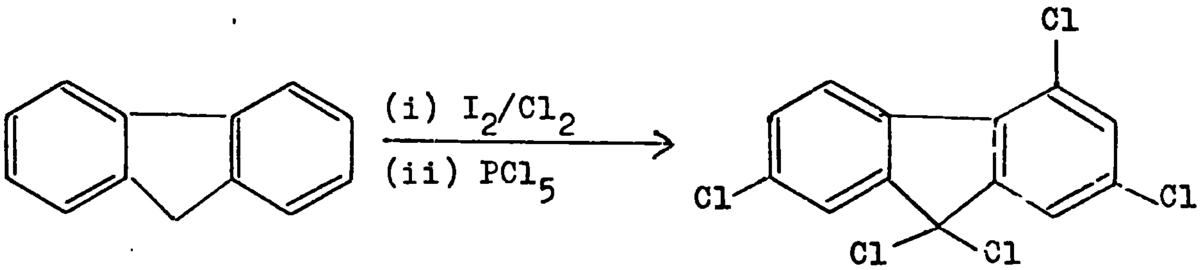
3.1 Fluorene

3.1.1 Catalytic Chlorination

Catalytic chlorination of fluorene produced only partially chlorinated species, similar to those observed by other workers. e.g. Boaver[116] obtained 2,7-dichlorofluorene by direct chlorination of fluorene in acetic acid solution.



A reaction in the presence of iodine as catalyst has been observed to give 2,4,7-trichlorofluorene,[117] further reaction of which, with PCl_5 at 200°C[118] gave 2,4,7,9,9-pentachlorofluorene.



The introduction of chlorine into the system deactivates it towards electrophilic substitution, and the two most active sites, viz.2- and 7- are first replaced; addition of a catalyst enables the 4-position to be substituted, but further substitution appears to be difficult. The allylic methylene group may be readily chlorinated using PCl_5, and replacements of this type are fairly common. A much more powerful chlorinating agent is thus required to achieve perchlorination.

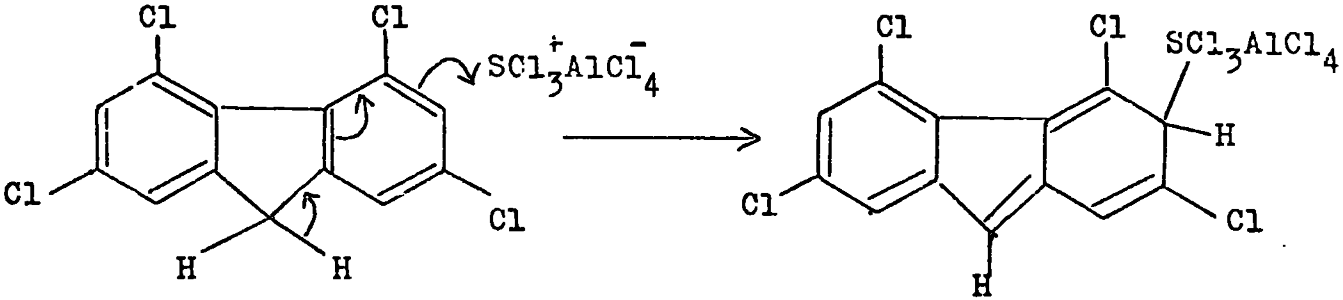
3.1.2 Chlorination with Reagent B.M.C.

Reagent B.M.C. has been used extensively[10,21,23] to chlorinate nuclear positions in aromatic and alkaromatic hydrocarbons. When fluorene was reacted with reagent B.M.C., skeletal breakdown was observed to occur, giving what is believed to be a substituted biphenyl as the product. Mass spectrometry (showed P = 541 with eleven chlorine atoms present, $C_{13}H\ Cl_{11}$ requires $M^+(^{35}Cl)$ 542. i.e. the peak observed is the parent minus the proton), analysis (gave a molecular formula of

$C_{13}HCl_{11}$), infra red (showed -C-H stretching vibrations) and consideration of the reaction process led to the conclusion that this compound was 2-dichloromethyl-2',3,3',4,4',5,5',6,6'-nonachlorobiphenyl. This product may be formed by partial chlorination of the bridgehead methylene group, coupled with chlorination occurring at the ring junction.

The following illustrates a possible reaction mechanism which would account for the observed product. Electrophilic substitution of chlorine into fluorene has been shown to occur most readily in the 2-, 4-, and 7- positions, the 5-position presumably being the next to be replaced.

Assuming 2,4,5,7-tetrachlorofluorene to be formed during the chlorination, the following seouence of reactions are possible.

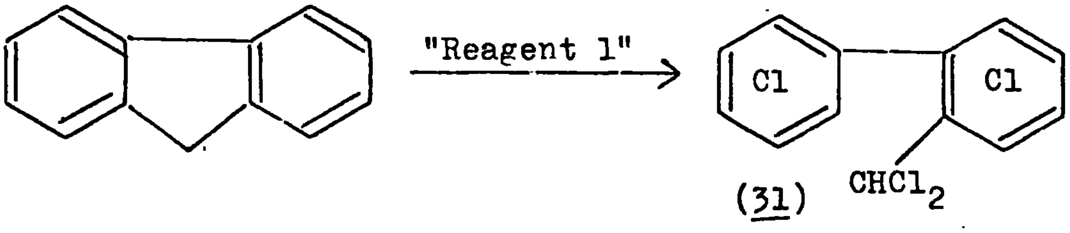


(21)

The 9-position in (21) is now conjugated to the aromatic ring and is susceptible to attack from the chlorinating agent (c.f. chlorination of β,β-dichlorostyrene with reagent B.M.C.)[10,17,18] This process, coupled with attack at the ring junction at some stage would account for the observed product.

3.1.3 Chlorination with $AlCl_3/SO_2Cl_2/S_2Cl_2$

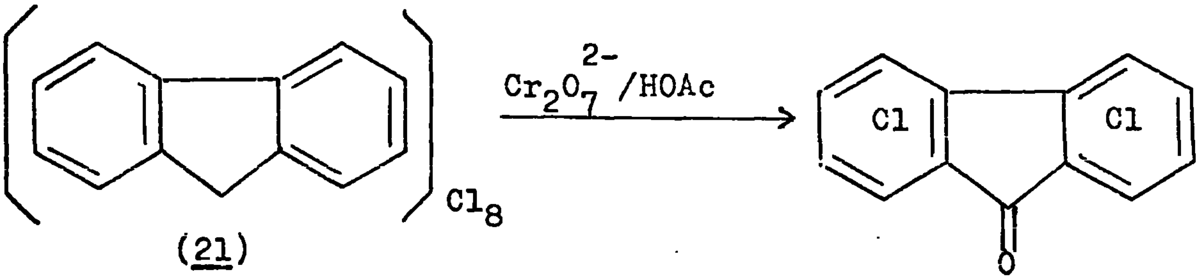
The chlorination of fluorene with "Reagent 1" again resulted in the formation of (31).



3.1.4 Preparation of Perchlorofluorene

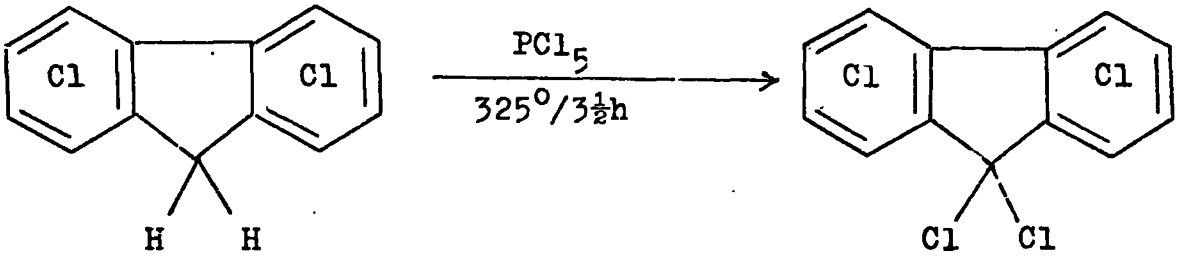
Chlorination of fluorene with "Reagent 2" resulted in the sole formation of 1,2,3,4,5,6,7,8-octachlorofluorene, (21) presumably the relatively milder reaction conditions (i.e. removal of reflux and concentration stages of the reaction) accounting for the carbon skeleton remaining intact, and the occurrence of nuclear chlorination alone.

The positions of chlorine substitution were confirmed by oxidising the product with sodium dichromate in acetic acid, giving some octachlorofluoren-9-one. Unfortunately this did not



prove to be a viable preparative route to octachlorofluoren-9-one, as only partial oxidation occurred and the product had to be separated from starting material by lengthy fractional crystallisations.

Perchlorofluorene was obtained by reaction of (<u>21</u>) with PCl_5, using a procedure similar to that described in the literature.[118]

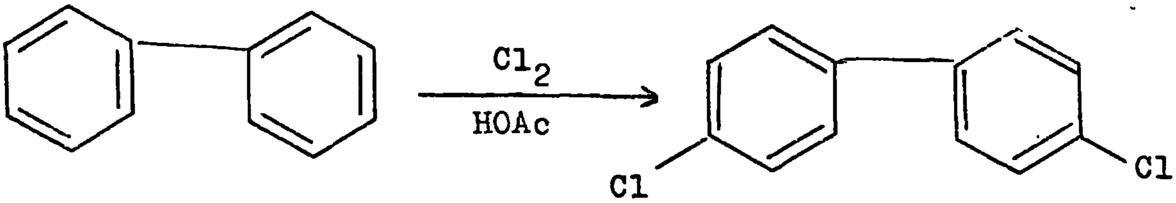


When too forcing conditions were used, (e.g. long reaction time, higher temperature) chlorinolysis occurred, giving low yields of decachlorobiphenyl.

3.2 Biphenyl

3.2.1 Preparation of 4,4'-dichlorobiphenyl

This was prepared by direct electrophilic chlorination of biphenyl, as described in the literature.[119]



An attempt to perchlorinate and cyclise with sulphur to give octachlorodibenzo(b,d)thiophen as described by Klug,[85] was unsuccessful and resulted in extensive tar formation.

3.2.2 Preparation of Decachlorobiphenyl

An almost quantitative yield of decachlorobiphenyl was obtained by reaction of the parent hydrocarbon with $AlCl_3/SO_2Cl_2/S_2Cl_2$ (Reagent 1). Ballester also describes this chlorination using reagent B.M.C.[18]

3.3 Dibenzo(b,d)thiophen

3.3.1 Preparation of Octachlorodibenzo(b,d)thiophen

Direct chlorination of the parent heterocycle with $AlCl_3/SO_2Cl_2/S_2Cl_2$ (Reagent 3) resulted in the formation of octachlorodibenzo(b,d)thiophen. (96%; M.p. (xylene) = 304.5°C)

3.4 Dibenzo(b,d)furan

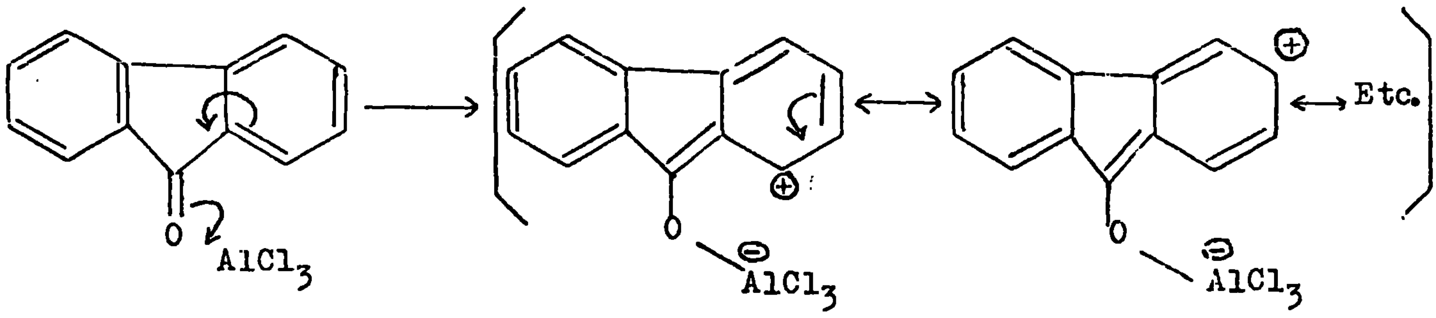
3.4.1 Preparation of Octachlorodibenzo(b,d)furan

Direct chlorination of the parent heterocyle with reagent 3 resulted in the formation of octachlorodibenzo(b,d) furan in 95% yield. (M.p. (chloroform) = 260°C)

3.5 Fluoren-9-one

3.5.1 Chlorination Using a Mixture of $SO_2Cl_2/AlCl_3/S_2Cl_2$

Chlorination of fluoren-9-one with reagent 1 gave a mixture of dichloro- and trichloro- fluoren-9-one, identified from their mass spectra. (i.e. P = 248 with Cl x 2, and P = 282 with Cl x 3. $C_{13}H_6Cl_2O$ requires $^m/e$ = 248, $C_{13}H_5Cl_3O$ requires $^m/e$ = 282). Complexation of aluminium chloride with the carbonyl group may be responsible for the low degree of chlorination observed, which probably occurs primarily in the 2,4 and 7-positions. i.e. the products are probably 2,7-dichloro- and 2,4,7-trichloro-fluoren-9-one.



The 1,3,6,8-positions will be unreactive towards electrophilic attack and this coupled with a low concentration of the chlorinating species would account for the observed results.

The use of reagent 3 yielded a mixture of tetra-, penta-, and hexa- chlorofluoren-9-one (mass spectrometry) but the perchlorocompound was not observed. The presence of larger quantities of aluminium chloride in the chlorinating mixture will have fascilitated the greater degree of chlorination observed. It is possible that addition of even more aluminium chloride, or the use of more forcing conditions (longer reflux time, more concentrated reagent etc.) will eventually yield octachlorofluoren-9-one. However, it was felt at the time that an alternative approach was required.

3.5.2 Acid Hydrolysis of Decachlorofluorene

Attempted hydrolysis by refluxing decachlorofluorene with 50%(^{V}/v) hydrochloric acid resulted in the recovery of starting materials only, whereas reaction with fuming sulphuric acid similar to that described by Ballester,[46] resulted in tarring. Refluxing decachlorofluorene in 80%(^{V}/v) phosphoric acid resulted in some hydrolysis occurring, giving a mixture of octachlorofluoren-9-one and starting material which was separated by fractional crystallisation. The ultimate yield of ketone was low and thus rendered the method impracticable from a preparative point of view.

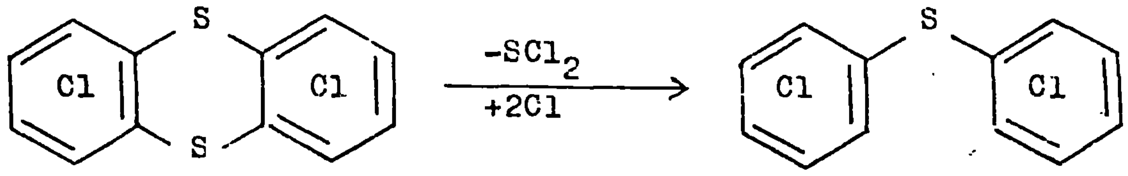
3.5.3 Oxidation of 1,2,3.4,5.6,7,8-Octachlorofluorene

The oxidation of fluorene to fluoren-9-one using sodium dichromate in acetic acid[120] has been described. Application of this oxidation procedure to (31) met with limited success. A low yield of the keto-compound was obtained, along with starting material. Solubility of these high molecular weight polychlorocompounds would seem to be a contributing factor to this low yield, insufficient material being in solution to undergo oxidation. If a single phase system can be achieved, i.e. a system in which sodium dichromate, acetic acid, octachlorofluoren-9-one, and (31) are all readily soluble, the reaction may go smoothly to completion giving octachlorofluoren-9-one in high yield upon removal of solvent. Crown polyether systems (See chapter IV) may be a possible approach to this problem.

3.6 Thianthrene

3.6.1 Preparation of Octachlorothianthrene

Octachlorothianthrene was obtained along with some bispentachlorophenyl sulphide, which could be separated by fractional crystallisation from xylene, when thianthrene was chlorinated with $AlCl_3/SO_2Cl_2/S_2Cl_2$ (reagent 3). The bispentachlorophenyl sulphide probably results from loss of sulphur chloride, from the thianthrene, followed by nuclear chlorination.



3.7 Phenothiazine

3.7.1 Attempted Chlorination Using a Mixture of SO_2Cl_2/S_2Cl_2/$AlCl_3$

Addition of sulphuryl chloride to phenothiazine resulted in violent reaction, coupled with the rapid evolution of gas and the formation of a black sludge. Other methods of chlorinating this substrate were not investigated.

3.8 Naphthalene

3.8.1 Preparation of Octachloronaphthalene

Octachloronaphthalene was obtained (95% yield) when naphthalene was chlorinated with reagent 1. Ballester has performed this chlorination with reagent B.M.C. and has obtained a perchlorodihydronaphthalene which was then dechlorinated to give octachloronaphthalene.[23,25] The only difference between the two methods is the quantity of sulphuryl chloride used, and it is not understood how this fact alone effects the outcome of the product to such an extent.

3.9 Toluene

3.9.1 Nuclear Chlorination, Using a Mixture of SO_2Cl_2/$AlCl_3$/S_2Cl_2

Chlorination of toluene with $SO_2Cl_2/S_2Cl_2/AlCl_3$ (Reagent 1) gave a quantitative yield of 1-methyl-2,3,4,5,6-pentachlorobenzene. (i.e. nuclear chlorination). Although the last chlorination to be described, this experiment was performed parallel with the chlorinations of fluorene. Its significance was to illustrate the nuclear chlorinating ability of the reagent, without the destruction or chlorination of the alkyl group. Unfortunately, this was not the case with fluorene.

3.9.2 Reaction of 1-methyl-2,3,4,5,6-pentachlorobenzene with PCl_5

Again, this reaction was performed as a parallel to fluorene, demonstrating the occurrence of chlorinolysis to yield hexachlorobenzene. (N.B. it should be remembered that decachlorobiphenyl was obtained in some reactions of octachlorofluorene with PCl_5 before conditions were optimised.)

CHAPTER III

Properties of Some Polyhalogeno Aromatic Compounds

1. General Introduction

1.1 The Aim and Scope of the Work Described in this Chapter

The initial aim of this work was to synthesise a series of perchloroaromatic systems as possible precursors to the corresponding perfluoro analogues by halogen exchange. Reactions of these perfluoro compounds could then be followed by techniques such as mass spectrometry, G.L.C., N.M.R., etc.

Unfortunately, so far, we have been unable to convert the polychlorocompounds into their perfluoro analogues and since there is no convenient tool to determine the structures of derivatives of polychloro compounds, very little investigative work has been undertaken. This chapter includes the reactions which were attempted, along with some nucleophilic substitution reactions involving fluorinated biphenyls, which were carried out as a possible approach to fluorinated dibenzofurans.

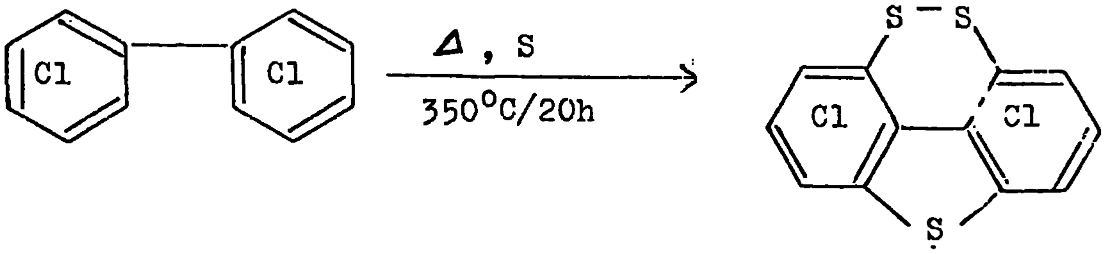
2. Cyclisation Reactions

2.1 Formation of 1,9-Epidithio-2,3,4,6,7,8-hexachlorodibenzo(b,d)thiophen

2.1.1 Reaction of Decachlorobiphenyl with Sulphur

Decachlorobiphenyl can be prepared conveniently in the laboratory, and an alturnative route to octachlorodibenzo(b,d)-thiophen could be cyclisation of decachlorobiphenyl with sulphur. Both sulphur and thiourea have been used as nucleophiles with haloaromatics, forming a polycyclic compound[111] and a disulphide[121] respectively.

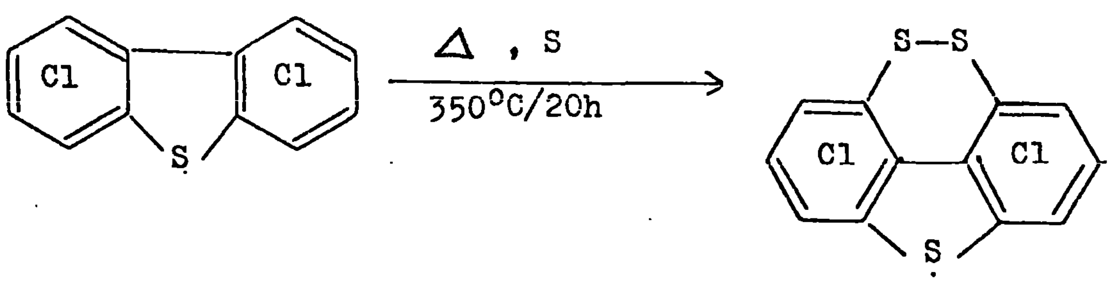
When biphenyl and sulphur were refluxed in xylene, or heated in an autoclave at temperatures less than 350°C, no reaction was observed. However, when they were heated together at 350°C for 20 hours in a stainless steel autoclave, a bright yellow compound identified as 1,9-epidithio-2,3,4,6,7,8-hexachlorodibenzo(b,d)thiophen (22) was separated in 35% yield, 65% conversion; (22) was readily recrystallised from xylene, and melted with decomposition at 331°C.



(22)

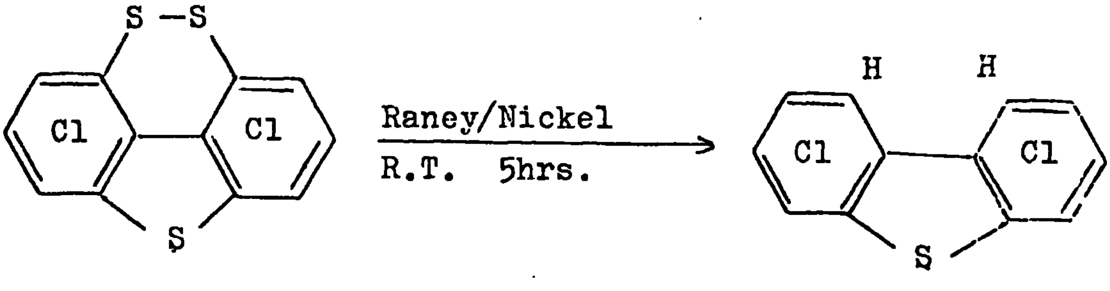
2.1.2 Reaction of Octachlorodibenzo(b,d)thiophen with Sulphur

When octachlorodibenzo(b,d)thiophen and sulphur were heated together at 350°C for 20 hours in a stainless steel autoclave, (22) was again obtained.



2.1.3 Reaction of (22) with Raney Nickel Catalyst

As a means of confirming the structure of (22) an attempt to desulphurise and reduce it to 3,3',4,4',5,5'-hexachlorobiphenyl was made. Only partial reduction occurred however, giving 2,3,4,6,7,8-hexachlorodibenzo(b,d)thiophen (23), identified from its mass spectrum (M$^+$(^{35}Cl) 388, $C_{12}H_2Cl_6S$



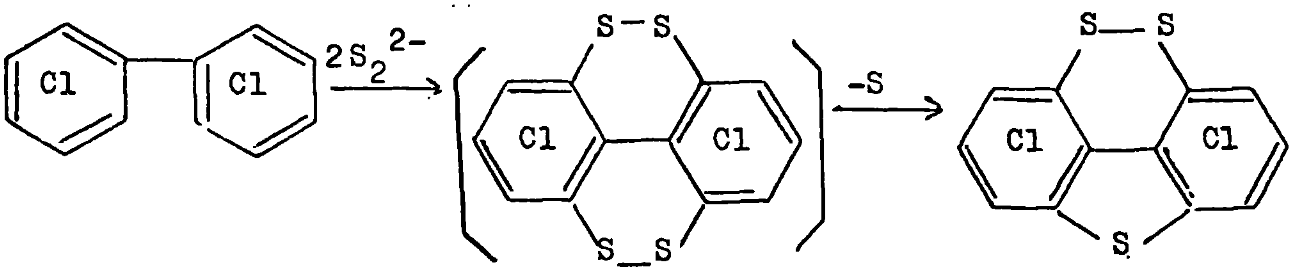
(22) (23)

requires $^m/e = 388$), analysis, and its P.M.R. spectrum, which showed a singlet at $\delta = 9.1$ p.p.m. relative to T.M.S.

2.1.4 General Conclusions and Comments

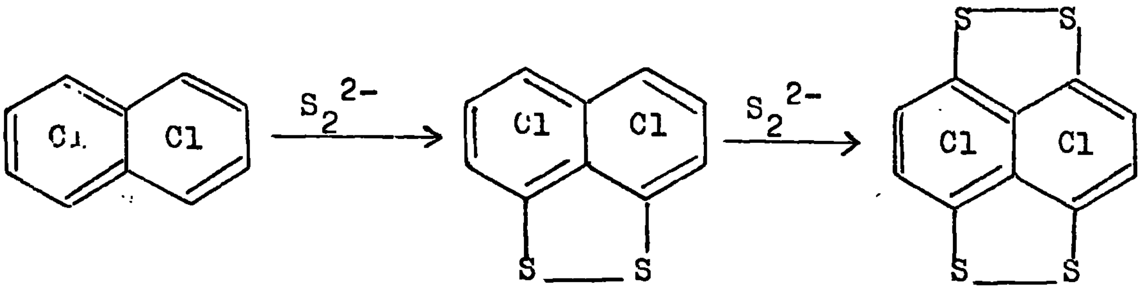
Two possible reaction pathways to (22) are possible, viz:

(i) simultaneous bidentate attack of S_2^{2-} at the 2,2'- and 6,6'-positions of decachlorobiphenyl, giving (24), followed by elimination of sulphur, forming (23). The initial stage would be similar to results observed by Klingsberg,[111] when octachloronaphthalene was reacted with sulphur giving (7) and (8).



(24)

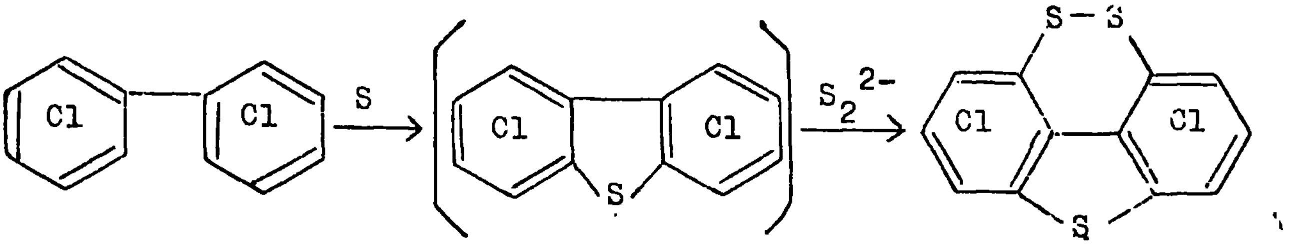
compare with:



(7) (8)

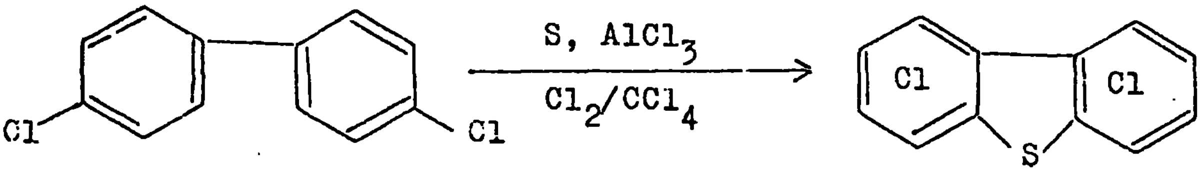
If this reaction pathway is followed, thermal elimination of sulphur from (24) at the reaction temperature may be responsible for the formation of (22).

(ii) Octachlorodibenzo(b,d)thiophen may be formed initially, which then undergoes bidentate attack by S_2^{2-} giving (22) i.e.



This second pathway is similar in its initial stage to a one reported by Klug,[85] for the formation of octachlorodibenzo(b,d)-thiophen from 4,4'-dichlorobiphenyl.

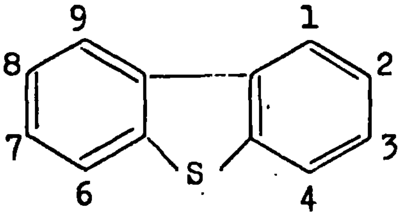
i.e.



As octachlorodibenzo(b,d)thiophen may be converted to (22), the second reaction pathway would seem to be more likely. However, no attempt was made to isolate the intermediate from the reaction.

The Raney-nickel reduction, along with the reaction of octachlorodibenzo(b,d)thiophen with sulphur confirm the structure of (22). The cyclisation reaction "places" one sulphur atom, and as only one P.M.R. signal was obtained from the product of reduction of (22), the remaining two sulphur atoms must be bonded, as a S_2 bridge, to two equivalent positions in the dibenzo(b,d)-

thiophen system i.e. 1,9; 2,8; 3,7; or 4,6.



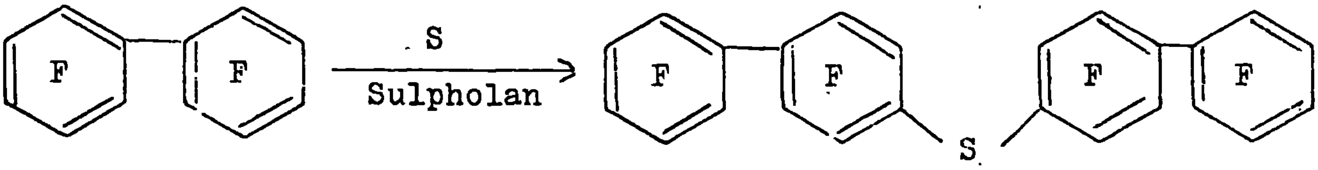
Steric considerations eliminate the last three alturnatives, which confirms the structure of $C_{12}Cl_6S_3$ as that shown in (22).

3. Nucleophilic Substitution Reactions

3.1 Perfluorobiphenyl

3.1.1 Reaction with Sulphur

Reaction of decafluorobiphenyl with sulphur in sulpholan resulted in the formation of a small quantity of perfluoro-(bis-(p-phenyl phenylene)) sulphide (26). This maroon solid



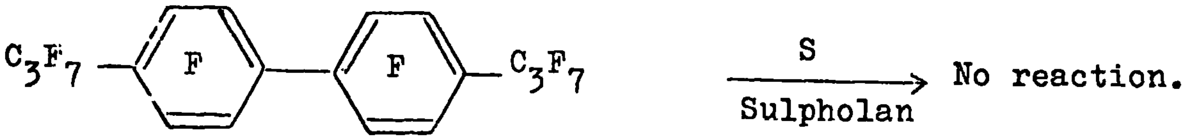
(26)

(M.p. 117°C) was identified from its mass spectrum, p = 662, ($C_{24}F_{18}S$ requires $^m/e$ = 662), and by comparison of its ^{19}F n.m.r. spectrum with that of decafluorobiphenyl.

3.2 Perfluoro-(4,4'-bisisopropylbiphenyl)

3.2.1 Reaction with Sulphur

The 4-position of decafluorobiphenyl is the most reactive towards nucleophilic substitution and a sulphide (26) is formed. If 2-substitution were induced, the possibility of cyclisation occurring to give octafluorodibenzo(b,d)thiophen becomes a feasible reaction. A sample of perfluoro-(4,4'-bis isopropyl biphenyl) (27) was supplied by Dr. A.C. Young, and the reaction repeated. Only starting materials were recovered.

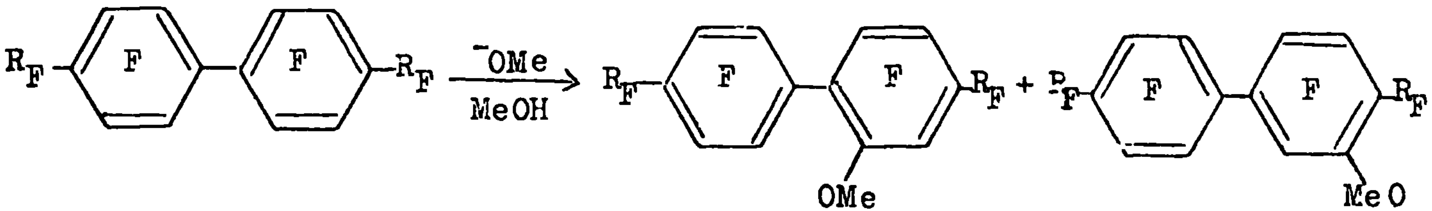


(27)

3.2.2 Reaction with Sodium Methoxide in Methanol

In an attempt to determine the preferred orientation of nucleophilic substitution in (27), the substrate was reacted with a solution of sodium methoxide in methanol. A white crystalline solid identified as monomethoxy-perfluoro-(4,4'-bisisopropylbiphenyl) was isolated in 80% yield. Identification was by mass spectrometry and analysis. N.M.R. showed the product to be a mixture of two isomers, with the methoxide substitution occurring both in the 2- and 3-positions.

A ^{19}F n.m.r spectrum showed complex resonances in the tertiary-F, the CF_3-F and the aromatic-F regions but were of little diagnostic use. A proton n.m.r. spectrum showed two distinct $-OCH_3$ resonances, one a singlet, the other a doublet, showing the presence of two methoxy derivatives (28) and (29). The doublet had J = 3Hz and corresponded to coupling to the tertiary fluorine of the adjacent perfluoro-isopropyl group.

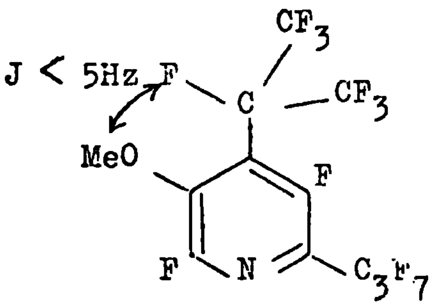


$R_F = C_3F_7$

(28)

(29)

This figure of 3Hz is similar to one previously observed for the compound (30)[122] The ratio of products (28) to (29) was approximately 1 to 3, measured from integration of the P.M.R. signals. i.e. The preferred orientation of nucleophilic substitution of methoxide into (27) is the 3-position, which shows the perfluoroisopropyl group to have a stronger directive influence to nucleophilic aromatic substituion then does the perfluoro aryl group. If 2-substitution were predominant, cyclisation to perfluorodibenzo(b,d)furan derivatives becomes feasible. Low yields of cyclised material may be obtained from the mixture of monomethoxy derivatives, but was not pursued at this stage.



(30)

4. Fluorination Reactions

4.1 Introduction

The introduction of fluorine into aromatic nuclei by halogen exchange with chlorine has been successfully employed to prepare a series of mono- and bi-cyclic nitrogen containing heterocycles, e.g. pentafluoropyridine, tetrafluoropyridazine, heptafluoroquinoline etc.

The usual procedure is to heat the substrate and an alkali metal fluoride together, either in an autoclave, or in an aprotic solvent such as sulpholan. An attempt to apply these techniques to tricyclic N-containing heterocycles has been recorded, but met with limited success.[2] The following includes the attempts to extend this method to members of the dibenzo-series, and related compounds.

4.2 Reactions with Potassium Fluoride in an Autoclave

4.2.1 Decachlorobiphenyl

Decachlorobiphenyl was heated with potassium fluoride in an autoclave over a range of temperatures. It was hoped that a simple halogen exchange reaction would occur, giving a fluorinated analogue of biphenyl. However no success was had at all using this technique.

An attempt to vacuum transfer volatile material from the hot autoclave resulted in the trapping of low molecular weight gases, and it was necessary to open the autoclave to try to extract tractable material. A black powdery residue remained. Refluxing the residue with different solvents did not extract any material and sublimation under vacuum gave a trace of a yellow solid, which was inadequate for further investigation.

Digestion of the residue with water yielded a black polymeric solid.

4.2.2 Decachlorofluorene

Decachlorofluorene again yielded a black intractable solid as the ultimate product, when it was heated with potassium fluoride.

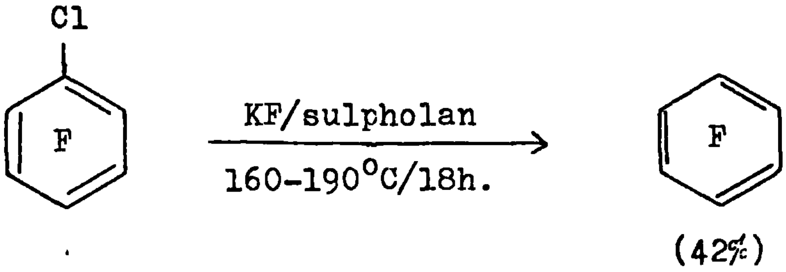
In an attempt to replace the two chlorine atoms in the 9-position with fluorine, decachlorofluorene was heated with antimony trifluoride. Again a black intractable solid was obtained.

4.2.3 Octachlorodibenzo(b,d)thiophen

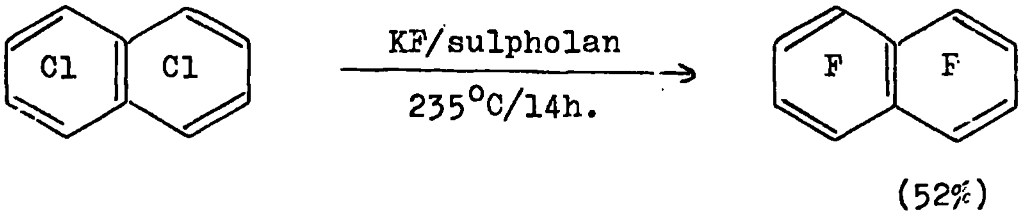
Octachlorodibenzo(b,d)thiophen was heated with potassium fluoride in an autoclave at various temperatures. At 300°C, starting materials were recovered and at 450°C a black intractable solid was obtained. An intermediate temperature reaction, at 330°C produced a mixture of partially fluorinated materials, in which up to four chlorine atoms had been replaced by fluorine. However, the small quantity of material isolated and the number of components present rendered it impracticable for preparative purposes. This reaction was the most promising of these series, but a fine balance seems to exist between degradation and fluorination. It may be possible to achieve perfluorination at some temperature between 330°C and 450°C, but after a series of attempts, it was concluded that this temperature is impracticably critical.

4.3 Reactions with Potassium Fluoride in a Solvent

Halogen exchange of chlorine for fluorine has also been achieved in solvents, e.g. reaction of chloropentafluorobenzene with potassium fluoride in sulpholan yields hexafluorobenzene in 42% yield.[123] With octachloronaphthalene as the substrate,



52% yield of the perfluoro compound is obtained.[123]



4.3.1 Decachlorobiphenyl

Reaction of decachlorobiphenyl with potassium fluoride in sulpholan yielded a small quantity of a complex mixture which contained some partially fluorinated biphenyls. The mass spectrum of the mixture corresponded to octachlorodifluorobiphenyl and nonachlorofluorobiphenyl. The low yield and complex nature of the product rendered the method impracticable.

4.3.2 Decachlorofluorene

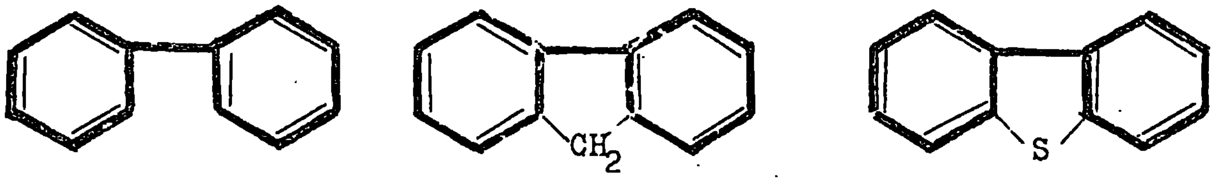
Again, a small quantity of partially fluorinated material was obtained, but did not warrent further investigation.

4.3.3 Octachlorodibenzo(b,d)thiophen

Only a mixture of partially fluorinated material was obtained. The degree of fluorination and the quantity of product isolated depended upon the reaction conditions used, but neither warrented further work.

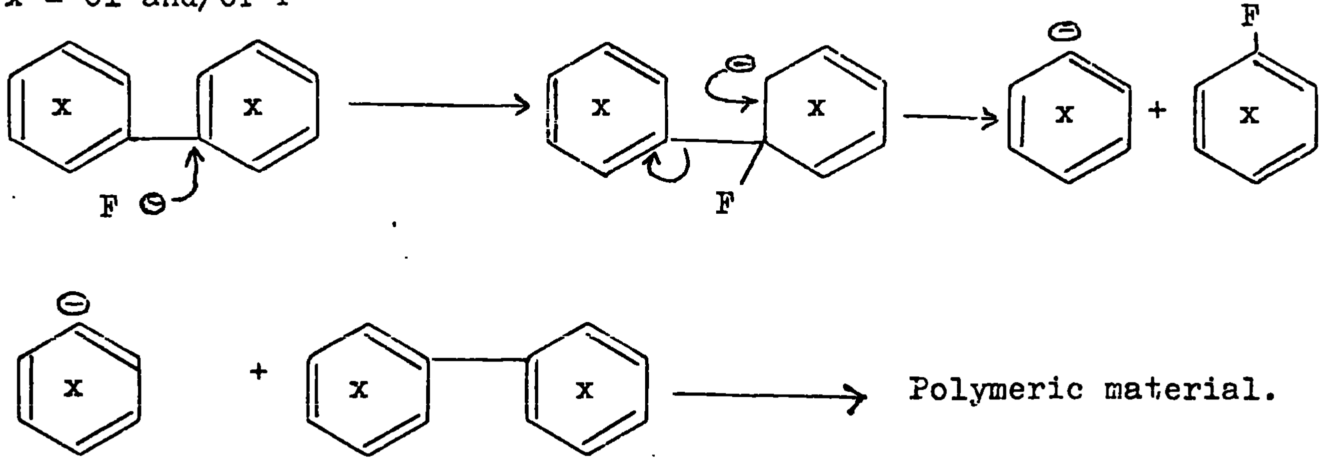
4.4 General Conclusions and Comments

Autoclave fluorination techniques cannot be readily applied to the systems described here. These systems must have some way of decomposing during reaction, which is not possible for the monocyclic and bicyclic systems to which the method has already been applied. All three compounds have a built in biphenyl system, not present in the mono- and bicyclic compounds.



Attack of fluoride ion at a ring junction may account for the failure of these reactions. Loss of a pentahalophenyl cation could then occur, which would react, further, to form the polymeric type materials observed. i.e.

x = Cl and/or F



A similar scheme may be envisaged involving the fluorene and dibenzo(b,d)thiophen systems.

The reactions in solution gave similar results, and a similar process to that described above may be occurring. However, in some cases, a small quantity of partially fluorinated material was recovered. The activation temperature for fluorination and the degradation temperature of the halogenated substrate appear to be very similar with a very fine balance between the two. A more active fluorinating species (thus lowering the reaction temperature) would clearly assist in solving this problem and crown polyethers seemed to be an obvious candidate to catalyse these reactions. This work is dealt with in Chapter IV.

5. Applications and Toxicological Properties of Some Polychloro Compounds

Decachlorobiphenyl has been used in the plastics and paints industries, the manufacture of lubricants and wax polishes, and also in the electrics industry. Its toxic limit is 0.5-1.0 mg. litre^{-1}., and its lipophilic character, which enables it to collect in the fatty tissues of the skin, may be responsible for this toxicity. Prolonged contact of decachlorobiphenyl with the skin can, in some cases, cause dermatitis.

The presence of small quantities of octachlorodibenzo(b,d)furan, normally found with decachlorobiphenyl may also be a contributing factor to its toxicity. Investigation into the toxicological properties of octachlorodibenzo(b,d)-furan is reported in the recent chemical literature.[124] It has recently been used along with antimony (III) oxide as a fire-proofing agent for polymers,[113] and also as an insecticide.

Chlorinated naphthalenes are toxic to the liver and have a pronounced dermatitic effect. However, they do have limited uses as high boiling point solvents, plasticisers and protective coatings, e.g. underwater paints.

CHAPTER IV

The Use of 18-Crown-6 polyether as a Fluorination Catalyst

1. Introduction

Chapter III of this thesis illustrated the difficulties encountered during the attempted fluorination of the polycyclic compounds under investigation.

The solubilisation of KF in aprotic solvents containing 18-crown-6, and the fluorinating properties of these solutions have been reported.[130] The potassium is said to be effectively complexed, by polyether, leaving a "naked" fluoride ion in solution.

The application of this effect to the polychloro systems being studied was now investigated. It was hoped that the production of a "naked" fluoride ion, an extremely powerful nucleophile, would replace Cl^- from the polycyclic substrates at relatively low temperatures, and reduce the chance of degradation and polymerisation occurring.

1.1 Preparation and Purification of 18-Crown-6 polyether

1.1.1 Chlorination of Trigol

Trigol was chlorinated to give 1,8-dichloro-3,6-dioxa-octane (31) as described in the literature.[125] The reaction involves nucleophilic displacement of -OH by -Cl using thionyl chloride.

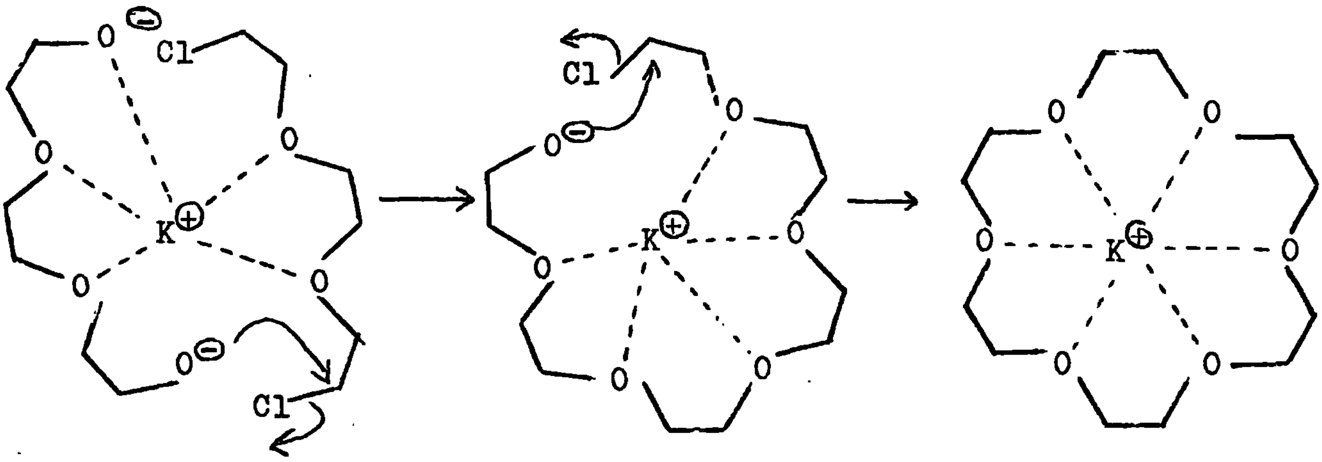
$$HO(CH_2CH_2O)_2CH_2CH_2OH \xrightarrow[C_6H_6/Py]{SOCl_2} Cl(CH_2CH_2O)_2CH_2CH_2Cl$$

(31)

1.1.2 Formation of Crude 18-Crown-6 polyether

Trigol was reacted with (31) in basic solution, using the procedure described by Gokel and co-workers.[126] Cyclisation occurred, giving crude 18-crown-6 polyether, which could be collected by distillation under reduced pressure (100-130°C/ 0.05mm Hg).

Greene has suggested a "template effect" to account for the high yield of cyclic compared with polymeric material obtained from the reaction.



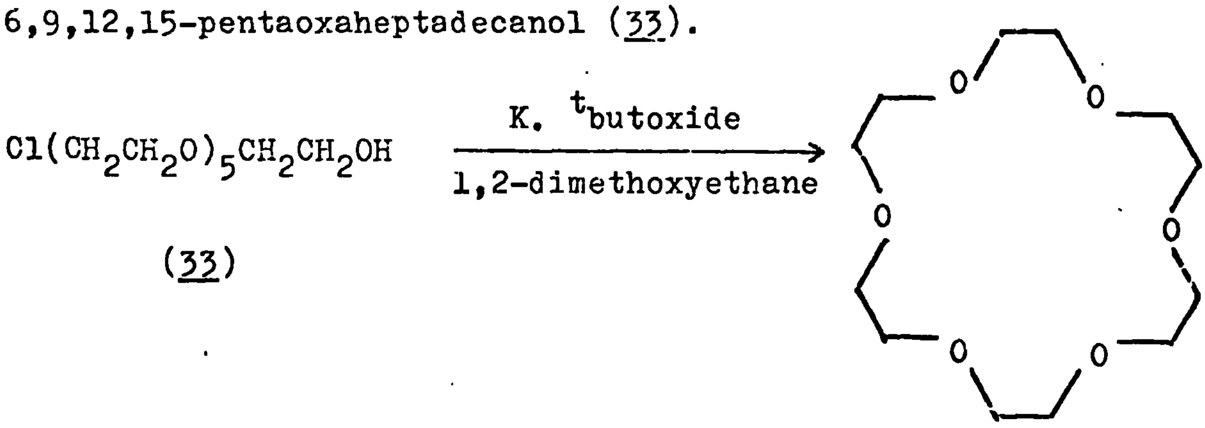
1.1.3 Purification of 18-Crown-6 polyether with Acetonitrile

Purification of the crude 18-crown-6 polyether was by complexing with acetonitrile.[126] The complexing seems to exclude impurities that distil with, or near to the pure polyether. The recrystallised complex is then broken down by pumping off the acetonitrile with slight heating under a good vacuum for several hours. The liquid 18-crown-6 solidifies with the evolution of heat, giving a sharp melting (39.5°C) white crystalline solid.

1.2 Background Work on the Uses of 18-Crown-6 polyether

1.2.1 Methods of Synthesis

Since 1967, several authors have reported the synthesis of 18-crown-6 polyether (32). Pedersen[127] obtained (32) in low yield (< 2%) from the base catalysed cyclisation of 17-chloro-3,6,9,12,15-pentaoxaheptadecanol (33).



(33)

(32)

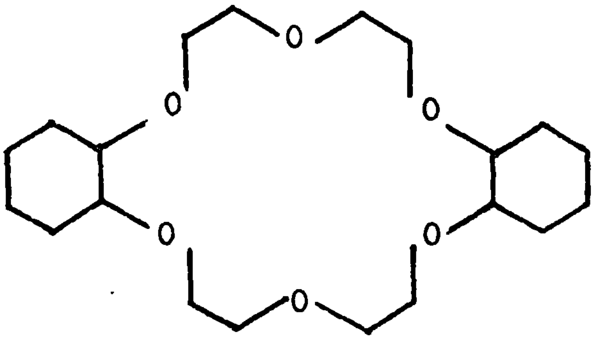
In 1972, Greene investigated the effect of solvent upon a base catalysed condensation reaction between trigol and triethylene glycol tosylate.[128] Although yields of (32) in T.H.F. were relatively low (30-60%), this proved to be the simplest technique to use.

Gokel and co-workers[126] reported a rapid synthesis of (32) in 40% yield, using Williamson's ether synthesis. This was the method employed in these laboratories.

More recently, it has been shown that (32) is obtained in low (4%) yield from the oligomerisation of ethylene oxide.[129]

1.2.2 Nomenclature

The macrocyclic polyethers can be assigned unique but very cumbersome names by application of the IUPAC rules for bridged hydrocarbons e.g. (34) would be called 2,5,8,15,18,21-hexaoxatricyclo (20.4.0.0^{9,14})hexacosane.



(34)

A simpler 'ad hoc' nomenclature was devised.[125] This incorporated digits and the word "crown" to signify the number of atoms in the ring. Thus (<u>34</u>) becomes dicyclohexyl-18-crown-6, the 18 signifying the number of atoms in the "crown", the six signifying the number of oxygen atoms in the ring and the dicyclohexyl describing the substituents attached to the "crown". The placement of substituents and oxygen atoms into the ring are as symmetrical as possible, exceptions are indicated by asym-.

1,2.3 Applications of 18-Crown-6 polyether/KF Complex

The solubilisation of potassium fluoride in acetonitrile and benzene containing 18-crown-6 has been demonstrated.[130] Several reactions have been studied, their reaction conditions are relatively mild, and the conversions are essentially quantitative. Table IV.1 illustrates some of the reactions which have been demonstrated.[130]

Table IV.1

Reactions of Various Substrates with Potassium Fluoride i.p.o. 18-crown-6

Substrate	Solvent	Products
benzyl bromide	CH_3CN	benzyl fluoride
1-bromo octane	CH_3CN	1-fluorooctane (92%) 1-octene (8%)
2-bromo octane	C_6H_6	2-fluorooctane (32%) 1- and 2-octenes
2,4-dinitrochlorobenzene	CH_3CN	2,4-dinitrofluorobenzene
Acetyl Chloride	CH_3CN	Acetyl fluoride

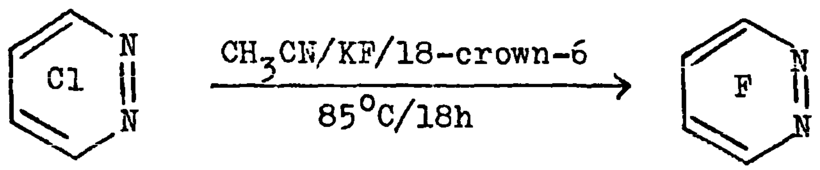
2. Fluorination of Halogenated N-containing Heterocycles

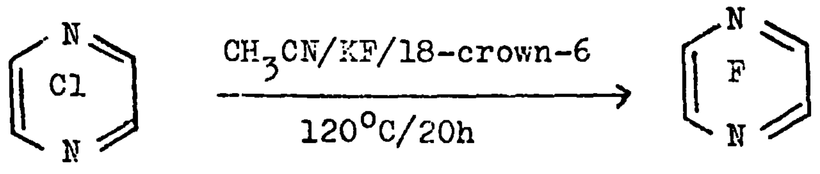
Before making any attempt to fluorinate the polycyclic compounds under investigation, it was necessary to determine the effect of (32) on various KF/solvent systems. Acetonitrile/18-crown-6/KF has been shown to be an efficient fluorinating system (see table IV.1, above) and was investigated first. Five monocyclic N-containing heterocycles were fluorinated, and the results are discussed below.

2.1 Using a CH_3CN/KF/18-crown-6 Fluorinating System

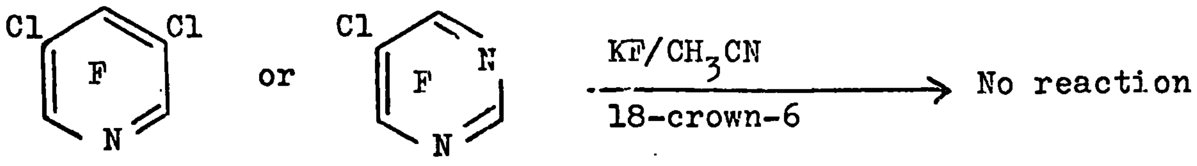
Using the acetonitrile/potassium fluoride/polyether system, pentachloropyridine, tetrachloropyrazine and tetrachloropyridazine were converted to 3,5-dichlorotrifluoropyridine, tetrafluoropyrazine and tetrachloropyridazine respectively. Control reactions under identical conditions (i.e. in the absence of (32)) did not afford any fluorinated materials. 3,5-Dichlorotrifluoropyridine could not be fluorinated any further. Tetrachloropyrimidine yielded 5-chlorotrifluoropyrimidine both in the presence and the absence of (32) as catalyst.

Clearly, (32) does have an activating influence towards fluorination, shown from the perfluorinations of tetrachloropyrazine and tetrachloropyridazine.





However, using the solvent system described, the 5-chlorine atom of tetrachloropyrimidine cannot be replaced, even though this system is reactive enough to undergo partial fluorination in the absence of catalyst. Both 5-chlorotrifluoropyrimidine (<u>35</u>) and 3,5-dichlorotrifluoropyridine (<u>36</u>) have the chlorine atoms meta- to nitrogen, which is known to have a deactivating influence towards nucleophilic attack in this position.



(<u>36</u>) (<u>35</u>)

A higher boiling, aprotic solvent (e.g. sulpholan) system may be sufficiently active to bring about this meta-chlorine displacement.

2.2 <u>Using a Sulpholan/KF/18-crown-6 Fluorinating System</u>

Fluorinated products, similar to those observed in Section 2.1 were obtained using this fluorinating system. In all cases, the same products were obtained, both in the presence of, and in the absence of (<u>32</u>). However, the system was still insufficiently reactive to replace the chlorine atoms meta to nitrogen, in either (<u>35</u>) or (<u>36</u>), even under relatively forcing conditions (longer reaction time, higher temperature etc.).

When tetrachloropyridazine was fluorinated using this system, prolonged reaction at high temperatures produced a completely gaseous product. (M^+ = 81, $\tilde{\nu}$: 1960,1945,1930,1250, 1240 cm^{-1}). The gas may arise from attack of F$^-$ on tetrafluoropyridazine, causing ring opening, with subsequent loss of nitrogen. Although potentially interesting, further work in the identification and formation of the unknown gas was not undertaken at this stage.

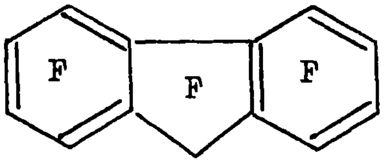
3. Fluorination of Halogenated Polycyclic Compounds

Section 2. of this chapter demonstrated the ability of (32) to act as a catalyst to fluorination. The more reactive sulpholan system was chosen to investigate the fluorination of polycyclics, using comparable conditions.

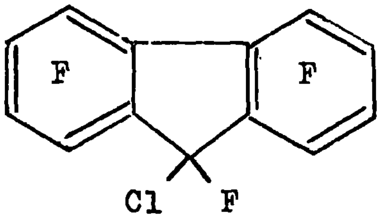
This section will be subdivided into three main parts, according to the results which were obtained. These are: (i) the fluorene system, the only one which indicated any success with the method; (ii) the biphenyl, dibenzo(b,d)furan and dibenzo(b,d)thiophen systems, which indicated the occurrence of reduction; and (iii) the decafluorobiphenyl system, which indicated some type of polymerisation.

3.1 The Fluorene System

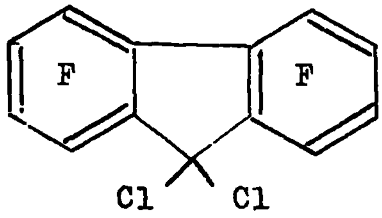
When decachlorofluorene was heated in the sulpholan/KF/18-crown-6 system, a yellow solid was obtained, (approx. 50% yield) the mass spectrum of which corresponded to a mixture of chlorofluorofluorenes, including the perfluorinated compound. A ^{19}F n.m.r. spectrum of the mixture was recorded, and a tentative assignment was made, on the basis of the structures (37), (38) and (39). Separation of the mixture was not pursued at this stage. Reaction with antimony trichloride under favourable conditions, may convert the mixture solely to perfluorofluorene.



(37)



(38)

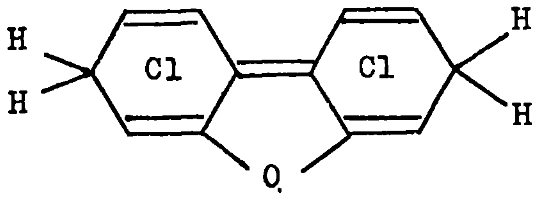


(39)

3.2 The Biphenyl, Dibenzo(b,d)thiophen and Dibenzo(b,d)furan Systems

In all three cases. the product of fluorination was a deeply coloured involatile material. The respective infra-red spectra of these products indicated $>c=c<$ ($\tilde{\nu}$ 1600cm^{-1} approx.) and -C-H ($\tilde{\nu}$ 2950cm^{-1} approx.) environments. Their mass spectra corresponded to compounds containing from four to seven chlorine atoms. However, parent peaks did not correspond to the respective fluoro/chloroheterocycles. e.g. the product when octachlorodibenzo(b,d)furan was the substrate showed a parent molecular ion at $M^+(^{35}Cl) = 374$ with six chlorine atoms. Assuming the dibenzo(b,d)furan skeleton to be intact, we have 374 - 210(6xCl) - 160($C_{12}O$) = 4.

i.e. a residual mass of 4, which can only correspond to four protons. i.e. a total molecular formula of $C_{12}H_4Cl_6O$. P.M.R. showed a single resonance at δ = 3.47p.p.m. relative to ext. T.M.S. This could correspond to a methylene group flanked by two vinyl systems. A structure (40) of the tetravinylethylene type would account for the observed spectroscopic data.



(40)

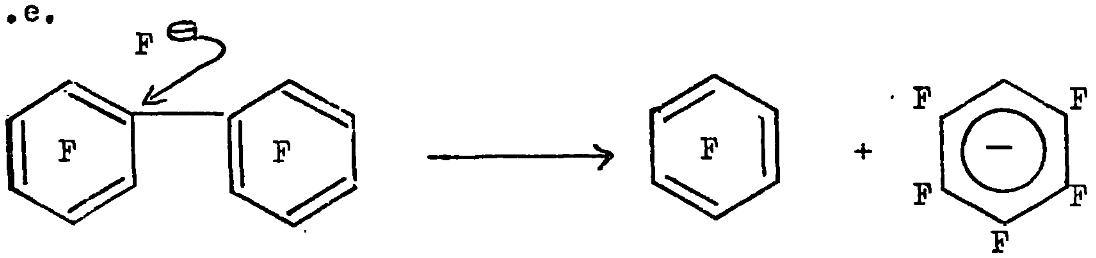
Comparable results were obtained for the biphenyl and dibenzo(b,d)thiophen systems, and reduced structures similar to (40) could be envisaged.

3.3 The Decafluorobiphenyl System

When decafluorobiphenyl was reacted with the sulpholan/KF/18-crown-6 system, a high M.W., deep red, involatile residue was obtained. The mass spectrum did not contain a peak at $M^+ = 334$, which corresponds to starting material.

It seems that even if decachlorobiphenyl could be perfluorinated using this method, further reaction of the perfluorocompound may occur giving high molecular weight materials. Formation of a pentahalophenyl anion may again be responsible.

i.e.



4. General Conclusion and Comments

The sulpholan/KF/18-crown-6 fluorinating system is sufficiently active to perfluorinate decachlorofluorene without degradation of the carbon skeleton. However, the reaction does not appear to go to completion. This was the only substrate which indicated that further work may produce a method for the preparation of a tricyclic perfluoro compound from its perchloro analogue by direct halogen exchange.

Biphenyl, dibenzo(b,d)furan and dibenzo(b,d)thiophen produced products which appeared to have been de-aromatised and reduced to some extent.

In general, the method is not readily applicable for halogen exchange of chlorine by fluorine in the substrates investigated, and alturnative techniques need to be explored.

These attempted fluorination reactions conclude the work with the perchloropolycyclic systems. Part II of this thesis which follows, deals with the preparation and properties of oligomers of some perfluorocycloalkenes.

CHAPTER V

Mass Spectrometry Applied to Highly Halogenated Polycyclic Compounds

1. General Introduction

Most of the compounds described in Part I of this thesis contain one or more chlorine atoms, and in many cases, mass spectrometry has been the major structural probe used for the determination of molecular weight, molecular composition, number of components etc. This has arisen mainly because of the combination of the relative insolubility of these compounds and the lack of a convenient nucleus with a spin number of ½, which would enable n.m.r. to be used as a structural probe. (The possibility of using ^{13}C n.m.r. as a structural probe with perchlorinated polycyclic compounds has been attempted,[2,131] but has met with limited success.)

Because of the afore mentioned factors, perhaps more reliance than would be usual, was placed upon the mass spectral data obtained for products which were isolated from reactions. It is felt that a brief note concerning the principals used in the analysis of mass spectra is necessary at this stage.

2. Isotopic Abundances of Chlorine

Chlorine has two naturally occurring isotopes with mass numbers of 35 and 37. The ratio of relative abundance of these isotopes is approximately 3:1 respectively (The exact percentages are given as 75.529 ± 0.016 and 24.471 ± 0.016[132,133] but for the purpose of this discussion the figures of approximately 3 to 1 are adequate). Hence, a compound containing one chlorine atom would show a peak in the mass spectrum at, say M, which would correspond to that proportion of the compound which contained only the ^{35}Cl isotope, and also, a peak at (M+2) which would correspond to that proportion containing only the ^{37}Cl isotope. As a consequence of the ratio of the natural abundance of ^{35}Cl to ^{37}Cl being approximately 3 to 1, the ratio of the peaks M and (M+2) would be approximately 3 to 1, i.e. a situation as shown in Fig V.1 would be observed. Similarly, a compound containing two chlorine atoms would be predicted to give an "isotopic splitting pattern" similar to that shown in Fig V.2.

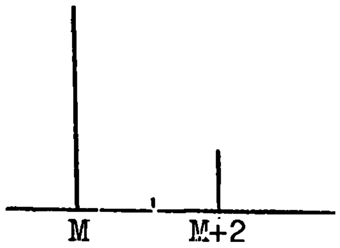


Fig V.1 Isotopic Distribution Observed in the Mass Spectrum of a Compound Containing One Chlorine Atom

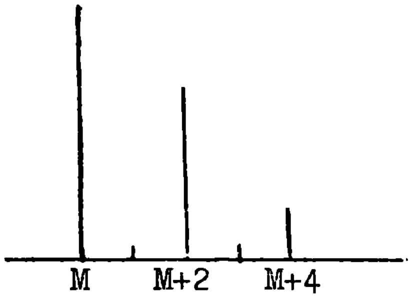


Fig V.2 Isotopic Distribution Observed in the Mass Spectrum of a Compound Containing Two Chlorine Atoms

A complete picture of the isotopic splitting patterns of compounds containing more chlorine atoms can thus be built up[134] by the use of Pascal's triangle and the expansion of the function $(x + y)^z$, where

x = the % of ^{35}Cl isotope

y = the % of ^{37}Cl isotope

z = the number of chlorine atoms being considered.

Table V.1 gives the peak intensity ratios for up to 14 chlorine atoms, and figure V.3 illustrates the "isotopic splitting patterns" observed in the mass spectrum. (N.B. The figures quoted in Table V.1 are calculated assuming the ratio of ^{35}Cl to ^{37}Cl to be 1 to 0.326).

The molecular weights quoted in this thesis are based on the molecule in which all of the chlorine atoms are of the ^{35}Cl isotope, and are therefore the lowest mass peak in the particular parent's isotope peaks grouping. As described above, the intensity pattern of the peaks in the molecular ion is highly characteristic of the number of chlorine atoms present in the molecule, and the numbers of chlorine atoms in compounds described in this thesis have been determined by measurements of these isotopic peak ratios.

3. Analysis of the Mass Spectra of Mixtures

In many cases, the products isolated from chlorination and fluorination reactions, described in Part I of this thesis, were mixtures. Thin layer chromatography did not readily distinguish between components and often showed the sample up as one large diffuse spot. Mass spectrometry however did give a good indication of the number of components present in a mixture and in some cases gave an approximate idea as to the ratios of these components.

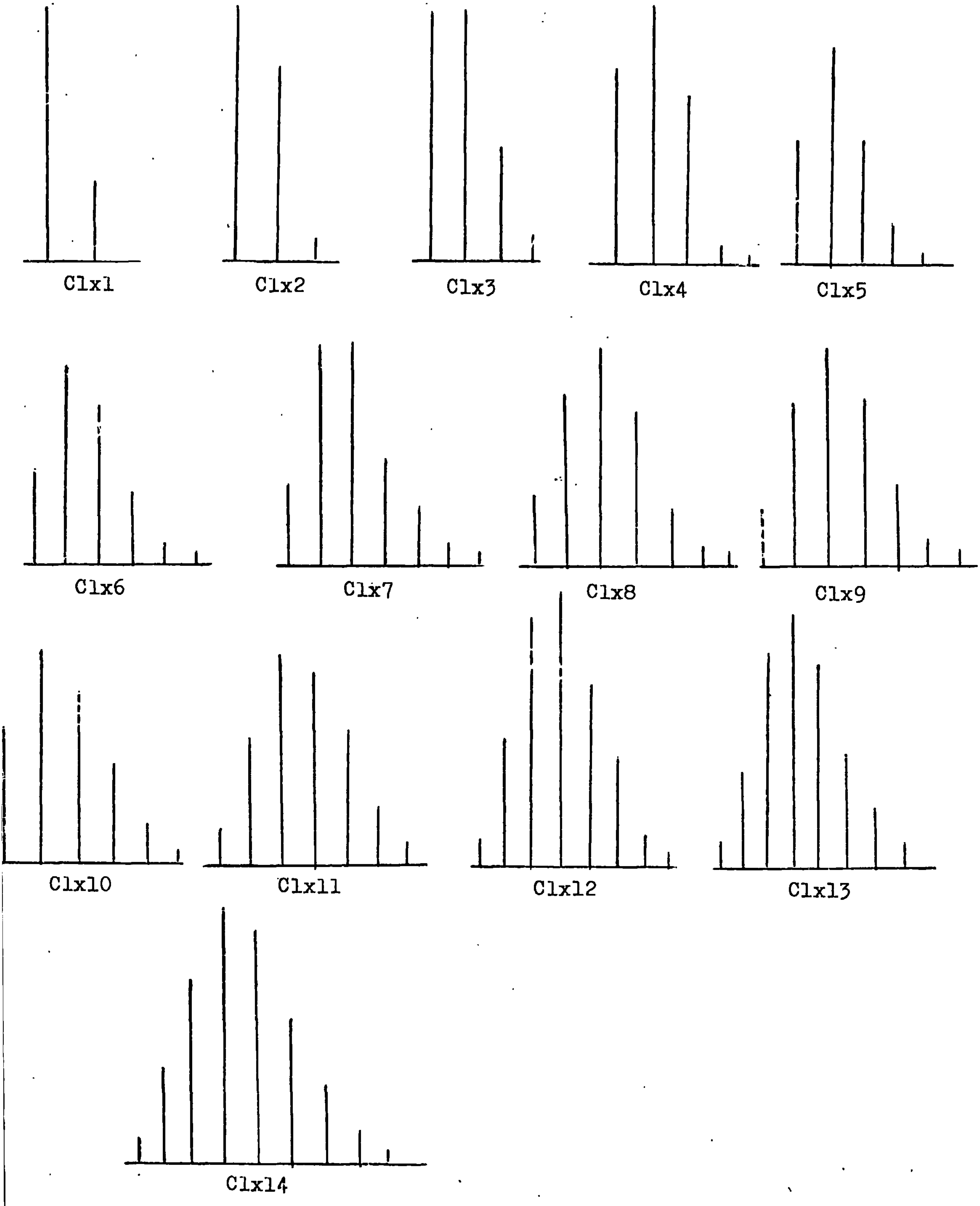
Bombardment of molecules with high energy (usually 70eV) caused extensive fragmentation to occur (although the parent

Isotopic Peak Intensity Ratios

No. of Cl atoms	P	P+2	P+4	P+6	P+8	P+10	P+12	P+14	P+16	P+18	P+20	P+22	P+24	P+26	P+28
14	1	4.56	9.67	12.59	11.31	7.41	3.60	1.34	0.39	0.08	0.01	0.001	$1x10^{-4}$	$7x10^{-5}$	$1x10^{-7}$
13	1	4.24	8.29	9.90	8.08	4.76	2.06	0.67	0.17	0.03	0.003	$3x10^{-4}$	$2x10^{-5}$	$5X10^{-7}$	
12	1	3.92	7.02	7.61	5.59	2.93	1.11	0.31	0.06	0.009	$7x10^{-4}$	$5x10^{-5}$	$1.4x10^{-6}$		
11	1	3.59	5.85	5.71	3.73	1.71	0.55	0.13	0.02	0.002	$1x10^{-4}$	$4x10^{-6}$			
10	1	3.26	4.78	4.15	2.37	0.93	0.25	0.05	0.006	0.004	$1x10^{-5}$				
9	1	2.93	3.83	2.91	1.42	0.47	0.10	0.01	0.001	$4x10^{-5}$					
8	1	2.61	2.98	1.94	0.79	0.21	0.03	0.003	$13x10^{-5}$						
7	1	2.28	2.23	1.21	0.40	0.08	0.008	$4x10^{-4}$							
6	1	1.96	1.61	0.69	0.17	0.023	0.011								
5	1	1.63	1.06	0.35	0.057	$37x10^{-4}$									
4	1	1.31	0.639	0.14	0.015										
3	1	0.998	0.319	0.035											
2	1	0.653	0.106												
1	1	0.326													

Fig V.3 Isotopic splitting Patterns Observed in the Mass Spectra of Compounds Containing up to 14 Cl atoms

The peaks are observed at P+2 intervals. (Not to scale)



Clx1 Clx2 Clx3 Clx4 Clx5

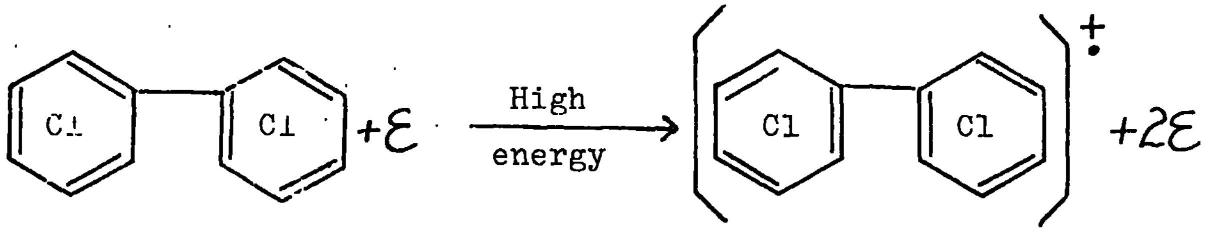
Clx6 Clx7 Clx8 Clx9

Clx10 Clx11 Clx12 Clx13

Clx14

peak was usually observed), which in the majority of cases showed as the successive loss of chlorine atoms from the parent molecular ion.

e.g.

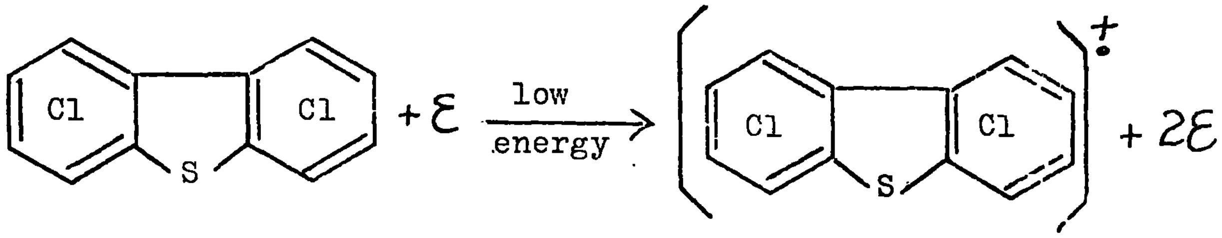


Parent molecular ion

$$(C_{12}Cl_{10})^{+\bullet} \xrightarrow[\text{energy}]{\text{high}} Cl^{\bullet} + (C_{12}Cl_{9})^{+} \xrightarrow{-Cl^{\bullet}} \text{Etc.}$$

However, low energy bombardment (nominally 12-14eV) did not cause any fragmentation at all in the majority of cases, and the parent molecular ion was the only one observed in the spectrum.

e.g.



If fragmentation did occur, it was to a far lesser extent than at 70eV. Hence, the ratio of parent ion to fragment ion increased at low eV bombardment. i.e. if groups of peaks remained in a low eV spectrum, and they were in the same ratio as they were in the high eV spectrum, it was almost certain that they themselves were parent compounds and not fragments of a higher molecular weight parent.

Although not a general rule, it was indicated in some cases, that measurement of the ratios of parent peaks in the mass spectrum of a mixture could give a rough estimate of the percentage of each component in the mixture. The following example serves to illustrate an application of this.

e.g. the following data was obtained from experimental measurements on a product of chlorination of fluoren-9-one with a modified B.M.C. reagent (See experimental, Chapter VI, Section 2.5.1).

i) Low and high energy mass spectra showed the presence of two components, viz: P = 248 with two chlorine atoms and P = 282 with three chlorine atoms. (Calc. for $C_{12}H_6Cl_2O$: $M(^{35}Cl)$, 248; Calc. for $C_{12}H_5Cl_3O$: $M(^{35}Cl)$, 282.).

i.e. we have a mixture of di- and tri-chlorofluoren-9-one

ii) The ratio (measured directly from the mass spectrum) of the parent peaks of the dichloro compound to the trichlorocompound was 50:12.

iii) Now, $C_{12}H_6Cl_2O$ contains 28.485% chlorine, $C_{12}H_5Cl_3O$ contains 37.533% chlorine. A mixture of the two components in a 50:12 ratio (Cl_2:Cl_3) is calculated to contain 30.230% chlorine. Chemical analysis of the chlorinated mixture gave a figure of 29.9% chlorine.

i.e. mass spectral analysis indicates a mixture of approximate composition 80% dichlorofluoren-9-one, 20% trichlorofluoren-9-one. These figures are supported by chemical analysis.

The above phenomenon may arise because of a combination of several factors, e.g.

i) because of the close similarity in structure of the compounds being examined properties such as vapour pressure and ionisation potential are likely to be very similar.

ii) the compounds under investigation require a relatively high ionisation chamber temperature (200-250°C) to enable a mass spectrum to be recorded. As a consequence of this, the total sample introduced into the spectrometer would probably be vapourised.

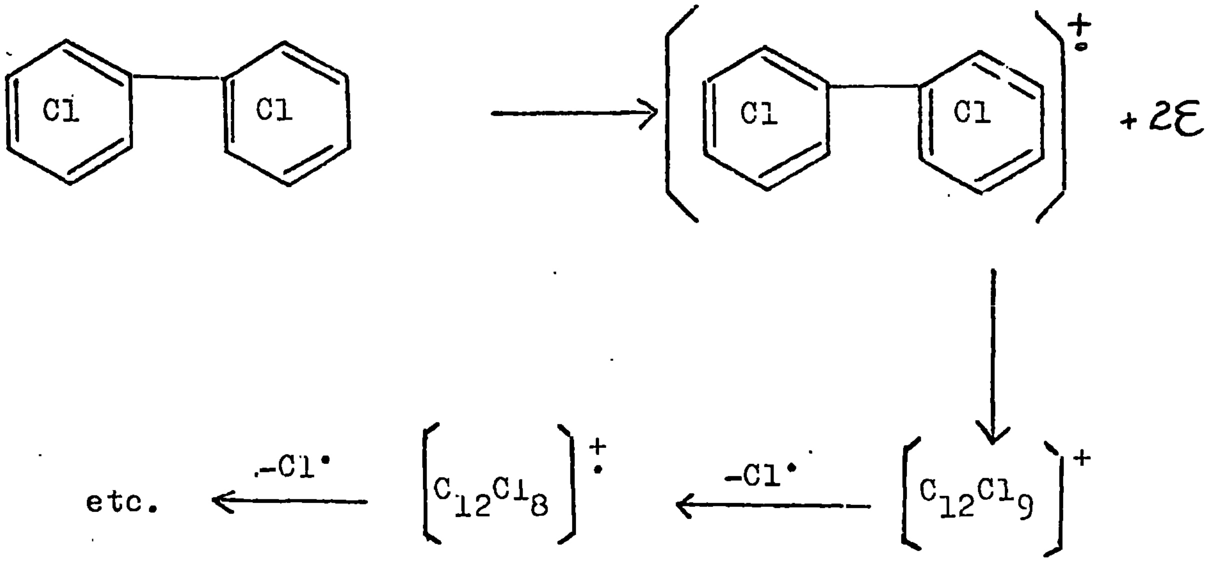
Assuming these factors to be those responsible for the approximation observed in the quoted example, it was hoped that this approximation could be applied in similar circumstances, along with low and high energy spectral data, to obtain a rough indication of the composition of mixtures.

4. Fragmentation of Polycyclic Compounds

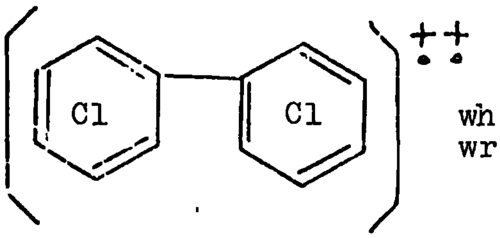
4.1 Carbocyclic Compounds

Hexachlorobenzene, decachlorobiphenyl, and decachlorofluorene were observed to fragment by successive loss of chlorine from the molecule. A parent peak was always observed and was relatively intense, indicating the stability of aromatic molecular ions, M^+

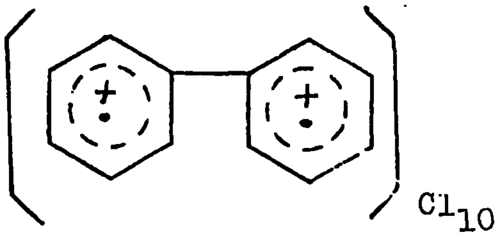
e.g. (i) In the case of decachlorobiphenyl, the following groups of peaks were the only ones observed in the upper mass range of the spectrum : P = 494(10,Cl); P = 459(9,Cl); P = 424(8,Cl); P = 379(7,Cl) etc. i.e. successive loss of chlorine from the molecule.



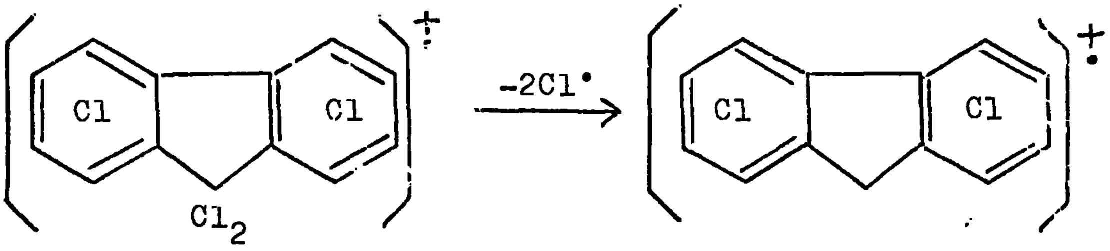
The tendency for decachlorobiphenyl to produce stable ions was emphasised by the appearance of $^{m}/2e$ type ions in its mass spectrum, i.e.



which may be written as



e.g. (ii) Decachlorofluorene again showed successive loss of chlorine, but the loss of 2,Cl from $C_{13}C_{10}$(P = 506) to give $C_{13}Cl_{8}$(P = 436) was extremely marked, indicating perhaps a tendency for primary loss of the two bridgehead chlorine atoms.



4.2 Heterocyclic Compounds

Octachlorodibenzo(b,d)furan and octachlorodibenzo (b,d)thiophen again showed a tendency to fragment by successive loss of chlorine from the molecule.

i.e. $C_{12}Cl_{8}O + \varepsilon \longrightarrow (C_{12}Cl_{8}O)^{\dot{+}} + 2\varepsilon$

$$\begin{tikzcd} (C_{12}Cl_{8}O)^{\dot{+}} \arrow[d, "-Cl^{\bullet}"] & & \\ (C_{12}Cl_{7}O)^{+} \arrow[r, "-Cl^{\bullet}"] & (C_{12}Cl_{6}O)^{\dot{+}} \arrow[r] & \text{etc.} \end{tikzcd}$$

However, another fragmentation route; viz the loss of CxCl(x = S,O) was evident in the mass spectra of these compounds.

i.e.

$$\begin{tikzcd} C_{12}Cl_8O + \mathcal{E} \arrow[r] & (C_{12}Cl_8O)^{\stackrel{+}{\bullet}} + 2\mathcal{E} \arrow[d, "-\ \dot{C}OCl"] & \\ & (C_{11}Cl_7)^{+} \arrow[r, "-Cl^{\bullet}"] & \text{etc.} \end{tikzcd}$$

EXPERIMENTAL

CHAPTER VI

EXPERIMENTAL WORK

1. General

1.1 Chemicals

Diphenyl, dibenzo(b,d)furan, phenothiazine and thianthrene were obtained from Aldrich Chemical Company Limited, dibenzo(b,d)-thiophene and fluorene from Koch Light Laboratories and fluoren-9-one from B.D.H. Limited.

Potassium fluoride was dried by strong heating in the air, followed by grinding, and then heating under high vacuum. It was stored under an atmosphere of dry nitrogen.

Caesium fluoride was dried by warming under vacuum, with frequent agitation and periodic grinding in a nitrogen glove bag. It, too, was stored under an atmosphere of dry nitrogen.

1.2 Solvents

Sulpholan was purified by collection of the middle fraction in a vacuum distillation. It was stored under an atmosphere of dry nitrogen and over type IVA molecular sieve.

Acetonitrile was dried by refluxing it with P_2O_5 suspended on glass wool, followed by distillation under an atmosphere of dry nitrogen. It was stored under an atmosphere of dry nitrogen.

1.3 Instrumentation

Ultraviolet spectra were recorded on a Pye-Unicam SP800 spectrophotometer.

Infra-red spectra were recorded on Perkin-Elmer 547 or 577 spectrophotometers. Solid samples were recorded as KBr discs, liquid or low melting point solids as contact films between KBr plates and gaseous or low boiling point liquids in a gas cell with KBr windows.

Mass spectra were recorded on an A.E.I. MS9 spectrometer or on a V.G. Micromass 12B linked with a Pye series 104 gas chromatograph. Molecular weights recorded in this thesis are from mass spectroscopic measurements, as are the number of chlorine atoms present in the molecule.

Proton nuclear magnetic resonance spectra were recorded on a Varian 56/60D spectrometer with an ambient probe temperature of 40°C. Fluorine nuclear magnetic resonance spectra were recorded on either a Varian 56/60D spectrometer (probe temp. 40°C) or a Brüker HX90 spectrometer operating at 84.67 MHz with an ambient probe temperature of 22°C. For protons, tetramethyl silane was used as external standard and downfield shifts are recorded as positive. For fluorine, fluorotrichloromethane was used as external standard and upfield shifts are recorded as positive.

Thin layer chromatographs were recorded on microscope slides, or "quarter plates" (200mm x 50mm) coated with an even layer of silica (Silica gel/CT, Reeve Angel Scientific Limited) containing a fluorescing agent. The positions of compounds on the plate were revealed by the way they quenched the fluorescence normally excited by ultra-violet light.

Analytical gas phase chromatography was carried out using either a Perkin-Elmer 452 chromatograph or a Pye series 104 chromatograph. For chromatographic measurements the columns used were packed with either silicone elastomer on celite (column 'O') or di-n-decylphthalate on celite (column 'A').

1.4 Analyses

Carbon, hydrogen and nitrogen analyses were carried out on a Perkin-Elmer 240 elemental analyser. Analysis for halogen was a slightly modified version of the method described in the literature.[135] Sulphur analyses were achieved by a modified form of the oxygen flask combustion method.[136] All theoretical analyses are calculated assuming a molecular weight of 35.45 for chlorine.

Melting points and boiling points were determined at atmospheric pressure and are uncorrected. B.p.s were measured by the Siwoloboff method.

2. Preparation of Polychloro-Derivatives

2.1 Fluorene

2.1.1 Attempted Chlorination Using Chlorine Gas in the Presence of Iodine as Catalyst

Fluorene (50g) was dissolved in carbon tetrachloride ($250cm^3$) and solid iodine (0.5g) added as a catalyst. The reactants were contained in a $750cm^3$ three necked flanged head vessel, fitted with a reflux condenser. The reaction mixture was agitated by means of a 'citenco' motor. Dry chlorine gas (c.H_2SO_4 scrubber) was passed into the reaction flask via a sintered glass disperser. The contents of the flask were heated to reflux temperature, and chlorine gas passed continually over a period of 12 hours. A sample was taken from the reaction vessel and evaporated to dryness to leave a white waxy solid. T.L.C. indicated the presence of at least four components. The mass spectrum indicated the presence of trichloro-,tetrachloro-, and pentachloro- substituted derivatives of fluorene. (i.e. P = 268 with Cl x 3, P = 302 with Cl x 4, and P = 336 with Cl x 5. $C_{13}H_7Cl_3$ requires $^m/e$ = 268, $C_{13}H_6Cl_4$ requires $^m/e$ = 302, $C_{13}H_5Cl_5$ requires $^m/e$ = 336). Further reaction did not afford any more highly chlorinated species.

2.1.2 Attempted Chlorination Using B.M.C. Reagent[10,21,23]

From a dropping funnel, a solution of fluorene (2g) and sulphur monochloride (1g, 0.6cm^3 approx.) in sulphuryl chloride (50cm^3) was added slowly (20 minutes approx.) to a boiling solution of anhydrous aluminium chloride (0.5g) in sulphuryl chloride (150cm^3 approx.) in a flask fitted with a reflux condenser and immersed in an oil bath (temperature 85°C approx.).

After the addition, the reflux condenser was replaced by a distilling condenser and the solution was concentrated to approximately 10cm^3. The resulting mixture was refluxed for 2-3 hours, small amounts of sulphuryl chloride being added down the condenser to keep the volume of the reaction medium constant.

Excess sulphuryl chloride was evaporated off under reduced pressure, at room temperature. The residue was treated with water (200cm^3 approx.) and solid sodium bicarbonate added until no more gas evolution took place. The aqueous suspension was heated on a steam bath for one hour, allowed to cool and carefully strongly acidified with concentrated HCl. The resulting solid (6g,91.2%) was filtered off at the pump, washed well with water, dried and recrystallised (carbon tetrachloride) to yield an off white powder 2-dichloromethyl-2',3,3',4,4',5,5',6,6'-nonachlorobiphenyl. M.p. 255°C. (Found:C,28.9; Cl, 70.9%; M^+ (^{35}Cl), 541 with 11 chlorine atoms. $C_{13}HCl_{11}$ requires: C,28.52; H,0.18; Cl,71.3%; M, 542. i.e. The observed peak is the parent minus the proton). See infra-red spectrum No.1.

2.1.3 Attempted Chlorination Using a Mixture of Sulphuryl Chloride, Sulphur Monochloride, and Aluminium Chloride (Reagent 1)

N.B. The essential difference between this procedure and that described under Section 2.1.2 is a reduction in the proportion of sulphuryl chloride used in the chlorination. Hence a relatively small reaction vessel may be used for chlorination of larger quantities of substrate.

From a dropping funnel, a solution of fluorene (40g) and sulphur monochloride (12cm^3) in sulphuryl chloride (400cm^3) was added slowly (1 hour approx.) to a gently boiling solution of anhydrous aluminium chloride (12.5g) in sulphuryl chloride (750cm^3) contained in a flask equipped with a reflux condenser and immersed in an oil bath (85°C approx.).

After the addition, the reflux condenser was replaced by a distilling condenser and the solution was concentrated to approximately 200cm^3. The reaction mixture was heated at 80°C for 3 hours, without the addition of further amounts of sulphuryl chloride.

The mixture was allowed to cool to room temperature and the residual sulphuryl chloride was evaporated off under reduced pressure. The residue was treated with water (3½ litres) and solid sodium bicarbonate added until no more gas evolution took place. The suspension was heated on a water bath for 1½-2 hours with frequent stirring. When cool the liquor was carefully strongly acidified with concentrated HCl, the pale yellow solid (110g, 83%) filtered off and washed well with water. A dried sample was recrystallised (carbon tetrachloride), to yield an off white powder (M.p. 255°C). Its infra-red spectrum was identical to that of the product obtained in Section 2.1.2, i.e. $C_{13}HCl_{11}$.

2.1.4 Preparation of 1,2,3,4,5,6,7,8-Octachlorofluorene Using a Mixture of Sulphuryl Chloride, Sulphur Monochloride, and Aluminium Chloride (Reagent 2)

Aluminium chloride (15g) was dissolved in sulphuryl chloride

(250cm^3) contained in a 2 litre, three necked, round bottomed flask, by gentle heating. A solution of fluorene (50g) and sulphur monochloride (15cm^3) in sulphuryl chloride (250cm^3) was slowly added to the reaction flask at such a rate so as to keep the reaction mixture boiling. (N.B. after the solution of aluminium chloride in sulphuryl chloride had been formed, external heating of the reaction flask was not necessary. Sufficient heat of reaction was evolved during the addition, so as to keep the solvent gently refluxing). The contents of the flask were constantly agitated by means of a 'citenco' motor, and vapours were condensed in a reflux condenser. (See Fig. VI.1) The condenser was connected to an empty trap immersed in an ice bath and to a scrubber bottle containing concentrated sulphuric acid before release to the atmosphere. A slow stream of dry nitrogen was passed through the system whilst the reaction proceeded.

When addition was complete (90-120 minutes), the reaction mixture was virtually solid. Water was carefully added from the dropping funnel to hydrolyse any excess sulphuryl chloride remaining in the reaction flask. As the addition of water proceeded, a yellow solid separated. When quenching was complete (addition of approximately 1 litre of water), the liquor was boiled gently for 1 hour, allowed to cool, transferred to a 5 litre beaker with more water and diluted to 3 litres (approx.). Solid sodium bicarbonate was added until effervescence ceased, and the liquor was heated to 80-90°C, with continuous stirring ('citenco' motor) for 1-2 hours. When cool, the liquor was carefully strongly acidified with concentrated HCl. The solid product (133g, 100%) was filtered off, washed well with water and dried in an oven at 110°C. A sample was twice recrystallised (chloroform), to yield an off white powder

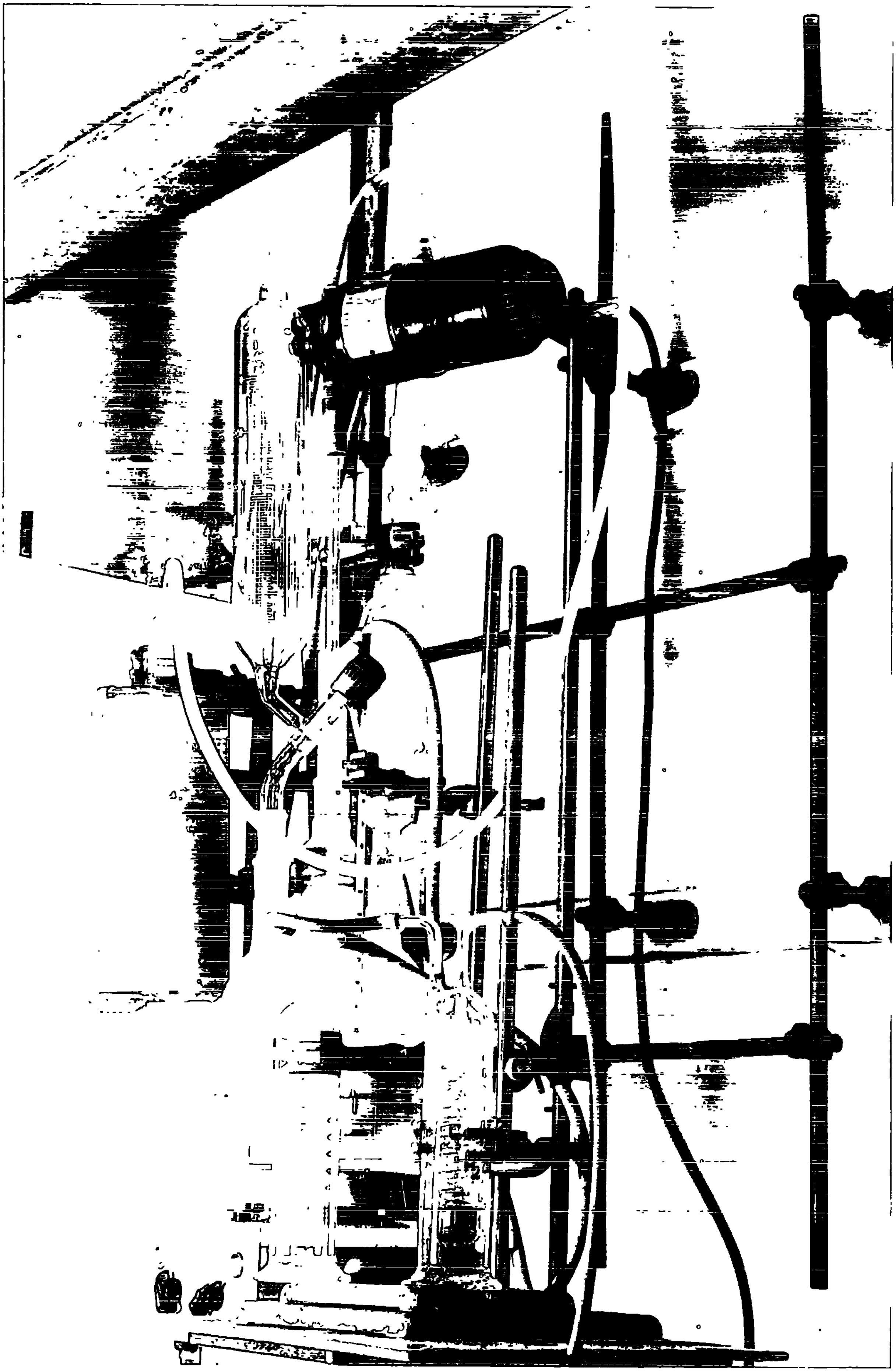


Fig. VI.1. Apparatus used for the preparation of
1,2,3,4,5,6,7,8-octachloro[illegible]

1,2,3,4,5,6,7,8-octachlorofluorene. M.p. 255°C. (Found: C,35.50; H,0.57; Cl, 63.9%; $M^+(^{35}Cl)$, 438 with 8 chlorine atoms present. $C_{13}H_2Cl_8$ requires: C, 35.32; H,0.46; Cl, 64.22%; M,438.). The positions of the chlorine atoms were shown by the fact that the compound could be oxidised to octachlorofluoren-9-one. (See later, Section 2.5.4). See infra-red spectrum No.2, N.M.R. spectrum No.1.

2.1.5 Reaction of 1,2,3,4,5,6,7,8-Octachlorofluorene with PCl_5 in an Autoclave

(a) Heating from Ambient Temperature (20°C) to 310°C Over a Period of 4½ Hours

1,2,3,4,5,6,7,8-Octachlorofluorene (20g) and phosphorus pentachloride (100g) were mixed together in a nickel lined, double ended autoclave. The autoclave was sealed and placed in a furnace at ambient temperature (approx. 20°C). The temperature of the furnace was raised to 310°C over a period of 4½ hours.

The autoclave was removed from the furnace, and vented in a fumes cupboard whilst still hot. The contents were poured onto crushed ice/water mixture, the solid material filtered off at the pump (8g, 34.5%) and a sample recrystallised (carbon tetrachloride/cyclohexane), to yield a pale yellow solid, perchlorofluorene. M.p. 260°C. Literature[46] value 256-258°C. (Found: C,30.54; Cl, 69.9%; $M^+(^{35}Cl)$, 506 with 10 chlorine atoms present. Calculated for $C_{13}Cl_{10}$: C,30.56; Cl,69.44%; M,506.). See infra-red spectrum No.3.

(b) Heating at 310-325°C for 20 Hours

The method is as described under 2.1.5 (a), except that the autoclave was placed in a furnace preheated to 310-325°C and left for 20 hours whilst the reaction proceeded.

Extraction of the quenched product afforded a minimal amount (circa 0.5g) of a yellow solid, decachlorobiphenyl. M.p. 297-299°C. Literature[137] value 296-298°C. (Found: C,28.82; Cl, 71.4%; $M^+(^{35}Cl)$, 494 with ten chlorine atoms present. Calculated for $C_{12}Cl_{10}$: C,28.89, Cl,71.11%; M,494.). See infra-red spectrum No. 4.

(c) Heating at 310-325°C for 3½ Hours

The method is as described under 2.1.5 (a), except that the autoclave was placed in a furnace preheated to 310-325°C and left for 3½ hours whilst the reaction proceeded. After extraction, perchlorofluorene (21g, 93%) was obtained as the product, identified by its infra-red spectrum.

2.2 Biphenyl

2.2.1 Preparation of 4,4'-Dichlorobiphenyl[119]

A sample of biphenyl (20g) was dissolved in gently boiling acetic acid (50cm^3). A stream of dry (c.H_2SO_4 scrubber) chlorine gas (45g) was passed through the solution over a period of 2-3 hours. The flask was fitted with a reflux condenser and immersed in an oil bath at 125-130°C. The flask was allowed to cool overnight, when white needle-like crystals were deposited. (6g. 21%). A sample was recrystallised (toluene/light petroleum), to yield white crystals of 4,4'-Dichlorobiphenyl. M.p.148°C. Literature[119] value 146.5-149°C. (Found: C,64.82; H,3.77; Cl,32.13%; $M^+(^{35}Cl)$, 222 with 2 chlorine atoms present. Calculated for $C_{12}H_8Cl_2$: C, 64.6; H,3.59; Cl,31.81%; M,222.). See infra-red spectrum No.5.

2.2.2 Preparation of Decachlorobiphenyl Using a Mixture of Sulphuryl Chloride, Sulphur Monochloride, and Aluminium Chloride (Reagent 1)

The procedure is as described under 2.1.3, using the following quantities of materials; Biphenyl (50g), S_2Cl_2 (15cm^3), $AlCl_3$ (12.5g) and SO_2Cl_2 (1250cm^3). A yellow solid (155g, 96%) was recovered and identified as decachlorobiphenyl by its infrared spectrum.

2.3 Dibenzo(b,d)thiophen

2.3.1 Attempted Preparation of Octachlorodibenzo(b,d)thiophen via a Cyclisation Reaction Using Sulphur, 4,4'-Dichlorobiphenyl and Chlorine Gas[85]

A sample of 4,4'-dichlorobiphenyl (5g) was dissolved in carbon tetrachloride (250cm^3). Aluminium chloride (0.3g) and sulphur (1.6g) were added to the solution. The reaction flask was fitted with a reflux condenser, a means of stirring (a 'citenco' motor in this case), a gas inlet, and was immersed in an oil bath. The reaction medium was refluxed, and a stream of dry (cH_2SO_4 scrubber) chlorine passed through the mixture over a period of 4-5 hours.

Excess carbon tetrachloride and other volatiles were distilled off at atmospheric pressure, to yield an intractable tar.

2.3.2 Preparation of Octachlorodibenzo(b,d)thiophen Using a Mixture of Sulphuryl Chloride, Sulphur Monochloride, and Aluminium Chloride (Reagent 3)

N.B. The essential difference between this reagent and that described under Section 2.1.3 is an increase in the proportion of aluminium chloride present in the chlorinating mixture.

From a dropping funnel, a solution of dibenzo(b,d)thiophen (5g) and sulphur monochloride (1.5cm^3) in sulphuryl chloride (50cm^3) was added slowly (1 hour approx.) to a gently boiling solution of anhydrous aluminium chloride (4g) in sulphuryl chloride (75cm^3) contained in a flask equipped with a reflux condenser and immersed in an oil bath (85°C approx.).

After the addition, the reflux condenser was replaced by a distilling condenser and the solution was concentrated to approximately 30cm^3. The reaction mixture was refluxed for 1-2 hours, adding fresh sulphuryl chloride as necessary, to keep the mixture mobile.

The mixture was allowed to cool to room temperature and the residual sulphuryl chloride was evaporated off under reduced pressure. The residue was treated with water (500cm^3 approx.) and solid sodium bicarbonate added until no more gas evolution took place. The liquor was heated to 80°C and stirred continually for 1-2 hours. When cool, the liquor was carefully, strongly acidified with concentrated hydrochloric acid. The pale yellow solid (12g. 96%) was filtered off and washed well with water. A dry sample was recrystallised (xylene), to yield white needle-like crystals of octachlorodibenzo(b,d)thiophen. M.p.304.5°C. Literature[85] value 302°C. (Found: C,31.15; Cl,61.9; S,6.9%; $M^+(^{35}Cl)$, 456 with 8 chlorine atoms present. Calc. for $C_{12}Cl_8S$: C,31.3; Cl,61.7; S,7.0%; M,456.). See infra-red spectrum No.6.

2.4 Dibenzo(b,d)furan

2.4.1 Preparation of Octachlorodibenzo(b,d)furan Using a Mixture of Sulphuryl Chloride, Sulphur Monochloride, and Aluminium Chloride (Reagent 3)

The method and reagents are as described under Section 2.3.2, using the following quantities of materials: dibenzo(b,d)-furan (5g), S_2Cl_2(1.5cm^3), $AlCl_3$ (4g) and SO_2Cl_2 (125cm^3).

A pale yellow solid was filtered off (12.7g. 96% yield) and washed well with water. A dry sample was recrystallised (chloroform) to yield a pale yellow "fluffy" solid, octachlorodibenzo(b,d)furan. M.p.260°C. Literature[64] value 257°C.

(Found: C,32.8; Cl,63.6%; $M^+(^{35}Cl)$, 440 with 8 chlorine atoms present. Calc. for $C_{12}Cl_8O$:C,32.46; Cl,63.93%; M,440.). See infra-red spectrum No.7.

2.5 Fluoren-9-one

2.5.1 Chlorination Using a Mixture of Sulphuryl Chloride, Sulphur Monochloride, and Aluminium Chloride (Reagent 1)

The method and reagents are as described under Section 2.1.3 using the following quantities of materials: fluoren-9-one (40g), S_2Cl_2 (12cm^3), $AlCl_3$(12.5g) and SO_2Cl_2 (400cm^3).

A bright yellow solid was filtered off (37g). The mass spectrum indicated the presence of dichloro- and trichloro-substituted derivatives of fluoren-9-one. (i.e. P = 248 with Cl x 2 and P = 282 with Cl x 3. $C_{13}H_6Cl_2O$ requires $^m/e$ = 248, $C_{13}H_5Cl_3O$ requires $^m/e$ = 282).

2.5.2 Chlorination Using a Mixture of Sulphuryl Chloride, Sulphur Monochloride, and Aluminium Chloride (Reagent 3)

The method and reagents are as described under Section 2.3.2 using the following quantities of materials: fluoren-9-one (5g), S_2Cl_2(1.5cm^3), $AlCl_3$ (4g) and SO_2Cl_2 (125cm^3).

A bright yellow solid (10g) was filtered off. The mass spectrum indicated the presence of tetrachloro-, pentachloro- and hexachloro- substituted derivatives of fluoren-9-one. (i.e. P = 316 with Cl x 4, P = 350 with Cl x 5, and P = 384 with Cl x 6. $C_{13}H_4Cl_4O$ requires $^m/e$ = 316, $C_{13}H_3Cl_5O$ requires $^m/e$ = 350, $C_{13}H_2Cl_6O$ requires $^m/e$ = 384).

2.5.3 Acid Hydrolysis of Decachlorofluorene

(a) Fuming Sulphuric Acid

Perchlorofluorene (2g) was heated with fuming sulphuric acid (10cm^3) for 15 minutes. A black intractable tar resulted as the product.

(b) 50% ($^{v}/v$) Hydrochloric Acid

Perchlorofluorene (2g) and hydrochloric acid (50cm^3 of 50% ($^{v}/v$)) were refluxed together for 48 hours. Unreacted perchlorofluorene (2g) was the only recovered product, identified by its infra-red and mass spectra.

(c) 80% ($^{v}/v$) Phosphoric Acid

Perchlorofluorene (2g) and phosphoric acid (50cm^3 of 80% ($^{v}/v$)) were refluxed together for 24 hours. A yellow solid (2g approx.) was filtered off and dried. It was shown by infra-red and mass spectrometry to be a mixture of unreacted perchlorofluorene plus some octachlorofluoren-9-one. Successive fractional crystallisation from chloroform yielded octachlorofluoren-9-one M.p. 295°C in low yield, ($<$ 0.5g) identified by its infra-red spectrum[46] and its melting point.[46] The mass spectrum showed a parent peak at P = 462 (Based on ^{35}Cl) with 8 chlorine atoms present. ($C_{13}Cl_{8}O$ requires $^{m}/e$ = 452). See infra-red spectrum No.8.

2.5.4 Oxidation of 1,2,3,4,5,6,7,8-Octachlorofluorene with Sodium Dichromate in Acetic Acid[120]

To a gently boiling solution of 1,2,3,4,5,6,7,8-octachlorofluorene (10.6g, 24m moles) in glacial acetic acid (25cm^3) was added dropwise, over a period of 1 hour, a warm solution of sodium dichromate (12g) in glacial acetic acid (16cm^3) and water (4cm^3). The mixture was refluxed for 2-3 hours and allowed to cool. The contents of the reaction flask were poured onto iced water (250cm^3 approx.), stirred and allowed to stand for 2 hours. The supernatant liquor was decanted off and the bright yellow solid residue stirred with water (400cm^3 approx.). The solid was filtered off at the pump, washed well with dilute sulphuric acid (250cm^3, 20% ($^{v}/v$)) and finally with water until chromium free.

The bright yellow residue was dried in an oven at 110°C. It was shown to be a mixture of octachlorofluoren-9-one and unreacted 1,2,3,4,5,6,7,8-octachlorofluorene from its infra-red and mass spectra. (i.e. P = 452 with Cl x 8, $C_{13}Cl_8O$ requires $^m/e$ = 452 (based on ^{35}Cl) and P = 438 with Cl x 8; $C_{13}H_2Cl_8$ requires $^m/e$ = 438 (based on ^{35}Cl).) An attempt to separate this mixture with "Girard's Reagent" was unsuccessful.

2.6 Thianthrene

2.6.1 Chlorination Using a Mixture of Sulphuryl Chloride, Sulphur Monochloride, and Aluminium Chloride (Reagent 3)

The method and reagents are as described under Section 2.3.2 using the following quantities of materials: Thianthrene (5g), S_2Cl_2(1.5cm^3), $AlCl_3$(4g) and SO_2Cl_2(125cm^3).

The pale yellow solid (11.5g) was filtered off at the pump, dried and shown by mass spectrometry to be a mixture of octachlorothianthrene and bis-(pentachlorophenyl)sulphide. (P = 488 with Cl x 8, $C_{12}Cl_8S_2$ requires $^m/e$ = 488 (based on ^{35}Cl); P = 528 with Cl x 10, $C_{12}Cl_{10}S$ requires $^m/e$ = 528 (based on ^{35}Cl)).

The mixture was fractionally recrystallised (xylene) to give brilliant white crystals of octachlorothianthrene. M.p. $>$360°C. Literature[86] value $>$ 360°C. (Found: Cl,57.3; S,13.08%; M(^{35}Cl), 488 with 8 chlorine atoms present. Calculated for $C_{12}Cl_8S_2$: Cl,57.67; S,13.04%; M,488.). See infra-red spectrum No.9.

2.7 Phenothiazine

2.7.1 Attempted Chlorination Using a Mixture of Sulphuryl Chloride, Sulphur Monochloride, and Aluminium Chloride

All attempts to form a solution of phenothiazine in sulphuryl chloride and sulphur monochloride prior to addition to the reaction flask, resulted in violent reaction and formation of a black sludge. Further modifications to the chlorinating procedure were not investigated.

2.8 Naphthalene

2.8.1 Preparation of Octachloronaphthalene Using a Mixture of Sulphuryl Chloride, Sulphur Monochloride, and Aluminium Chloride (Reagent 1)

The procedure is as described under Section 2.1.3 using the following quantities of materials: Naphthalene (10g), S_2Cl_2 (3cm^3), $AlCl_3$(2.5g) and SO_2Cl_2 (250cm^3). A pale yellow solid (30g, 95.2%) was recovered. A sample was recrystallised (carbon tetrachloride) to yield off white crystals of octachloronaphthalene. M.p.197°C. Literature[137(a)] value 198°C. (Found: C,29.74; Cl,70.3%; $M^+(^{35}Cl)$, 400 with 8 chlorine atoms present. Calc. for $C_{10}Cl_8$: C,29.73; Cl,70.27%; M,400.). See infra-red spectrum No. 10.

2.9 Toluene

2.9.1 Preparation of 1-methyl -2,3,4,5,6- pentachlorobenzene Using a Mixture of Sulphuryl Chloride, Sulphur Monochloride and Aluminium Chloride (Reagent 1)

The procedure is as described under Section 2.1.3 using the following quantities of materials: Toluene (50g, 57.5cm^3), S_2Cl_2 (15cm^3), $AlCl_3$(12.5g) and SO_2Cl_2 (1250cm^3). A white solid (143g, 100%) was recovered. A sample was recrystallised (carbon tetrachloride) to give brilliant white, needle like crystals of 1-methyl-2,3,4,5,6 - pentachlorobenzene M.p. 225.5°C. Literature[137(c)] value 223°C. (Found: C,31.4; H,1.14; Cl,67.1%; $M^+(^{35}Cl)$, 262 with 5 chlorine atoms present. Calc. for $C_7H_3Cl_5$: C,31.79; H,1.14; Cl,67.07%; M,262.). See infra-red spectrum No.11. N.M.R. Spectrum No.7.

2.9.2 Reaction of 1-methyl -2,3,4,5,6-pentachlorobenzene with PCl_5 in an Autoclave

1-methyl -2,3,4,5,6-pentachlorobenzene (20g) and phosphorus pentachloride (100g) were mixed together in a nickel lined, double ended autoclave. The autoclave was sealed, placed in a furnace preheated to 325°C and left for 3½ hours for reaction to proceed.

The autoclave was removed from the furnace and vented in a fumes cupboard whilst still hot. The contents of the autoclave were poured onto crushed ice/water mixture, the solid material filtered off (10g, 46.4%) and a dry sample recrystallised (carbon tetrachloride) to yield a white solid, hexachlorobenzene M.p.231°C. Literature[137(b)] value 227°C. (Found: C,25.58; Cl,74.3%; $M^+(^{35}Cl)$, 282 with 6 chlorine atoms present. Calc. for C_6H_6 : C,25.29; Cl,74.71%; M,282.) See infra-red spectrum No.12.

3. Reactions of Some Polyhalogeno Compounds

3.1 Decachlorobiphenyl

3.1.1 Attempted Cyclisation Reactions with Sulphur

(a) In Xylene

Perchlorobiphenyl (5g) and sulphur (1g) were added to xylene ($100cm^3$) contained in a $250cm^3$ round bottomed flask. The flask was equipped with a reflux condenser and immersed in an oil bath. Reaction was allowed to proceed, under reflux for 48 hours. Removal of solvent left a pale yellow solid (5.9g) which was shown to be a mixture of starting materials. The mass spectrum showed two components with P = 256 and P = 494 with 10 chlorine atoms present. (S_8 requires $^m/e = 256$; $C_{12}Cl_{10}$ requires $^m/e = 494$ (Based on ^{35}Cl)).

(b) In an Autoclave at 300°C for 20 Hours

Decachlorobiphenyl (25g) and sulphur (5g) were mixed together in a stainless steel autoclave. The autoclave was evacuated, sealed and placed in a furnace at 300°C. Reaction was allowed to proceed for 20 hours. Extraction of the reaction medium afforded a yellow solid (23g) which was shown to be a mixture of starting materials.

(c) In an Autoclave at 350°C for 20 Hours

Decachlorobiphenyl (25g) and sulphur (5g) were mixed together in a stainless steel autoclave. The autoclave was evacuated, sealed and placed in a furnace at 350°C. Reaction was allowed to proceed for 20 hours.

The solid reaction products were digested with xylene ($500 cm^3$ approx.) and decolourising charcoal (1-2g). The solvent was filtered hot, and the filtrate deposited a yellow solid (5g, 34.4%, 64% conversion) which was filtered off and shown to be 2,3,4,6,7,8-hexachloro-1,9-epidithiodibenzo(b,d)thiophen. M.p. 331°C.d. (Found: C, 31.95; Cl,47.12; S,20.88%; M^+(^{35}Cl), 450 with 6 chlorine atoms present, $C_{12}Cl_6S_3$ requires : C,31.79; Cl,46.96; S,21.25%; M,450.). See infra-red spectrum No.13.

Evaporation of solvent from the mother liquor yielded 9g of unreacted decachlorobiphenyl, identified from its infrared and mass spectra.

3.2 Octachlorodibenzo(b,d)thiophen

3.2.1 Cyclisation Reaction with Sulphur in an Autoclave at 350°C for 20 Hours

Octachlorodibenzo(b,d)thiophen (20g) and sulphur (4g) were mixed together in a stainless steel autoclave. The autoclave was evacuated, sealed and placed in a furnace at 350°C. Reaction was allowed to proceed for 20 hours.

The reaction product was digested with xylene ($500cm^3$ approx.) and decolourising charcoal (1-2g). The solvent was filtered hot and the filtrate deposited a deep yellow solid (3.5g) which was identified as 2,3,4,6,7,8-hexachloro-1,9-epidithiodibenzo(b,d)thiophen from its infra-red and mass spectra.

3.3 2,3,4,6,7,8-hexachloro-1,9-epidithiodibenzo(b,d)thiophen

3.3.1 Attempted Reduction with Raney/Nickel Catalyst

2,3,4,6,7,8-hexachloro-1,9-epidithiodibenzo(b,d)thiophen (0.25g) and Raney/Nickel catalyst (6g approx.) were transferred to a $250cm^3$ round bottomed flask with xylene ($100cm^3$). The mixture was stirred at room temperature for 5 hours. Insolubles were filtered off and the filtrate dried over $MgSO_4$. Removal of $MgSO_4$ and solvent yielded an off white solid (0.17g, 77.3%) which was recrystallised (xylene) to give a white "fluffy solid", 2,3,4,6,7,8-hexachlorodibenzo(b,d)thiophen M.p. 276°C. (Found: C,37.0; H,0.5; S,8.37%; $M^+(^{35}Cl)$ 388 with 6 chlorine atoms present. $C_{12}H_2Cl_6S$ requires: C,36.85; H,0.51; S,8.21%; M, 388.). See infra-red spectrum No.14.

3.4 Decafluorobiphenyl

3.4.1 Attempted Cyclisation Reaction with Sulphur in Sulpholan

Decafluorobiphenyl (5g, 15m moles), sulphur (1g, 31m moles), and sulpholan ($25cm^3$), were transferred, under an atmosphere of dry nitrogen to a $50cm^3$ B24 necked, conical flask. The flask was evacuated, sealed and immersed in an oil bath at 150°C for 1 week. When cool, the flask was let down to atmospheric pressure with dry nitrogen gas, the contents poured onto water (3 litres approx.), stirred well and allowed to settle overnight. Solid material was filtered off under suction through a "hyflo" pad to yield a pink residue, which was digested with acetone ($150cm^3$ approx.) to extract tractable material. Removal of solvent and vacuum sublimation of the red solid (4.5g) afforded a white sublimate (approx. 4g) (shown to be unreacted decafluorobiphenyl, from its infra-red and mass spectra) and a maroon solid which was probably perfluoro(bis-(p-phenyl phenylene)) sulphide M.p.113°C, as identified from its mass and ^{19}F n.m.r. spectra (M^{+},662; $C_{24}F_{18}S$ requires M = 662). See n.m.r. spectrum No.2, infra-red spectrum No.15. (N.B. insufficient material was recovered to obtain elemental analysis).

3.5 Perfluoro-(4,4'-bisisopropylbiphenyl)

3.5.1 Attempted Cyclisation Reaction with Sulphur in Sulpholan

Perfluoro-(4,4'-bisisopropylbiphenyl) (2g, 3.15m moles), sulphur (0.4g, 12.5m moles), and sulpholan ($25cm^{3}$) were transferred, under an atmosphere of dry nitrogen, to a $50cm^{3}$, B24 necked, conical flask. The flask was evacuated, sealed and the contents stirred at 150°C for 1 week.

The flask and contents were allowed to cool, the flask let down to atmospheric pressure with dry nitrogen, and the contents poured onto water (3 litres approx.). The resulting emulsion was stirred well and allowed to settle overnight. Solid material was filtered off under suction through a "hyflo" pad to yield a pale orange residue, which was digested with acetone ($150cm^{3}$ approx.) to extract tractable material. Removal of solvent afforded an off white solid (1.9g) which was sublimed (0.005mm Hg; 48°C) to yield a white crystalline solid (1.9g) shown to be starting material, from its infra-red (see spectrum No.16) and mass spectra. (M^{+}, 634) ($C_{18}F_{22}$ requires M = 634).

3.5.2 Nucleophilic Substitution with Sodium Methoxide in Methanol

Perfluoro-(4,4'-bisisopropylbiphenyl) (0.5g, 0.8m moles) and dry methanol ($25cm^{3}$) were gently refluxed in a $100cm^{3}$, two necked, round bottomed flask. A solution of sodium methoxide (20cm^3, 0.04M) in methanol was carefully added from a dropping funnel. The reaction mixture was refluxed for 48 hours, allowed to cool, poured onto dilute H_2SO_4 (500cm^3 20%, $^v/v$) and stirred well.

The aqueous phase was ether extracted (3x50cm^3), the extracts bulked and dried over calcium chloride. Removal of $CaCl_2$ and solvent left an oily liquid, sublimation (90°C; 0.05mm Hg) of which afforded a white crystalline solid (0.4g, 78.5%) which was <u>mono-methoxy-perfluoro-(4,4'-bisisopropylbiphenyl</u>) (Found: C,35.36; H,0.52; F,62.16%; M$^+$,646. $C_{19}OH_3F_{21}$ requires: C,35.29; H,0.46; F,61.77%; M,646.). See infra-red spectrum No.17, N.M.R. spectra Nos.3 and 4.

4. Attempted Fluorination Reactions

4.1 2-Dichloromethyl-2',3,3',4,4',5,5',6,6'-nonachlorobiphenyl

4.1.1 In a Solvent

The general procedure and outcome for the two reactions was the same and the quantitative details are given in Table VI.1 below. Run 1 is typical and is described here.

Table VI.1

Summary of Reaction Conditions for the Attempted Solvent Fluorination of 2-Dichloromethyl-2',3,3',4,4',5,5',6,6'-nonachlorobiphenyl

Run	Amount of Substrate	Amount of Fluorinating Agent	Volume Sulpholan	Reaction Temp.	Rctn. Time
1	5g	10g KF	25cm^3	145°C	17h
2	5g	25g CsF	25cm^3	145°C	17h

2-Dichloromethyl-2',3,3',4,4',5,5',6,6'-nonachlorobiphenyl (5g), potassium fluoride (10g), and sulpholan (25cm^3) were transferred under an atmosphere of dry nitrogen gas to a 50cm^3, B24 necked, conical flask. The flask was connected, via a gas tap to a variable volume reservoir (a football bladder in this case) to allow for expansion and any gaseous products evolved during the course of the reaction. The contents were stirred at 145°C for 17 hours.

When cool, the contents of the flask were poured onto water (3 litres approx.) and stirred vigorously. The liquor was allowed to settle overnight. Solid material was filtered off under suction through a "hyflo" pad to yield a deep brown/black residue, which was refluxed for one hour with carbon tetrachloride (250cm^3 approx.). Insolubles were filtered off and the solution dried ($CaCl_2$). Removal of $CaCl_2$ and solvent afforded an intractable tar.

4.1.2 In the Solid Phase

A general procedure was followed throughout and the reaction conditions are summarised in Table VI.2 below. Run 2 is typical and is described here.

2-Dichloromethyl-2',3,3',4,4',5,5',6,6'-nonachlorobiphenyl (10g) and dry potassium fluoride (35g) were mixed and transferred to a thoroughly dried stainless steel autoclave (approx. 100cm^3 capacity) as quickly as possible. The autoclave was evacuated, sealed and placed in a furnace at 300°C for 18 hours.

Table VI.2

Summary of Reaction Conditions for the Attempted Autoclave Fluorination of 2-Dichloromethyl-2',3,3',4,4',5,5',6,6'-nonachlorobiphenyl

Run	Amount of Substrate	Amount of Fluorinating Agent	Reaction Temperature	Reaction Time
1	10g	35g KF	350°C	18h
2	10g	35g KF	300°C	18h
3	10g	35g KF	250°C	18h

Volatile reaction products were vacuum transferred from the hot autoclave into a cold trap (liquid air). Only material which was gaseous at room temperature was obtained this way. When cool, the autoclave was let down to an atmosphere of dry nitrogen gas, and opened. It was found to contain a black powdery mass, on which various techniques were employed in an attempt to extract tractable material.

Sublimation of the black residue under vacuum (150°C, 0.005mm Hg) gave a trace of a yellow solid which was inadequate for further investigation. Solvent extraction by means of refluxing a sample of residue (5g) with different solvents ($250cm^3$) (e.g. acetone, carbon tetrachloride, chloroform or chlorobenzene) was also unsuccessful. Digestion of the residue with water ($500cm^3$) left a black polymeric solid.

4.2 Decachlorobiphenyl

4.2.1 In a Solvent

The procedure was as described under Section 4.1.1, using the following quantities of material and conditions: Decachlorobiphenyl (5g), potassium fluoride (20g), sulpholan ($25cm^3$). Reaction was allowed to proceed at 200°C for 20 hours.

After quenching, a brown acetone soluble extract (2g) was obtained, which when heated under vacuum (100°C; 0.005mm Hg) yielded a small quantity of a pale yellow solid, which was shown by mass spectrometry to comprise a mixture of chloro/fluorobiphenyls, with as many as eight chlorine atoms remaining (e.g. $^m/e = 462$, with 8 chlorine atoms, $^m/e = 446$, with 7 chlorine atoms, $^m/e = 334$ was not observed, which would correspond to the perfluorinated species, $C_{12}F_{10}$).

4.2.2 In the Solid Phase

The general procedure was as described under Section 4.1.2, and the quantitative details and reaction conditions are summarised in Table VI.3 below.

Table VI.3

Summary of Reaction Conditions for the Attempted Autoclave Fluorination of Decachlorobiphenyl.

Run	Amount of Substrate	Amount of Fluorinating Agent	Reaction Temperature	Reaction Time
1	10g	35g KF	350°C	20h
2	10g	35g KF	500°C	20h
3	10g	35g KF	425°C	20h

At 350°C, decachlorobiphenyl was recovered, identified from its infra-red and mass spectra. However, treatment of the residues from the reactions at 500°C and 425°C similarly to that described under 4.1.2 (i.e. sublimation and solvent extraction) was unsuccessful and yielded only intractable tars and polymeric material.

4.3 Decachlorofluorene

4.3.1 In a Solvent

A general procedure was employed throughout and quantitative details are given in Table VI.4. Run 3 is typical and is described below.

Decachlorofluorene (5g), potassium fluoride (25g) and sulpholan (25cm^3) were transferred, under an atmosphere of dry nitrogen, to a 50cm^3, B24 necked, conical flask. The flask was connected via a gas tap to a variable volume reservoir (a football bladder in this case) to allow for expansion and any gaseous products evolved during the course of the reaction. The flask was immersed in an oil bath at 200°C (a silicone oil bath was employed to achieve this temperature) and the contents were stirred for 21 hours.

When cool, the contents of the flask were poured onto water (3 litres approx.) and stirred vigorously. The liquor was allowed to settle overnight. Solid material was filtered off under suction through a "hyflo" pad to yield a black residue, which was refluxed with acetone to extract tractable material. Removal of insolubles and solvent left a black tar, sublimation (100°C; 0.005mm Hg) of which afforded a pale yellow sublimate ($<$0.5g) shown by its mass spectrum to be a mixture of chlorofluoro fluorenes. (i.e. $^m/e$ = 378 with two chlorine atoms, $^m/e$ = 362 with one chlorine atom and $^m/e$ = 346 chlorine absent, i.e. perfluorofluorene) N.B. Although decafluorofluorene was observed in the mass spectrum of the product, the complex nature of the mixture, the low yield and the presence of higher molecular weight material rendered the method impracticable as a preparative route to decafluorofluorene.

Table VI.4

Summary of Reaction Conditions for the Attempted Solvent Fluorination of Decachlorofluorene.

Run	Amount of Substrate	Amount of Fluorinating Agent	Volume Sulpholan	Reaction Temperature	Reaction Time
1	5g	10g KF	25cm^3	200°C	20h
2	5g	10g KF	25cm^3	200°C	40h
3	5g	25g KF	25cm^3	200°C	21h
4	5g	23g KF	25cm^3	200°C	168h

Run 4 differed from 1, 2 and 3 in that the fluorinating agent was added batchwise over the extended reaction period. Additions and times are shown in Table VI.5.

Table VI.5

Additions of KF during the course of run 4

Reaction Time	Amount KF Added
0h	10g
24h	2g
48h	2g
138h	9g

4.3.2 In the Solid Phase

A standard procedure was employed in both cases, as previously described under Section 4.1.2. Reaction conditions are summarised in Table VI.6.

Table VI.6

Summary of Reaction Conditions Used in the Attempted Autoclave Fluorination of Decachlorofluorene.

Run	Amount of Substrate	Amount of Fluorinating Agent	Reaction Temperature	Reaction Time
1	10g	35g KF	480°C	3½h
2	10g	35g KF	450°C	1¾h

In both cases, no success was achieved in attempts to extract tractable material. Once again, black polymeric material resulted as the ultimate product.

4.3.3 Using Antimony Trifluoride

(a) Solution Reaction

Perchlorofluorene (2g), antimony trifluoride (1g) and chloroform (100cm^3) were heated together under reflux for 48 hours. The reaction mixture was filtered whilst hot, allowed to cool and solvent removed. The recovered pale yellow solid product (1.8g) was shown to be unreacted perchlorofluorene, from its infra-red and mass spectra.

(b) Solid Phase Reaction

Perchlorofluorene (2g), and antimony trifluoride (1g) were mixed together and quickly transferred to a stainless steel autoclave. The autoclave was evacuated, sealed and placed in a furnace at 325°C for 20 hours.

Volatile reaction products were vacuum transferred from the hot autoclave into a cold trap (liquid air). Only material which was gaseous at room temperature was obtained this way. After cooling the autoclave was let down to an atmosphere of dry nitrogen gas. When opened, a black intractable, polymeric solid was recovered.

4.4 Octachlorodibenzo(b,d)thiophen

4.4.1 In a Solvent

A standard procedure was employed throughout, as described previously under Section 4.1.1. Table VI.7 summarises the reaction conditions used.

Table VI.7

Summarised Reaction Conditions for the Attempted Solvent Fluorination of Octachlorodibenzo(b,d)thiophen.

Run	Amount of Substrate	Amount of Fluorinating Agent	Volume Sulpholan	Reaction Temperature	Reaction Time
1	5g	10g KF	25cm^3	200°C	92h
2	5g	10g KF	25cm^3	200°C	18h
3	3g	10g KF	25cm^3	195°C	24h

Run 1 yielded an intractable tar. Run 2 afforded a small amount of chlorofluorodibenzo(b,d)thiophens (shown by the mass spectrum. i.e.

$^m/e$ = 408 with 5 chlorine atoms, $^m/e$ = 392 with 4 chlorine atoms etc.).

Run 3, however, yeilded 2.3g of an off white solid after solvent extraction. Mass spectrometry indicated this to be a mixture of chlorofluorodibenzo(b,d)thiophens, ranging from tetrachlorotetrafluoro dibenzo(b,d)thiophen to heptachloromonofluorodibenzo(b,d)thiophen. Unreacted starting material, $C_{12}Cl_8S$ was also indicated in the spectrum.

4.4.2 In the Solid Phase

A standard reaction procedure was followed throughout, as described under Section 4.1.2. The reaction conditions are summarised in Table VI.8.

Table VI.8

Summary of the Reaction Conditions for the Attempted Autoclave Fluorination of Octachlorodibenzo(b,d)thiophen.

Run	Amount of Substrate	Amount of Fluorinating Agent	Reaction Temperature	Reaction Time
1	7.5g	35g KF	300°C	3½h
2	4.5g	30g KF	330°C	48h
3	2.5g	15g KF	450°C	20h

Run 1 yielded unreacted octachlorodibenzo(b,d)thiophen, identified by its infra-red and mass spectra. Run 2 yielded a mixture of chlorofluorodibenzo(b,d)thiophens, in which up to four chlorine atoms had been replaced by fluorine identified from the mass spectrum which showed groups of peaks with $^m/e$ = 424 with six chlorine atoms, $^m/e$ = 408 with five chlorine atoms etc. No peaks corresponding to higher fluorinated species were observed. Run 3 yielded only intractable polymeric material.

5. Fluorination Reactions of Some Polyhalogenoheterocycles in the Presence of 18-Crown-6 polyether

5.1 Preparation of 18-Crown-6 polyether

5.1.1 Chlorination of Trigol[125]

Trigol (150cm^3, 1.1 moles), benzene (1000cm^3) and pyridine (147cm^3, 2.45 moles) were added to a three litre, two necked, round bottomed flask fitted with a reflux condenser and a dropping funnel. The mixture was gently refluxed. Thionyl chloride (175cm^3, 2.45 moles) was carefully added over a period of about 3 hours, during which time a white precipitate formed. Reflux was continued for a further 18 hours.

When cool, hydrochloric acid (250cm^3, 20% $^v/v$) was added dropwise from the funnel over a period of about one hour. When addition was complete, the contents of the flask were carefully shaken, allowed to settle, and the two layers separated: a lower yellow layer and an upper benzene layer. Solvent was removed from the benzene layer using a rotary evaporator, to yield a yellow liquid (200-250cm^3), which was vacuum distilled, the fraction distilling at 100°C/6mm Hg being collected (166g, 80%). This was shown by G.L.C./M.S. (column $O_{2\frac{1}{2}}$, 150°C) to be approximately 95% pure 1,8-dichloro-3,6-dioxaoctane. M^+,137, with one chlorine atom (loss of CH_2Cl from $C_6H_{12}O_2Cl_2$ gives $^m/e = 137$). See infra-red spectrum No.18, N.M.R. spectrum No.5.

5.1.2 Preparation of Crude 18-Crown-6 polyether[126]

To a one litre, two necked, round bottomed flask was added trigol (38.25g) and tetrahydrofuran (125cm^3). A teflon coated magnetic stirrer was used to agitate the solution. A solution of potassium hydroxide (27.5g, 85%) in water (15cm^3) was added in one portion to the contents of the flask, which warmed but did not boil. The flask was fitted with a reflux condenser and a dropping funnel. The contents of the flask were stirred for 30 minutes, when darkening of the lower of the two layers occurred.

A solution of 1,8-dichloro-3,6-dioxaoctane (35g) in tetrahydrofuran (25cm^3) was added gradually to the reaction vessel. The contents of the flask were boiled, under reflux for 20 hours.

When cool, solvent was removed on the rotary evaporator and methylene chloride (125cm^3) added to the residue. The mixture was stirred at room temperature for 45 minutes, filtered onto dry magnesium sulphate, shaken and allowed to stand. Removal of $MgSO_4$ and solvent afforded a deep red coloured oil, which was vacuum distilled, the fraction distilling at 100-130°C/0.05mm Hg being collected. (27g, 54%). This distillate was used in Section 5.1.3 for acetonitrile purification, and no attempt to characterise it at this stage was made.

5.1.3 Purification of Crude 18-Crown-6 polyether using Acetonitrile[126]

The crude distillate (27g) from Section 5.1.2, acetonitrile (70cm^3) and a teflon coated magnetic stirrer were transferred to a 150cm^3 round bottomed flask equipped with a reflux condenser and a $CaCl_2$ drying tube. The contents of the flask were warmed until a clear solution was obtained. The solution was allowed to cool slowly, with constant stirring, when white crystals were seen to deposit. Stirring was continued at ambient temperature for 18 hours. Precipitation was completed by immersing the flask in an acetone/ice bath.

The white crystals were quickly filtered off with suction and transferred to a $100cm^3$ round bottomed flask equipped with a magnetic stirring bar, a vacuum take off and a gentle source of heat. The crystals were gently heated (40-50°C), with continuous stirring. Acetonitrile was pumped off under vacuum (0.005mm Hg) over a period of 2-3 hours.

The flask was let down to atmospheric pressure with dry nitrogen gas, and the contents allowed to cool. The liquid residue solidified with the evolution of heat, to give a white crystalline solid, (8g, 30%) 18-crown-6 polyether. M.p. 39.5°C. Literature[126] value 39-40°C. (Found: C,54.49; H,9.47%; M^+, 264. Calc. for $C_{12}H_{24}O_6$: C,54.54; H,9.11%; M,264.). See infra-red spectrum No.19, N.M.R. spectrum No.6.

5.2 Fluorination of Halogenated N-containing Heterocycles

5.2.1 General Procedures used for 18-Crown-6 polyether Catalysed Fluorinations

(a) Using Acetonitrile or Xylene as a Solvent

A general reaction procedure was used throughout, and is described below, a typical reaction set up is shown in Fig. VI.2. Quantitative reaction conditions are given under the respective heterocycles being fluorinated.

Substrate, potassium fluoride, 18-crown-6 polyether, and solvent were transferred to a reaction vessel (see Fig. VI.2) which was then evacuated and sealed. The vessel was immersed in an oil bath and reaction allowed to proceed with continuous stirring.

Volatile reaction products were vacuum transferred to a cold trap (liquid air) and identification was by G.L.C./M.S.

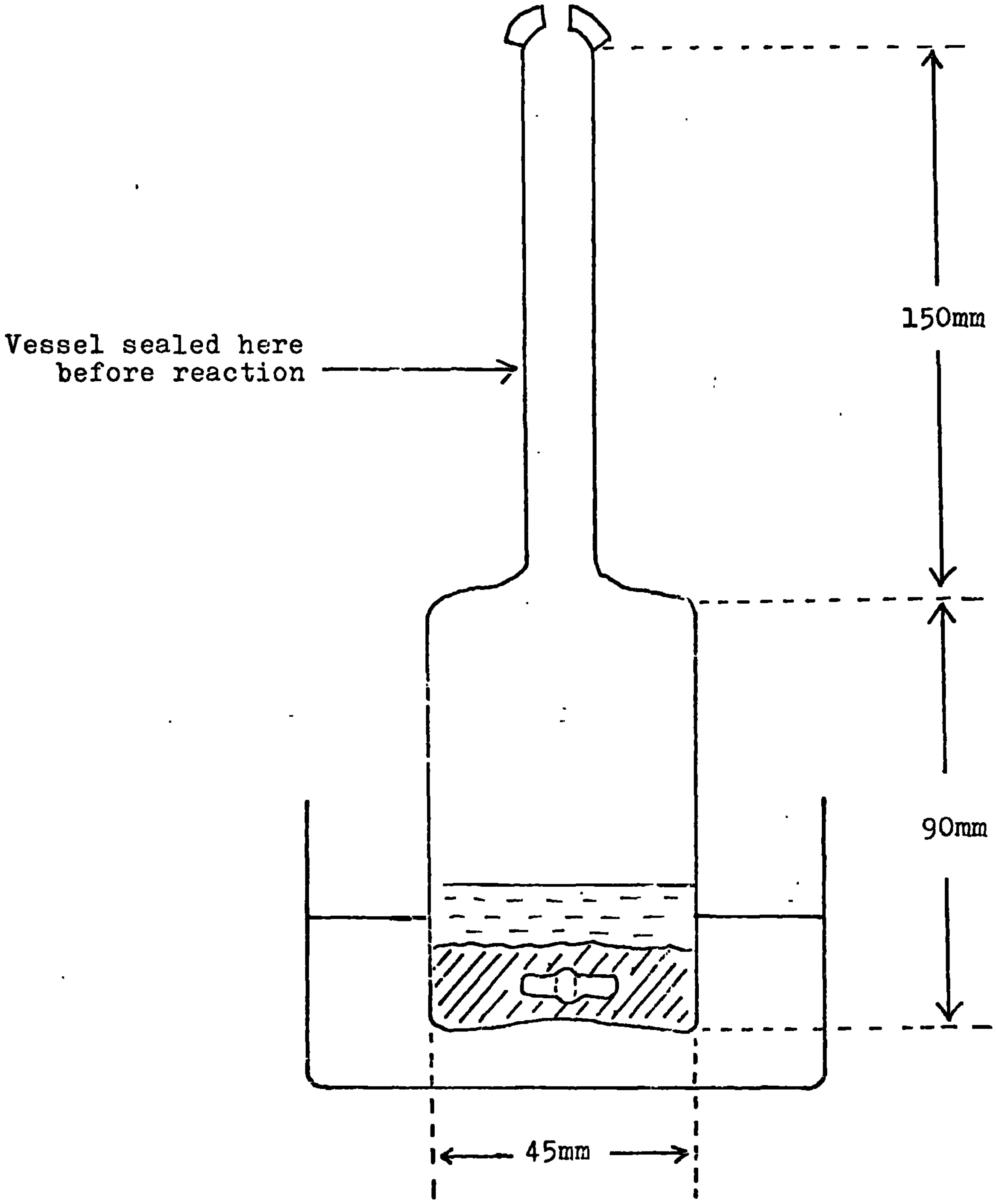


Fig. VI.2 Typical Reaction Vessel Used During 18-crown-6 Polyether Catalysed Fluorinations

(b) Using Sulpholan as a Solvent

Substrate, potassium fluoride, 18-crown-6 polyether, and sulpholan were quickly transferred, under an atmosphere of dry nitrogen gas, to a 50cm^3, B24 necked, conical flask and connected via a gas tap to a variable volume reservoir. The flask was immersed in an oil bath and the reaction allowed to proceed with continuous stirring. Volatile reaction products were again vacuum transferred and identified by G.L.C./M.S.

5.2.2 Pentachloropyridine

Practical details are as described under Sections 5.2.2 (a) and (b). Quantitative reaction conditions are listed in Table VI.9.

Table VI.9

Run	Pentachloro-pyridine	Solvent	Amount KF	Amount 18-C-6	Rctn. Temp.	Rctn. Time
1	2.5g	CH_3CN (10cm^3)	6g	2.5g	100°C	60h
2	2.5g	CH_3CN (10cm^3)	6g	-	100°C	60h
3	2.5g	CH_3CN (150cm^3)	50g	2.5g	Reflux	60h
4	2.5g	Xylene (10cm^3)	12g	2.5g	180°C	100h
5	3g	Sulpholan(20cm^3)	10g	0.5g	150°C	42h
6	3g	Sulpholan(20cm^3)	10g	-	150°C	42h

Run 1 gave 3,5-dichlorotrifluoropyridine as the product, identified by its G.L.C. retention time (column 'A', 150°C, solution in CH_3CN) and its mass spectrum, (M^+ (^{35}Cl), 201 with two chlorine atoms present). Run 2, (a control expt.) did not yield any fluorinated species. Runs 3 and 4 again afforded 3,5-dichlorotrifluoropyridine as the product. Run 5 gave

$C_5Cl_2F_3N$ (1.4g,58%), isolated yield, as did Run 6, (1.3g,54%), the corresponding control experiment.

5.2.3 3,5-dichlorotrifluoropyridine

Practical details are as described under Sections 5.2.1 (a) and (b). Quantitative reaction conditions are listed in Table VI.10.

Table VI.10

Run	3,5-dichloro-trifluoro pyridine	Solvent	Amount KF	Amount 18-C-6	Rctn. Temp.	Rctn. Time
1	2.5g	Xylene (10cm^3)	12g	2.5g	200°C	240h
2	8.3g	Sulpholan(20cm^3)	10g	0.5g	170°C	24h
3	3g	Sulpholan(20cm^3)	10g	0.5g	200°C	90h

In all three cases, starting material was recovered and no more highly fluorinated species were observed.

5.2.4 Tetrachloropyridazine

Practical details are as described under Sections 5.2.1 (a) and (b). Quantitative reaction conditions are given in Table VI.11.

Runs 1 and 4 yielded tetrafluoropyridazine as the sole fluorinated product, identified by G.L.C./M.S. (column 'A', 150°C; solution in acetonitrile). Run 2 (a control expt.) did not yield any fluorinated material, nor did run 3, even though 18-crown-6 polyether was present as catalyst.

Runs 5, 6 and 7 gave tetrafluoropyridazine as the sole fluorinated product in the following isolated yields: 1.05g, 50%; 1.0g, 49%; 0.6g, 29% respectively. Run 8 afforded a totally gaseous product, (M^+,81;$\bar{\nu}$, 1960,1945,1930,1250,1240cm^{-1}).

Table VI.11

Run	Tetrachloro-pyridazine	Solvent	Amount KF	Amount 18-C-6	Rctn. Temp.	Rctn. Time
1	2.5g	CH_3CN (10cm^3)	12g	1.5g	85°C	18h
2	2.5g	CH_3CN (10cm^3)	12g	-	85°C	18h
3	50g	Xylene (200cm^3)	60g	2.5g	Reflux	24h
4	5g	CH_3CN (10cm^3)	12g	0.5g	120°C	24h
5	3g	Sulpholan(25cm^3)	10g	0.5g	100°C	72h
6	3g	Sulpholan(25cm^3)	10g	-	100°C	72h
7	3g	Sulpholan(25cm^3)	10g	0.5g	150°C	42h
8	3g	Sulpholan(25cm^3)	10g	0.5g	150°C	120h

5.2.5 Tetrachloropyrimidine

Practical details are as described under Sections 5.2.1 (a) and (b). Quantitative reaction conditions are given in Table VI.12.

In all cases, 5-chlorotrifluoropyrimidine was obtained as the sole fluorinated product, identified by G.L.C./M.S. (column 'A', 110°C, solution in CH_3CN). The isolated yields of $C_4ClF_3N_2$ for runs 3 and 4 were: 1.3g, 56% and 1g, 44% respectively.

Table VI.12

Run	Tetrachloro-pyrimidine	Solvent	Amount KF	Amount 18-C-6	Rctn. Temp.	Rctn. Time
1	2.5g	CH_3CN (10cm^3)	12g	0.5g	120°C	24h
2	2.5g	CH_3CN (10cm^3)	12g	-	120°C	24h
3	3g	Sulpholan(20cm^3)	10g	0.5g	150°C	42h
4	3g	Sulpholan(20cm^3)	10g	-	150°C	42h

5.2.6 Tetrachloropyrazine

Practical details are as described under Sections 5.2.1 (a) and (b). Quantitative reaction conditions are given in Table VI.13.

Table VI.13

Run	Tetrachloro-pyrazine	Solvent	Amount KF	Amount 18-C-6	Rctn. Temp.	Rctn. Time
1	2.5g	CH_3CN (10cm^3)	12g	1g	120°C	20h
2	2.5g	CH_3CN (10cm^3)	12g	-	120°C	20h
3	3g	Sulpholan(20cm^3)	10g	0.5g	150°C	72h
4	3g	Sulpholan(20cm^3)	10g	-	150°C	72h

Runs 1, 3 and 4 gave tetrafluoropyrazine as the sole fluorinated product, identified by G.L.C./M.S. (column 'A', 50°C, solution in CH_3CN). See infra red spectrum No.20. Run 2 however (a control expt. for Run 1) gave no fluorinated product.

The isolated yields of tetrafluoropyrazine from runs 3 and 4 were: 1.05g, 50% and 1.0g, 48% respectively.

5.3 Fluorination of Halogenated Polycyclics

5.3.1 General Procedure

Substrate, potassium fluoride, 18-crown-6 polyether, and sulpholan were quickly transferred, under an atmosphere of dry nitrogen gas, to a 50cm^3, B24 necked, conical flask and connected via a gas tap to a variable volume reservoir. The flask was immersed in an oil bath and the reaction allowed to proceed with continuous stirring. Quantitative reaction conditions are given in Table VI.14.

When cool, the contents of the flask were poured onto water (3 litres approx.) and stirred vigorously, the liquor was allowed to settle overnight. Solid material was filtered off under suction ("hyflo" pad) and the residue was refluxed with methylene chloride ($250cm^3$ approx.) for 1 hour. Insolubles were filtered off, and the filtrate dried over $MgSO_4$. Removal of $MgSO_4$ and solvent left residues ranging from green to deep red to black in colour.

5.3.2 Decachlorobiphenyl

Run 1 of Table VI.14 yielded a black residue from which only a trace of white solid could be sublimed (150°C/0.005mm Hg), which was inadequate for further investigation. Run 2 of Table VI.14 afforded a deep red residue from which no sublimate could be obtained. A mass spectrum of the residue indicated a complex mixture of halogenated species with the most prominent parent peaks at $^m/e = 396$ with seven chlorine atoms, $^m/e = 380$, with six chlorine atoms and $^m/e = 364$ with five chlorine atoms. An I.R. Spectrum indicated C-H ($\bar{\nu}$:2960, $2920cm^{-1}$), C = C ($\bar{\nu}$: $1615cm^{-1}$) environments. A proton n.m.r. spectrum (solution in D6-acetone) showed a single resonance at $\delta = 3.0$ p.p.m. relative to external T.M.S. See discussion, Ch.IV.

5.3.3 Decachlorofluorene

Run 3 of Table VI.14 gave a purple-black residue, from which a yellow solid (1g approx.) M.p. 71-75°C, was sublimed (140°C/0.005mm Hg). A mass spectrum of this solid indicated it to be a mixture of chlorofluorofluorenes, i.e. parent peaks at $^m/e = 378$, with two chlorine atoms; $^m/e = 362$, with one chlorine atom; and $^m/e = 346$, chlorine absent. ($C_{13}Cl_2F_8$ requires $^m/e = 378$; $C_{13}ClF_9$ requires $^m/e = 362$; $C_{13}F_{10}$ requires $^m/e = 346$).

5.3.4 Octachlorodibenzo(b,d)thiophen

Run 4 of Table VI.14 afforded a dark green solid, from which a sublimate could not be obtained. A mass spectrum of the residue indicated a complex mixture of halogenated species, with the most prominent parent peaks at $^{m}/e = 390$, with five chlorine atoms; $^{m}/e = 374$, with five chlorine atoms; and $^{m}/e = 358$, with four chlorine atoms. An I.R. spectrum indicated C-H ($\tilde{\nu}$:2960, 2920cm^{-1}), C = C ($\tilde{\nu}$:1590, 1560cm^{-1}), C-F and C-Cl environments. A proton n.m.r. spectrum (solution in D6-acetone) showed a single resonance at $\delta = 3.13$ p.p.m. relative to external T.M.S. See discussion, Ch.IV.

5.3.5 Octachlorodibenzo(b,d)furan

Run 5 of Table VI.14 yielded a black residue, from which a sublimate could not be obtained. A mass spectrum of the residue indicated a complex mixture of halogenated species, with the most prominent parent peaks at $^{m}/e = 374$, with six chlorine atoms and $^{m}/e = 358$ with five chlorine atoms. An I.R. spectrum indicated C-H ($\tilde{\nu}$:2960, 2920cm^{-1}), C = C ($\tilde{\nu}$: 1615cm^{-1}) and C-Cl environments. A proton n.m.r. spectrum (solution in D6-acetone) showed a single resonance at $\delta = 3.09$ p.p.m. relative to external T.M.S. See discussion, Ch.IV.

5.3.6 Decafluorobiphenyl

Run 6, Table VI.14 yielded a deep red, involatile residue. The mass spectrum of this residue showed it to contain high molecular weight material with $^{m}/e > 650$. A peak at $^{m}/e = 334$ was not observed, which would correspond to unreacted starting material ($C_{12}F_{10}$ requires $^{m}/e = 334$). No further investigation of the residue was carried out.

Table VI.14

18-crown-6 Catalysed Fluorinations of Perhalogeno Polycyclics

Run	Substrate	Amount of Substrate	Amount of KF	Amount of 18-C-6	Volume of Sulpholan	Reaction Temp.	Reaction Time
1	Decachloro-biphenyl	3g	15g	0.7g	20cm^3	180°C	71h
2	Decachloro-biphenyl	3g	20g	1g	20cm^3	180°C	115h
3	Decachloro-fluorene	2.4g	10g	0.5g	25cm^3	170°C	24h
4	Octachloro-dibenzo(b,d) thiophen	3g	15g	0.7g	25cm^3	200°C	68h
5	Octachloro-dibenzo(b,d) furan	1.5g	10g	1g	25cm^3	140°C	72h
6	Decafluoro-biphenyl	2g	15g	0.5g	25cm^3	150°C	90h

PART II

SOME POLYFLUOROCYCLOALKENE DIMERS

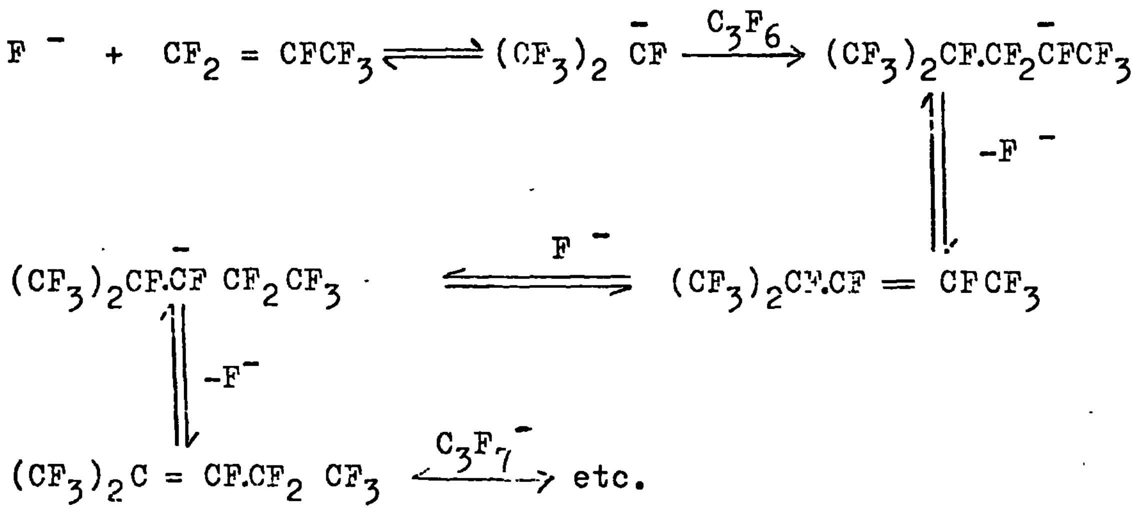
INTRODUCTION

CHAPTER VII

Fluoride Ion Induced Oligomerisation of Perfluorocycloalkenes

1. Introduction

Polyfluoroalkenes are susceptible to nucleophilic attack, and theoretically, fluoride ion induced polymerisations are possible. However, because side chain termination is a favourably competing reaction with polymerisation, only oligomers are formed. e.g. hexafluoropropene readily forms dimers and trimers in the presence of fluoride ion[138,139,140] and a possible reaction scheme is shown below



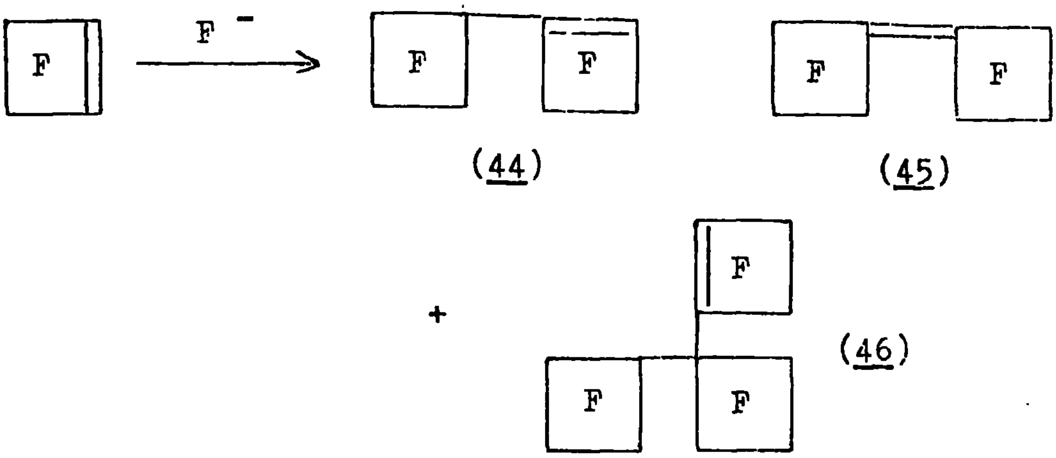
An olefin containing more than three linear carbon atoms will undergo double bond migration rather than self condensation, the initial carbanion eliminating fluoride ion and not attacking another molecule of olefin. In olefins where β-elimination of F^- is not possible, or self condensation does not readily occur, highly branched internally unsaturated oligomers are formed.

Perfluoroisobutene[139] and octafluorobut-2-ene[147] have been observed to form dimers. Tetrafluoroethylene forms a mixture of oligiomers[141,142] ranging from tetramer to heptamer, the relative proportion of each depending upon the experimental conditions used. Oligomers of acyclic fluoro olefins have been described elsewhere,[143] and the remainder of this introduction will be concerned with the oligomers of cyclic fluoro olefins.

2. Oligomers of Cyclic Fluoro olefins

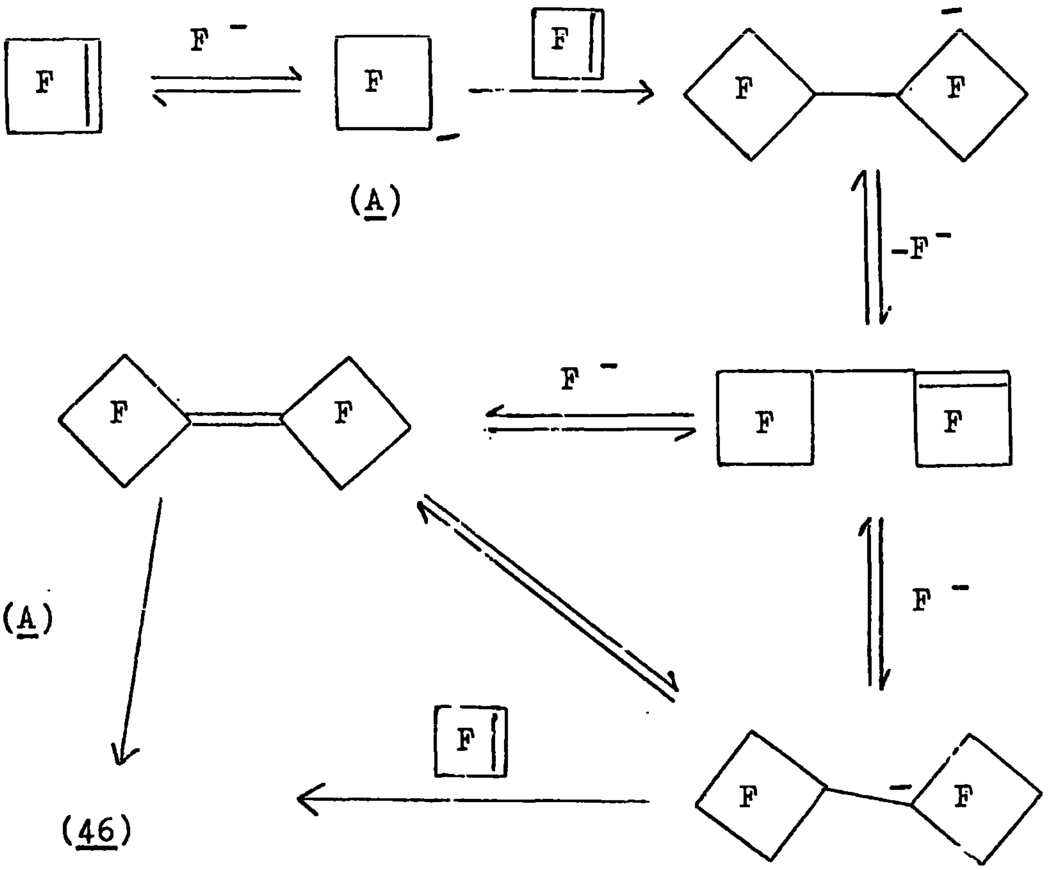
2.1 Perfluorocyclobutene

The oligomerisation of perfluorocyclobutene using different initiators has been studied.[144,145,146] A reaction with fluoride ion in D.M.F.[145] gave two dimers (44) and (45), along with a trimer (46), whereas a reaction in sulpholan at 125°C has been observed to give solely the trimer in 67% yield.[146]



(44) (45) (46)

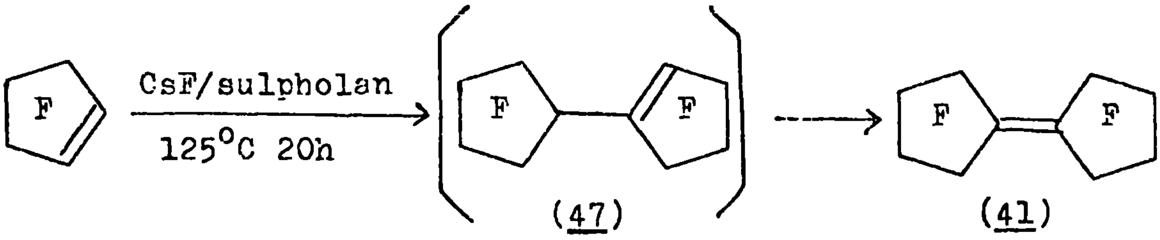
Chambers and co-workers[146] varified the structure of (46) using N.M.R. techniques, and suggested the following reaction mechanism for its formation:



More recently, Clarke[148] has published E.S.C.A. data which also corresponds to (46) and confirms Chambers' results.

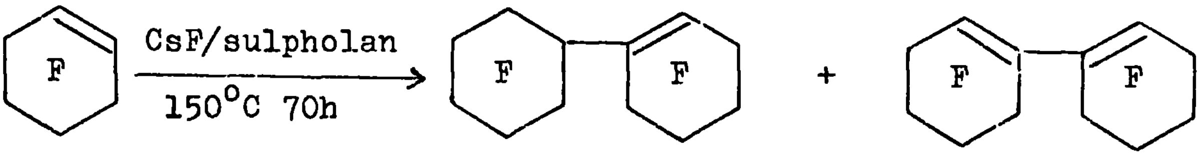
2.2 Perfluorocyclopentene

Perfluorocyclopentene has been shown to undergo fluoride ion induced dimerisation in sulpholan.[146] The expected product (47) undergoes rearrangement, giving the more thermodynamically stable (41).



2.3 Perfluorocyclohexene

Oligomerisation of perfluorocyclohexene is relatively difficult, and unlike perfluorocyclopentene, forms an unsymmetrical dimer (42).[146] Some defluorination has been observed during this reaction, giving (48).



(42) (48)

DISCUSSION

CHAPTER VIII

Reactions of Some Polyfluorocycloalkene Oligomers

1. General Introduction

The chemistry of perfluorobi(cyclopentylidene) (41), and related derivatives is potentially very interesting, as, unlike common fluoro olefins, there is no readily displaceable group attached directly to the double bond. Hence, reactions may proceed with addition, or with intramolecular rearrangement, with or without ring opening.

Photolysis and pyrolysis reactions also offer some fascinating possibilities for rearrangement and defluorination.

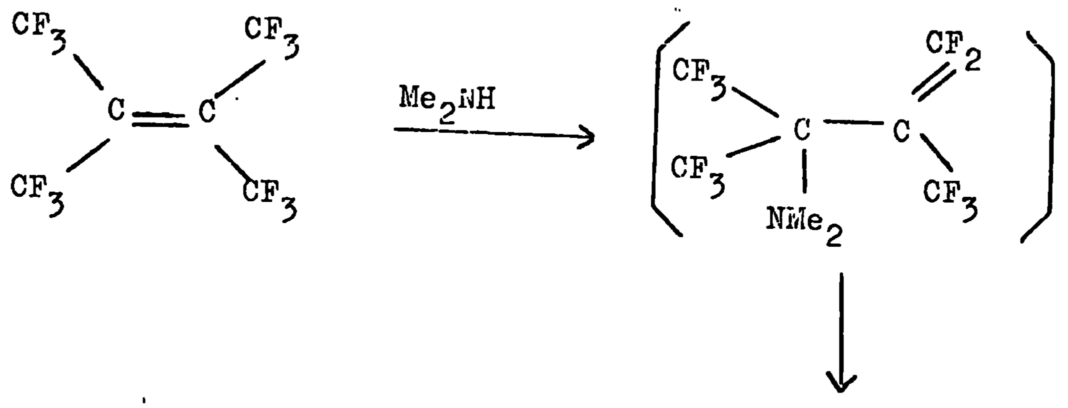
The following work was undertaken as a preliminary investigation of the reactivity of the oligiomeric species which were available.

2. Nucleophilic Substitution Reactions of Perfluorobi-(cyclopentylidene) (41)

2.1 Introduction

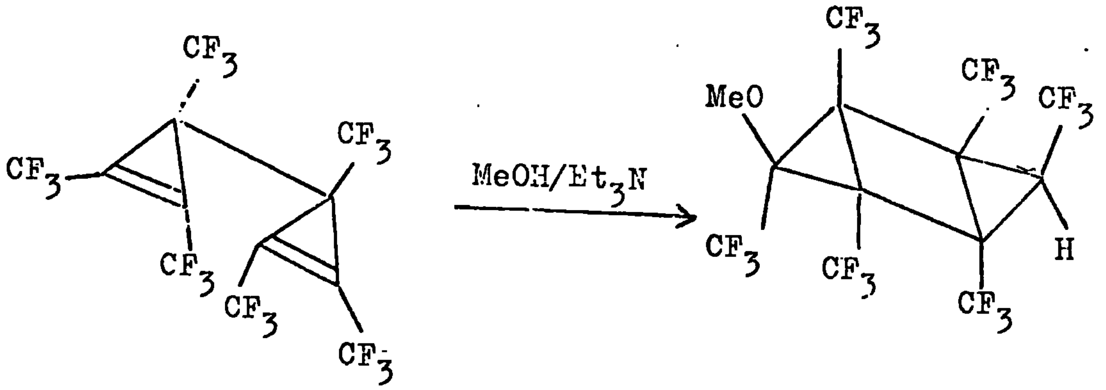
Ionic reactions of fluoro olefins have been reviewed,[151] and consequently, only work directly related to those reactions carried out by the author will be dealt with here. Nucleophilic substitution reactions of some perfluorotetraalkyl olefins have been described[143,152,153,154] and more recently, Tatlow and co-workers[153] have reported some ionic reactions of (70), which complement those described in Section 2.2.1 of this chapter.

e.g.

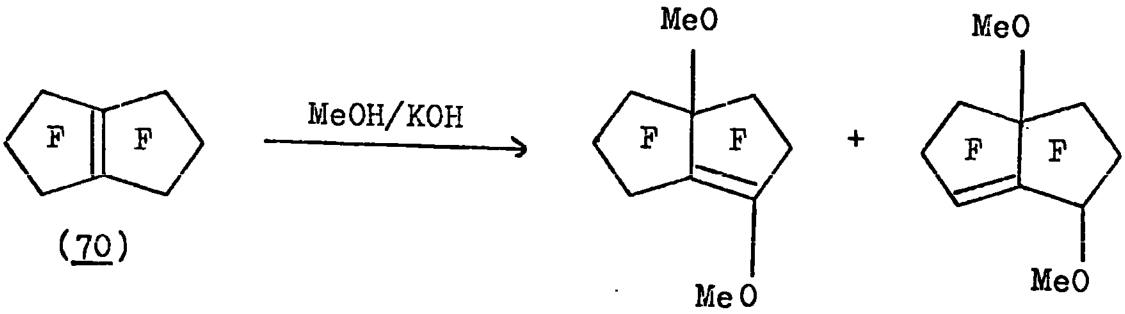


(Ref:152)

further reaction,
giving complex product



(Ref:154)



(70)

(Ref:153)

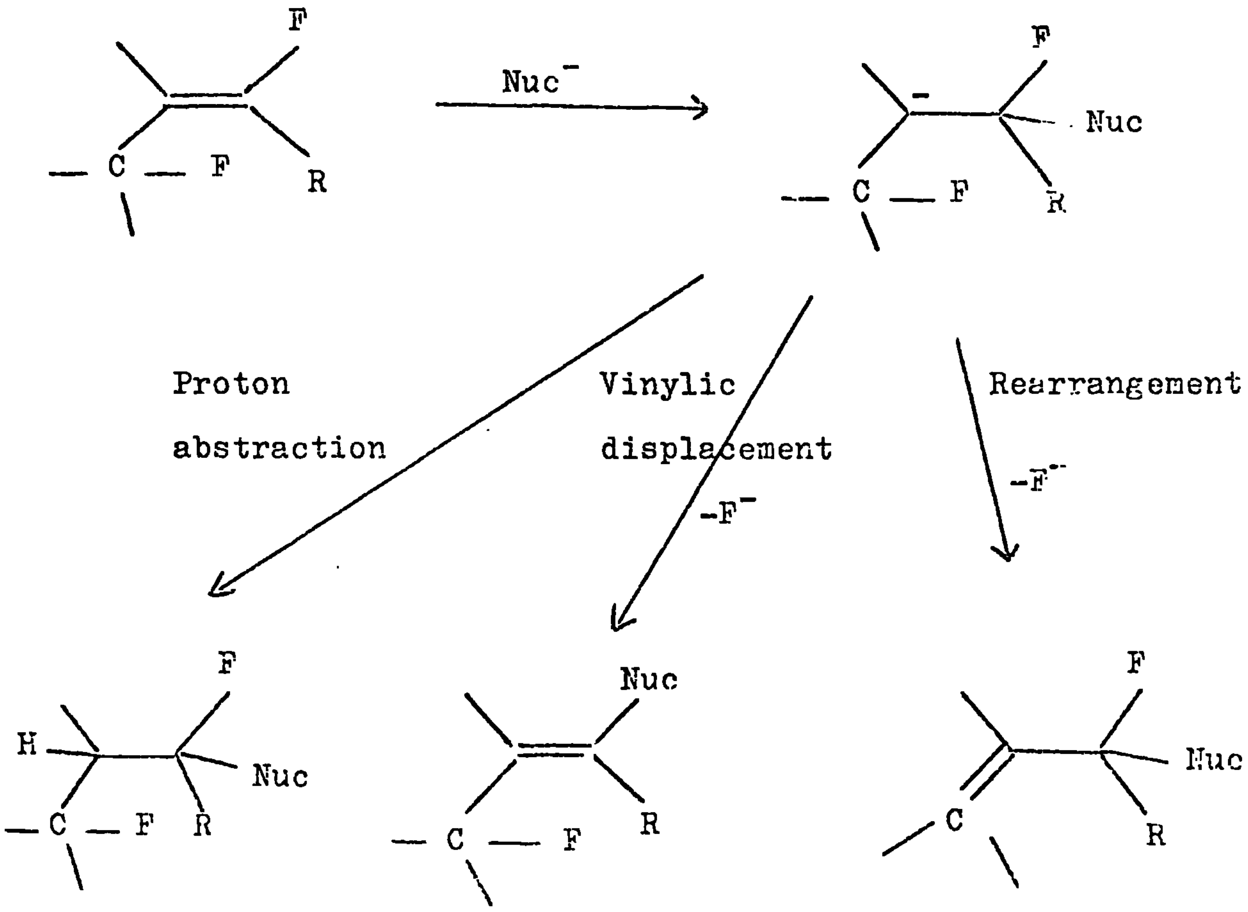
In general, there are three distinct reaction pathways open to a fluoro olefin undergoing nucleophilic substitution (reaction), viz:

(i) Addition of the nuclophile, followed by abstraction of a proton from the solvent, by the resulting carbanion.

(ii) Direct vinylic displacement of fluorine by the nucleophile.

(iii) Displacement of fluorine by the nucleophile, with rearrangement.

These three possibilities are illustrated in the reaction scheme shown below:



2.2 Reaction with Methoxide Ion

2.2.1 Under Relatively Controlled Conditions

When (<u>41</u>) was reacted with sodium methoxide in methanol under reflux for 24 hours, a colourless liquid comprising two main products was ultimately isolated. Other minor products ($<$10% product total) corresponded (G.L.C./M.S.) to mono- and tri-methoxy substituted derivatives of (<u>41</u>).

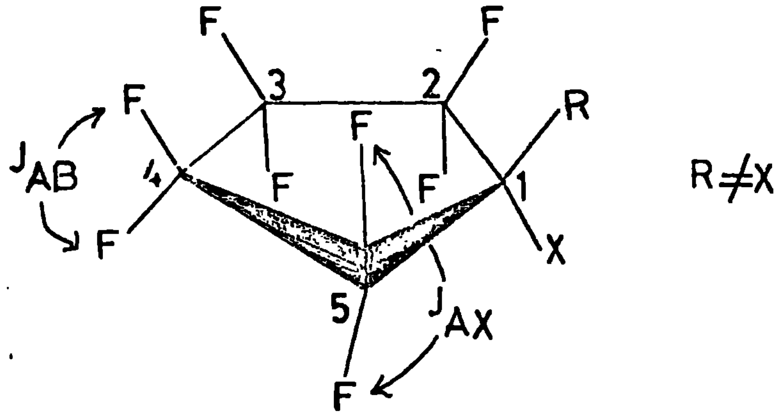
The major products were separated by preparative G.L.C. to give two colourless liquids (<u>49</u>) and (<u>50</u>) (B.P. $>$ 200°C) which were identified as follows:

Elemental analysis and mass spectral data of both compounds were consistent with a molecular formula of $C_{12}H_6O_2F_{14}$. i.e. dimethoxy substituted derivatives of (<u>41</u>).

Nuclear magnetic resonance data was recorded for both compounds, but only one set could be completely assigned. A detailed account of the analysis of the ^{19}F n.m.r. data of (<u>49</u>) is included here, as similar arguments for structure elucidation will be used in future sections of this chapter.

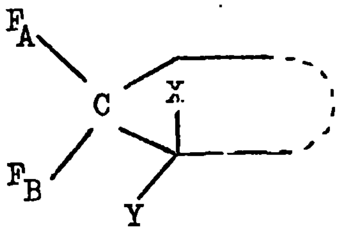
P.M.R. spectra of both components showed two single resonances in the $-OCH_3$ region (i.e. δ = 3 to 4 p.p.m.) One signal, (δ = 3.1 p.p.m.) common to both spectra was ultimately assigned to a tertiary methoxy group.

The simpler ^{19}F n.m.r. spectrum (i.e. that of (<u>49</u>)) showed three broadened singlets in the $-CF_2-$ region, along with eight other signals which were eventually assigned to AB and AX doublets. Fig. VIII.1 illustrates this spectrum, and shows the typical AB/AX signals obtained for compounds of this type. i.e.



(60)

N.B. The $-CF_2-$ groups 2 and 5 are equivalent, as are 3 and 4. Figures of approximately 250Hz have been observed for compounds of the general type (60a) exhibiting AB coupling.[155,156]

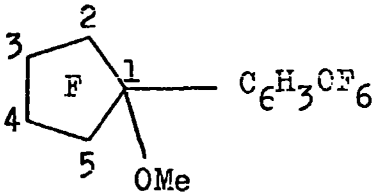


(60a)

i.e. $F_A \neq F_B$

$X \neq Y$

The ^{19}F n.m.r. spectrum of (49) gave J_{AB} and J_{AX} values of approximately 250Hz and were assigned on the basis of the information available for (49) as shown here:



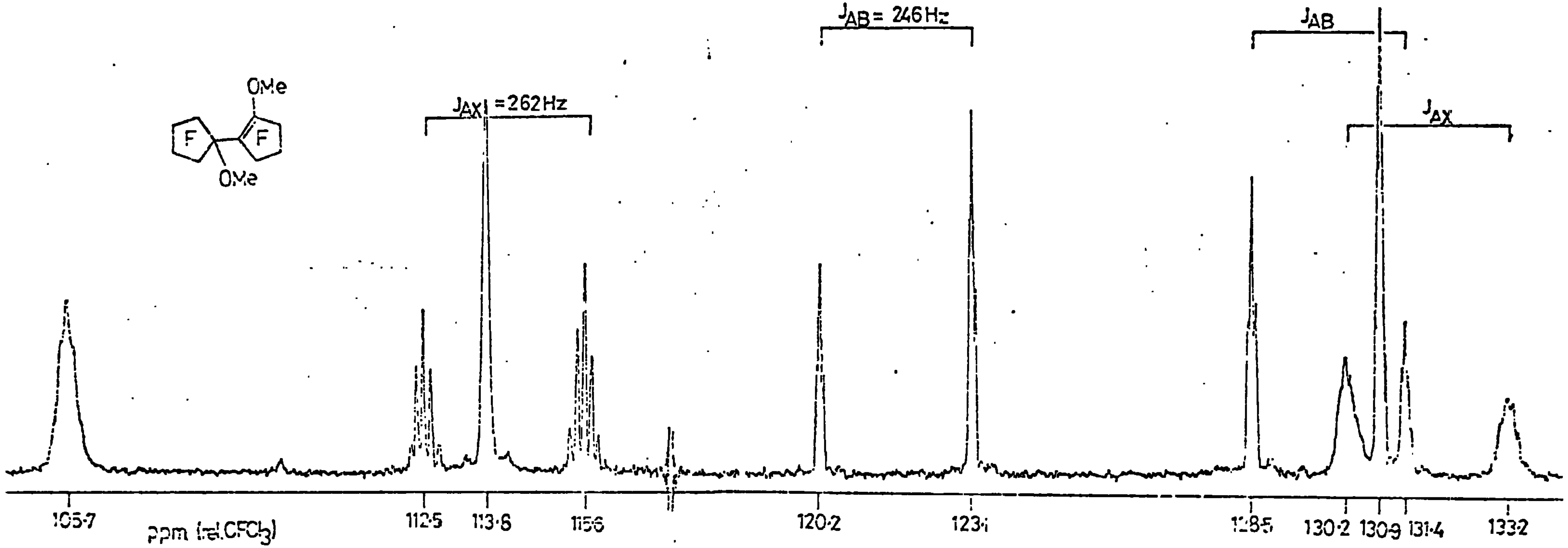
(49)

$(CF_2)_{2\ \&\ 5}$ J_{AX} = 262Hz

$(CF_2)_{3\ \&\ 4}$ J_{AB} = 246Hz

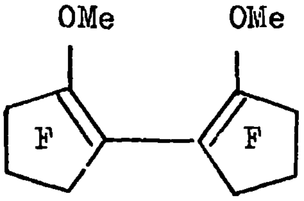
The distinction between the AX and AB doublets, and their

Fig. VIII.1 A typical ^{19}F n.m.r. spectrum of a perfluorobi(cyclopentylidene) derivative illustrating the AX/AB signals observed for systems of this type.



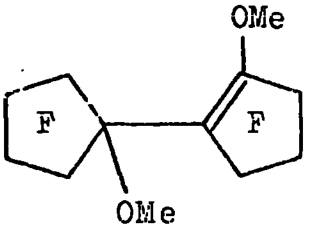
assignments was made upon the basis of their relative proximities to C_1. The $-CF_2-$ groups 2 and 5 are closer to the disturbing environments, and hence exhibit an AX effect, whereas the $-CF_2-$ groups 3 and 4, which are further removed from the disturbing environment exhibit an AB effect.

No vinylic or tertiary fluorine resonances were observed, only three broadened singlets of equal intensity in the $-CF_2-$ region at 108.3, 116.7 and 134.2 p.p.m. (relative to ext. $CFCl_3$). The ^{19}F n.m.r. spectrum of (58) has been observed[150] to exhibit three single resonances at 107.2, 116.3 and 131.9 p.p.m.



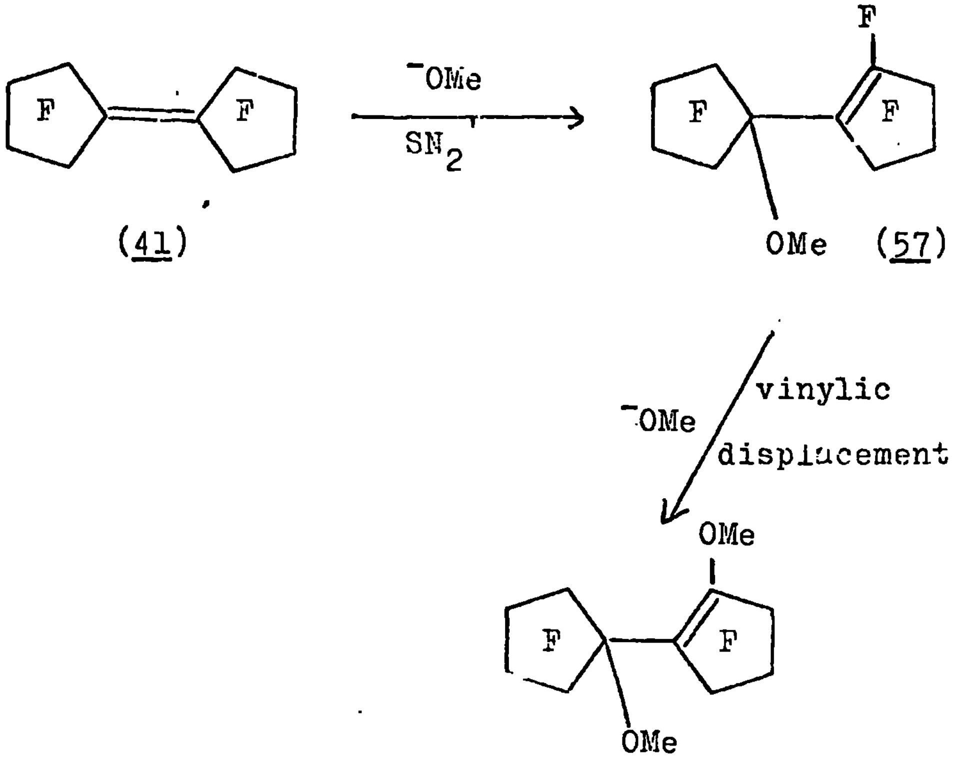
(58)

i.e. comparison of these values (recorded for (58)) with those obtained for (49) confirms the presence of a 2-methoxyhexafluorocyclopentyl group, and as will be seen later, difluoromethylene groups of this type did not usually show any significant coupling. The n.m.r. data and mass spectral/analytical data can only be consistent with structure (49)., below:



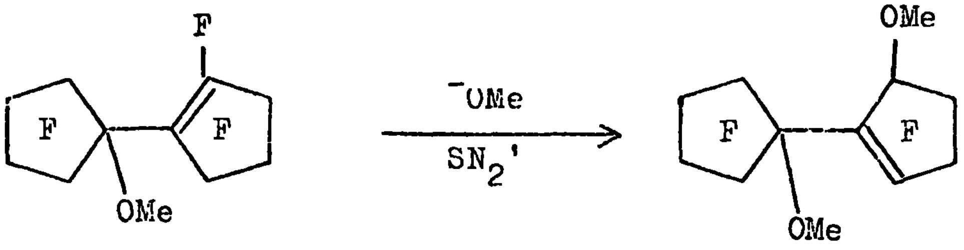
(49)

This derivative may be thought to be formed via two distinct nucleophilic substitution reactions. Initially (41) undergoes an SN_2' type reaction with $^-$OMe, followed directly by a vinylic displacement of F^- by $^-$OMe. i.e.



(41) (57) (49)

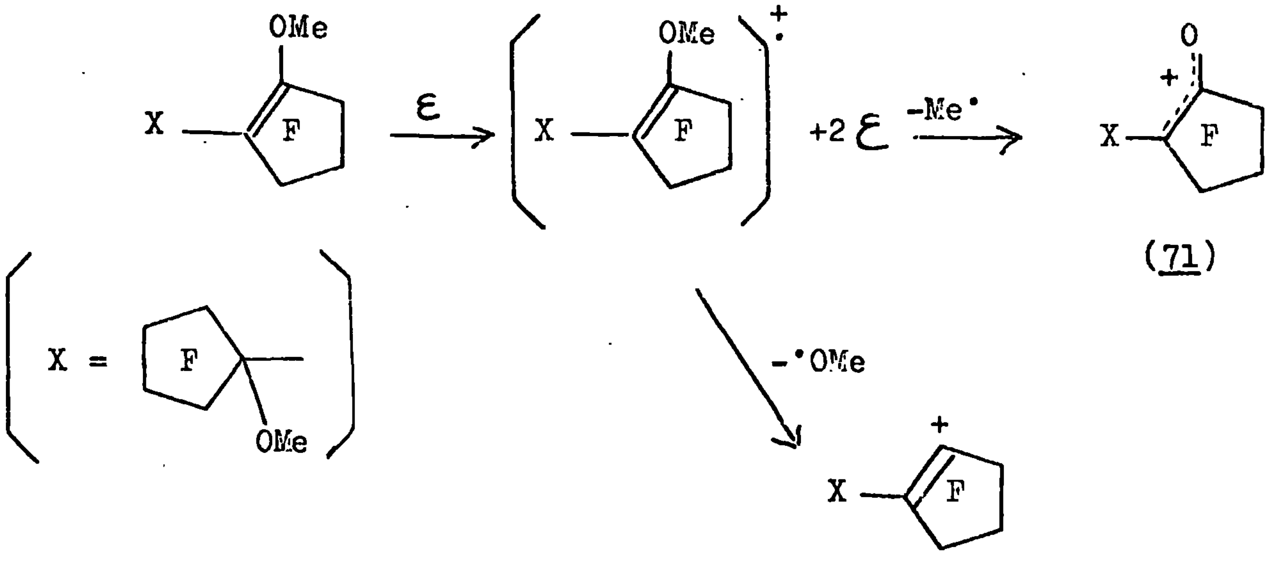
The second dimethoxy derivative was identified (see below) as (50) and may be formed via a second SN_2' type reaction occurring between (57) and $^-$OMe. i.e.



(57) (50)

Although a complete assignment of the ^{19}F n.m.r. data obtained for (50) was not carried out, its structure was derived on the following basis:

(A) Comparison of its Mass spectral fragmentation pattern with that of (49): i.e. the mass spectrum of (49) showed a parent peak (P), of relative intensity (r.i.) = 1; P-15, the base peak of r.i. = 5.66 (loss of $-CH_3$); P-19 of r.i. = 1.21 (loss of -F); and P-31 of r.i. = 0.92 (loss of $-OCH_3$) as its four highest $^m/e$ values. It might be expected that loss of the vinylic group (-OMe in this case), a ucually favourable fragmentation process (the +ve charge being stabilised by the π-electron system) may be predominant. However, as can be seen this group is not lost as readily as $-CH_3$ alone. The relatively low abundance of $^m/e$ = P-31 and the occurrence of the base peak at $^m/e$ = P-15 may be accounted for in terms of the cations (71) and (72), formed in the fragmentation processes outlined below:

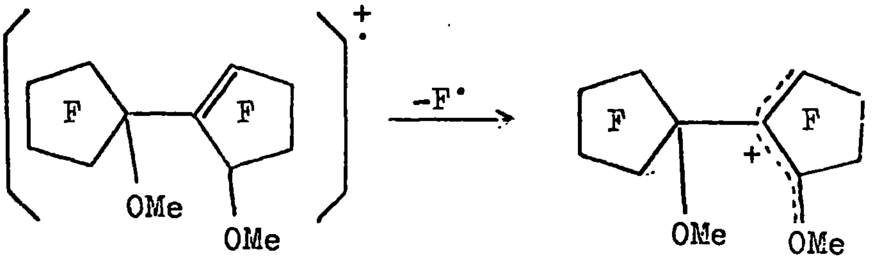


(71)

(72)

The cation (71) formed by loss of $^{\bullet}$Me is stabilised across the π - system and the lone pair of the oxygen: a much more favourable situation than if $^{\bullet}$OMe were lost, giving (72), which leaves only the π - system to deal with the resulting positive charge.

If we now consider the mass spectrum of (50), the corresponding $^{m}/e$ values and relative intensities are: P, r.i = 1; P-15, r.i = 3.3; P-19, r.i = 11.1; and P-31, r.i = 5.43. We now see that although similar losses to those observed for (49) occur, by far the most favourable process is loss of a fluorine atom.



(73)

Fluorine atoms in a tertiary position or occupying the same carbon atom as a methoxy group are easily hydrolysed and it is probable that fluorine atoms so placed would be easily "cracked off" in a mass spectrometer. i.e. it is the "tertiary" fluorine atom that is probably lost, giving rise to the stabilised cation (73). (N.B. a process of this type is not possible for (49)). These relative fragmentation processes of (49) and (50) are shown in figures VIII.2 and VIII.3 respectively.

Fig. VIII.2 Primary Fragmentation Routes of (49)

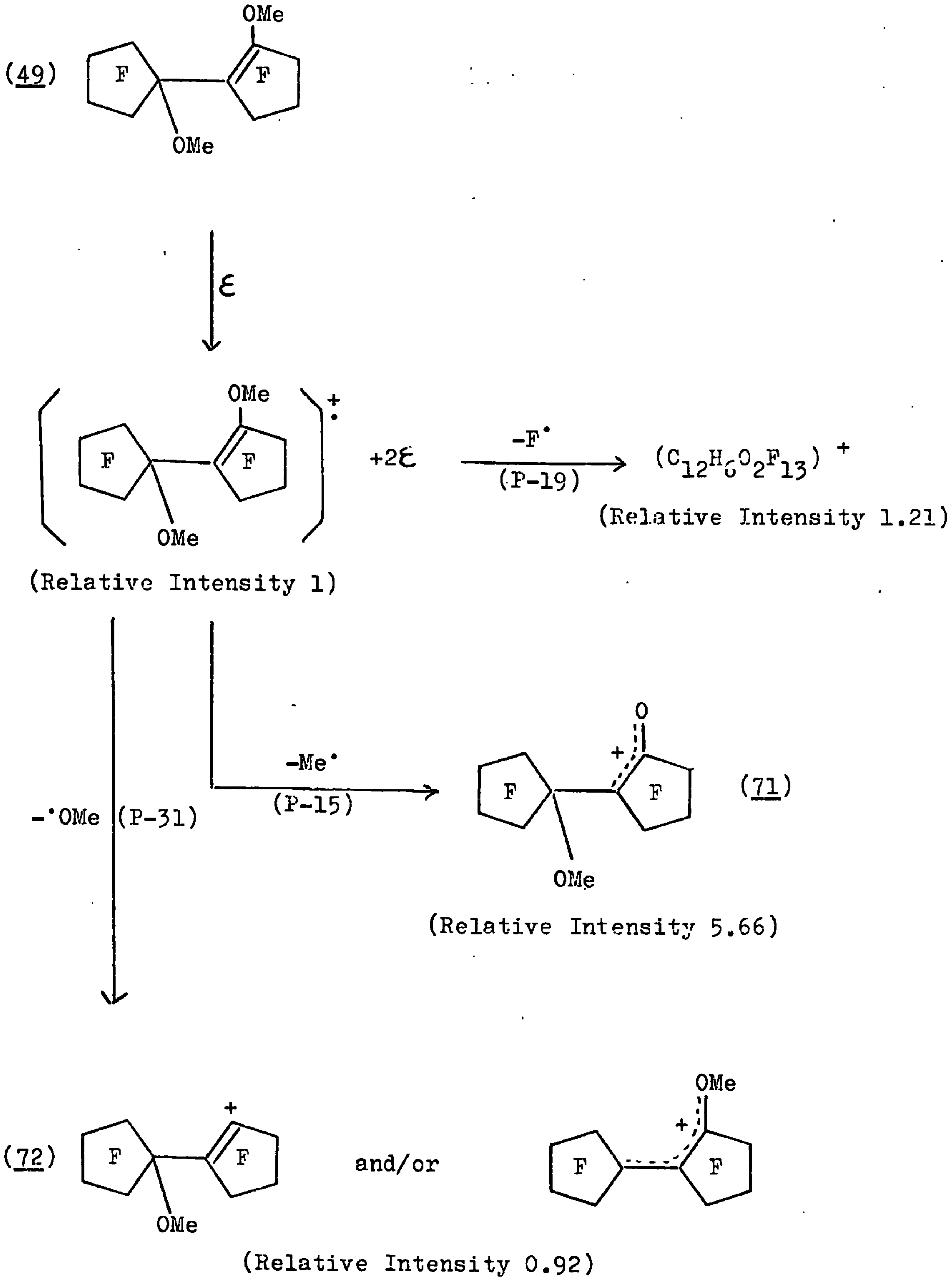
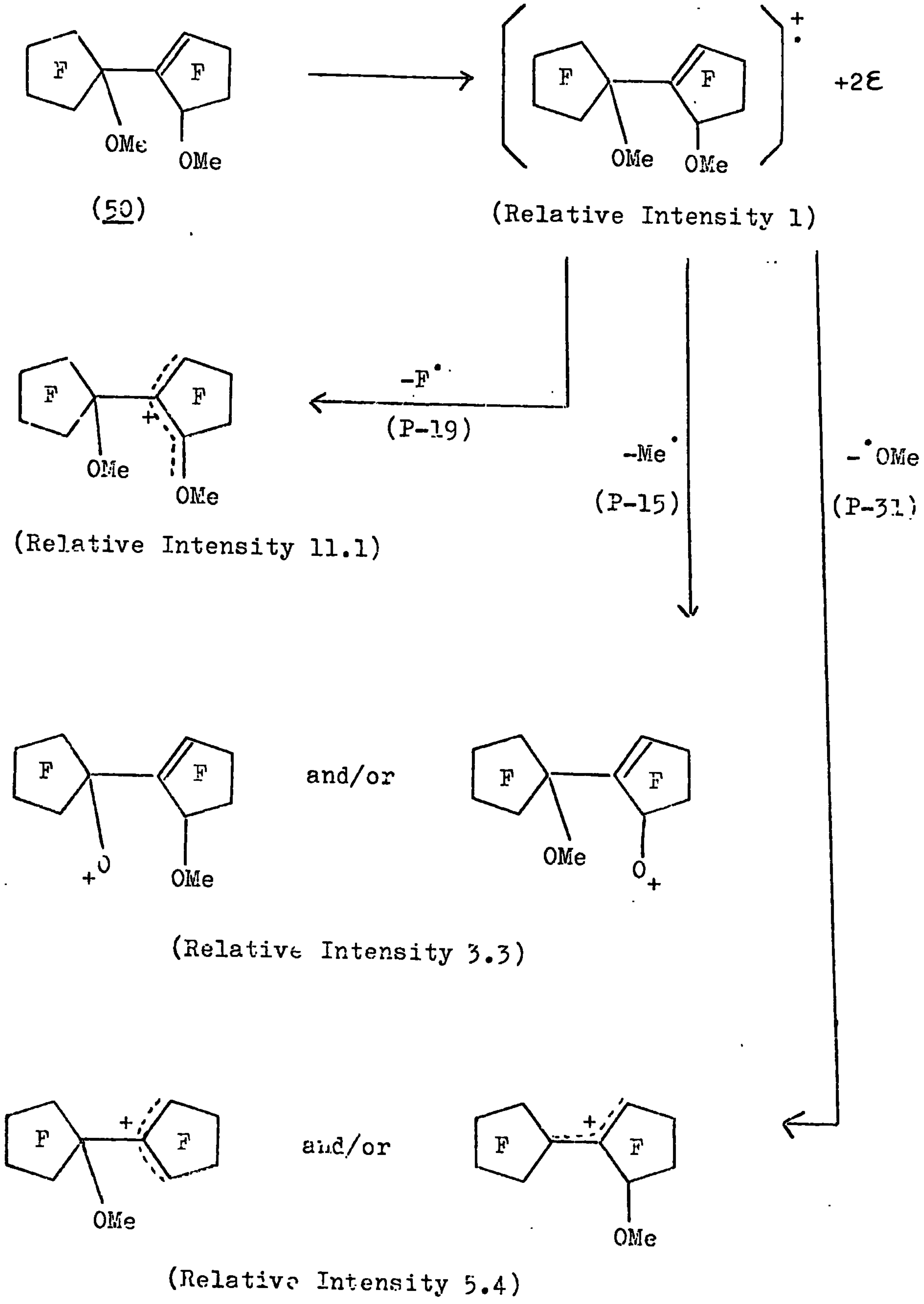


Fig. VIII.3 Primary Fragmentation Routes of (50)



(B) Comparison of its P.M.R. spectrum with that of (49)

Two signals were observed in the P.M.R. spectrum of (49), viz. δ = 3.09 p.p.m. (tertiary -OMe) and δ = 3.80 p.p.m. (vinylic $-OCH_3$). Two signals were also observed in the P.M.R. spectrum of (50), one of which was identical to that observed for (49), i.e. δ = 3.09 p.p.m., the tertiary methoxy group attached to the perfluorocyclopentyl ring. The second signal was at δ = 3.35 p.p.m., i.e. moved downfield, as may be expected from the relative change in environment, vinylic to tertiary.

(C) Comparison of its ^{19}F n.m.r. spectrum with that of (49)

Although very complex, the ^{19}F n.m.r. spectrum of (50) had two features which complemented the information in A and B above, and helped to confirm the structure of (50), viz: the occurrence of a signal in the vinylic fluorine region (i.e. approx. 107 p.p.m.) which integrated to one fluorine atom, and the occurrence of signals which resembled the AB/AX doublets which were observed in the spectrum of (49).

2.2.2 Exhaustive Methoxylation

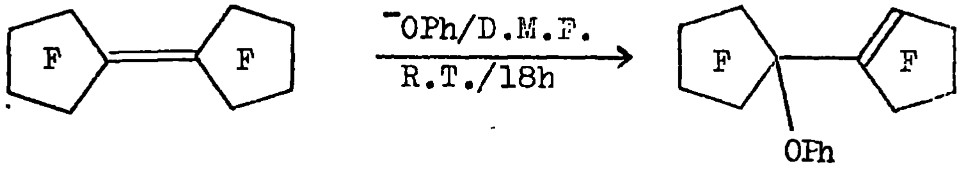
When (41) was stirred with methoxide ion over an extended reaction time, a pale yellow liquid which corresponded (G.L.C./M.S.) to a mixture of tri- and tetra-methoxy substituted derivatives of (41) was obtained (i.e. P = 460 and P = 472; $C_{13}H_9O_3F_{13}$ requires $^m/e$ = 460, and $C_{14}H_{12}O_4F_{12}$ requires $^m/e$ = 472). No attempt was made to separate and characterise these derivatives; they were used as a mixture in a subsequent hydrolysis reaction, described in Section 4.3.3.

A number of possibilities exist for the structures of these polymethoxy derivatives, depending upon whether the reaction has proceeded via S_N2', or vinylic substitution, or both, but these cannot be assigned.

2.3 Reactions with Other Nucleophiles

2.3.1 Phenoxide Ion in Dimethylformamide

When (41) was stirred with a solution of sodium phenoxide in dimethylformamide, a mixture of products was obtained. Although no one pure derivative could be isolated and characterised, sufficient spectroscopic data was obtained to suggest that the predominent reaction was mono-nucleophilic substitution of phenoxide into the system, via an S_N2' type displacement. i.e.



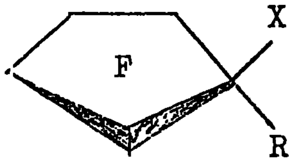
(41) (51)

The structure of (51) was arrived at on the following basis:

(i) G.L.C./M.S. showed the major component of the reaction product to have a molecular weight of 498 ((51) requires $^m/e$ = 458) and fragments corresponding to losses of -Ph and -OPh were evident in the spectrum.

(ii) A ^{19}F n.m.r. spectrum of (51) showed the basic characteristics of a compound with a structure of the type

(60). i.e. 4 doublets with J ~ 260Hz corresponding to AX/AB type systems (see also fig VIII.1).



(60)

Also present were resonances corresponding to a vinylic fluorine environment, and three broadened singlets in the $-CF_2-$ region. Structure (51) is the only one which is consistent with all of the available spectroscopic data.

Separation and purification of (51) by a variety of means, e.g. molecular distillation, preparative scale V.P.C., resulted in the formation of a resinous type material. After a considerable number of attempts, further efforts to isolate (51) pure were abandoned.

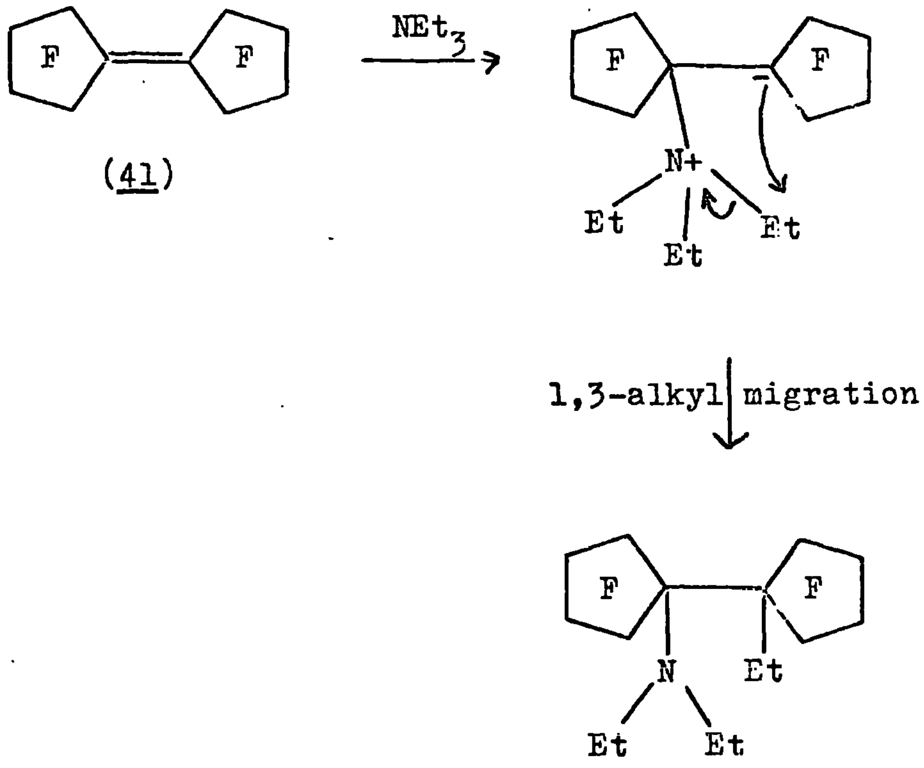
2.3.2 Triethylamine in Tetraglyme

When (41) was stirred with triethylamine in tetraglyme, a multicomponent mixture was obtained, and once again, as in the case of the phenoxide reaction, a pure derivative could not be isolated. In fact, identification of the major product was not achieved. The following section contains some tentative suggestions as to the structural features of the major product, based upon the spectroscopic data which was recorded.

The mass spectrum of the major component gave a molecular weight of 448, and the most favourable fragmentation process was shown (low eV spectrum) to follow a sequence which involved losses of $^m/e = 19$ (F), $^m/e = 29$ (C_2H_5), and $^m/e = 48$ (C_2H_5F). The base peak occurred at $^m/e = 253$ (i.e. a loss of 195). The even molecular weight of the parent peak showed that the compound contained either NO nitrogen, or an even number of nitrogen atoms (unlikely because of consideration of molecular weight).

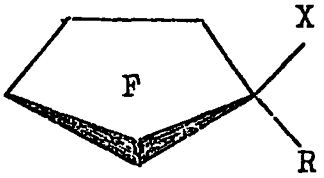
i.e. the product probably contains an ethyl group, but does not appear to contain nitrogen. An ethyl group may be introduced into the molecule via a 1,3-alkyl migration, following an initial nucleophilic attack of NEt_3 upon (41).

i.e.


(41)

An infra red spectrum of the product indicated the presence of a double bond in the system ($\bar{\nu} \sim 1720 cm^{-1}$) along with an alkyl group ($\bar{\nu}$ 2800 - 3000cm^{-1}). i.e. further evidence towards the presence of an ethyl group, along with the possible retention of unsaturation in the molecule.

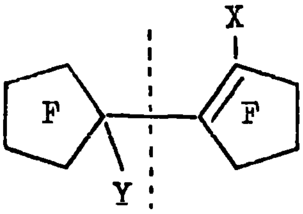
A ^{19}F n.m.r. spectrum gave resonances which once again corresponded to a structure of the type (60).



(60)

i.e. the presence of 4 AB/AX doublets with J ~ 260Hz. Also observed were three broadened singlets in the $-CF_2-$ region, but no resonances corresponding to either vinylic -CF or tertiary -CF were seen. (N.B. integration of $-CF_2-$ gps. to each AX/AB doublet was fairly good). Unfortunately, it was not possible to obtain a satisfactory P.M.R. spectrum of the product.

Collecting together the available data leads to the derivation of a structure of the type (61), the left hand side of this molecule being virtually confirmed from the n.m.r. data.

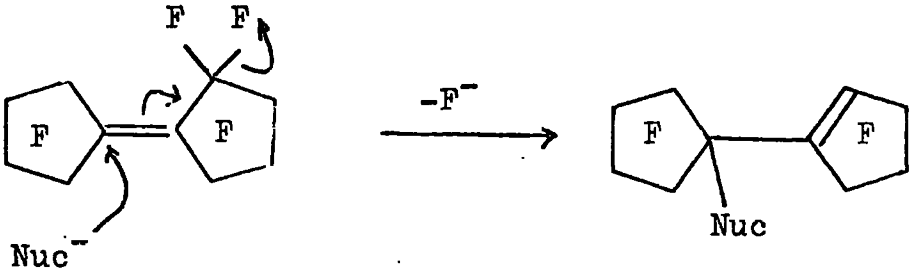


(61)

However, on this basis, if either X or Y is taken as being $-C_2H_5$, a residual mass of 33 is left to correspond to the second substituent ($-CH_2F$?). Further work in this area needs to be undertaken in an attempt to elucidate the structure of the product. The possibility of some interesting rearrangements exists, as indicated by the limited data recorded so far.

2.4 Conclusions

Although (41) does not possess a readily replaceable vinylic group, it does react with nucleophiles under relatively mild conditions. The reactions which have been investigated are by no means simple; rearrangement usually occurring along with substituion. An initial SN_2' type process appears to be the most favourable reaction route, although when triethylamine is the nucleophile, this is not wholly certain.



The possible occurrence of polysubstitution has been illustrated; however we now have two competing reactions, viz: vinylic substitution versus SN_2' type replacement and this can lead to complex multicomponent product formation as illustrated in the polymethoxylation reaction. Separation and identification of products of this type does not seem to be a practically viable proposition.

3. Addition Reactions

3.1 Introduction

As well as undergoing ionic addition via nucleophilic attack, fluoro olefins have also been observed to add via electrophilic reaction. The π -system of fluoro olefins has a relatively low electron density, and this renders them resistant to electrophilic attack. However reactions involving the addtion of halogens, hydrogen halides and alkyl halides in the presence of Lewis acid are thought to follow an electrophilic process.

Non ionic additions to fluoro olefins are known, and a probable free radical mechanism would be

initiation

$$X - Y \xrightarrow{\text{initiator}} X^{\bullet} + Y - \text{init.}$$

addition

$$X^{\bullet} + R_2C = CR_2 \longrightarrow X - R_2C - {}^{\bullet}CR_2$$

propagation

$$X - CR_2 - {}^{\bullet}CR_2 + R_2C = CR_2 \rightarrow X\text{-}CR_2.CR_2.CR_2.CR_2^{\bullet}$$

chain termination

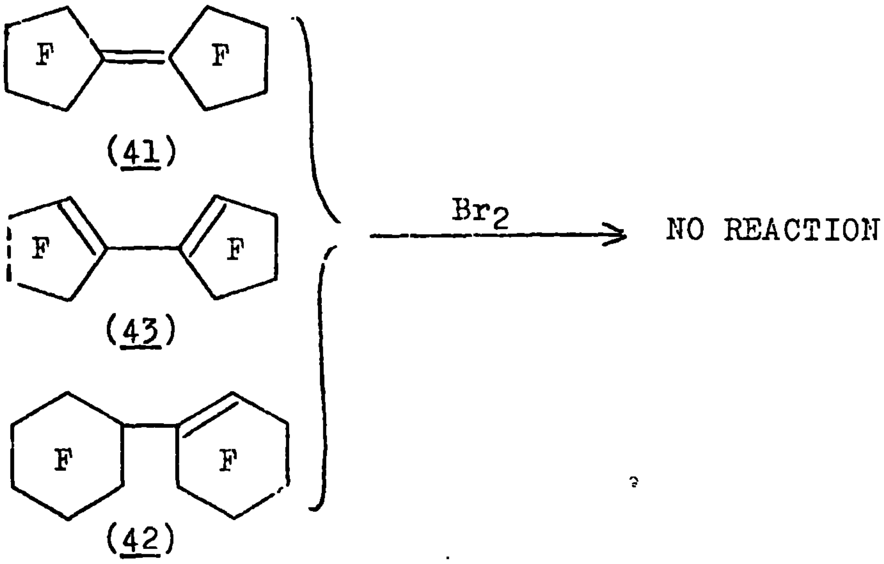
$$X\ (CR_2)_3CR_2^{\bullet} + XY \longrightarrow X\ (CR_2)_4Y + X^{\bullet}$$

Obviously, polymerisation will be a competing reaction with addition, but if the X-Y bond is fairly weak, and the ratio of XY to olefin is high, 1:1 addition across the double bond may be achieved. It should be noted that the orientation of radical addition to an unsymmetrical fluoro olefin is not completely stereospecific, as illustrated by the following example:

$$CHF = CF_2 \xrightarrow{HBr} \underset{58\%}{CHFBr.CHF_2} + \underset{42\%}{CH_2F.CF_2Br} \quad (Ref:157)$$

3.2 Attempted Bromination Reactions

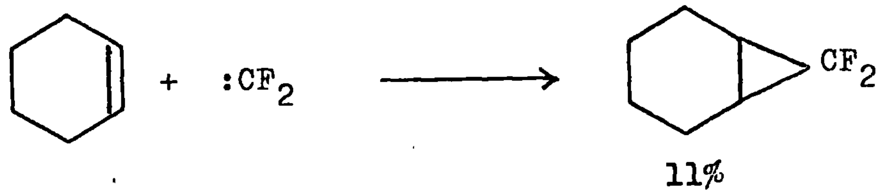
Neither bromine water, nor a solution of bromine in carbon tetrachloride underwent decolourisation when it was dropped into solutions of either (41), (42) or (43), even upon heating; indicating the relative deactivation of the π -electron systems of these cyclic fluoro olefins to electrophilic attack. It may be possible to induce free radical bromination, as observed in the case of perfluorocyclobutene, by irradiation of the reaction medium with ultraviolet light.



3.3 Attempted Difluorocarbene Insertion into (41)

Thermal breakdown of sodium chlorodifluoroacetate has been shown to form difluorocarbene,[158] which may be trapped with cyclohexene, to form difluoronorcarane in 11% yield.[159]

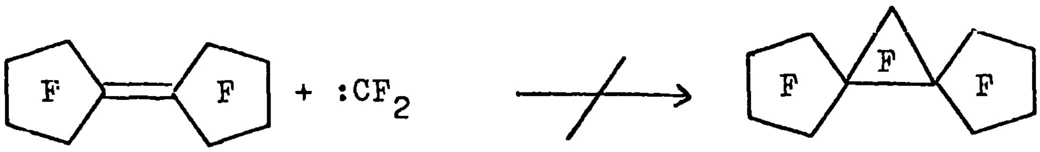
$$CF_2Cl.CO_2^- \xrightarrow{\Delta} CO_2 + CF_2Cl^- \longrightarrow Cl^- + :CF_2$$



Fluorinated cyclopropane derivatives have also been prepared by pyrolysis of fluorine substituted diazo compounds,[160] difluorodiazirine[161] etc., in the presence of olefins.

In an attempt to induce difluorocarbene insertion into (<u>41</u>), a mixture of sodium chlorodifluoroacetate and (<u>41</u>) were heated together at 250°C for 48 hours. Although decomposition of the salt had occurred, only unreacted (<u>41</u>) ($>$ 95% recovery) was obtained as a tractable product.

It may be that (<u>41</u>) is insufficiently nucleophilic to undergo addition with difluorocarbene, on extremely electron deficient species, or that the difluorocarbene generator is insufficiently active. Sodium chlorodifluoroacetate has been shown to be a relatively poor difluorocarbene producer, in comparison with the lithium salt and group II metal salts.[158] Also, pyrolysis of hexafluoropropylene epoxide has been shown to be a useful method of generating difluorocarbene.[162] Further work utilising these more potent difluorocarbene generators needs to be undertaken, as reaction of (<u>41</u>) with $:CF_2$ to form (<u>62</u>) does on the face of it seem relatively straight forward.



(41) (62)

3.4 Conclusions

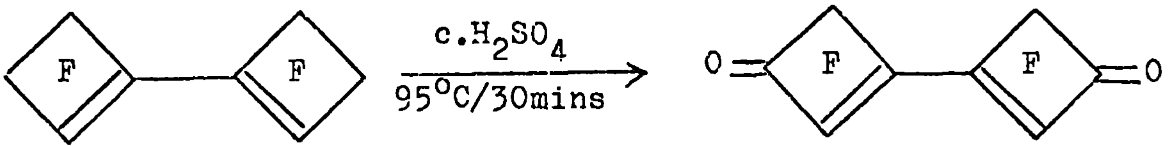
Generally, (41) does not undergo electrophilic addition reactions; also perfluorobicyclopentenyl (42) and perfluoro-(1-cyclohexylcyclohexene) (43) indicate a tendency towards the same type of unreactivity, shown by their failure to add bromine.

The double bond in (41) does not seem to be sufficiently susceptible to electrophilic attack, to react with electrophiles such as bromine and difluorocarbene, but free radical induced reactions may be viable propositions (e.g. γ -irradiation induced additions, photolytically induced additions of bromine etc.)

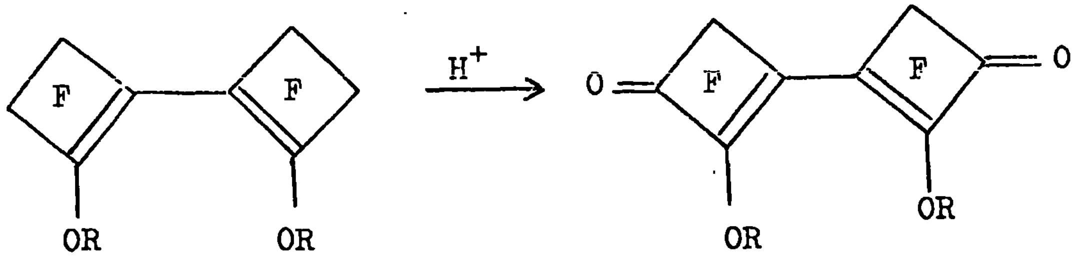
4. Hydrolysis Reactions

4.1 Introduction

It has been shown that decafluorobicyclobutenyl (63) and its alkoxy derivatives (64) are readily hydrolysed by concentrated sulphuric acid to their corresponding diketo derivatives ((65) and (66) respectively) by displacement of the allylic fluorine atoms.[163,164]



(63) (65) (Ref:163)

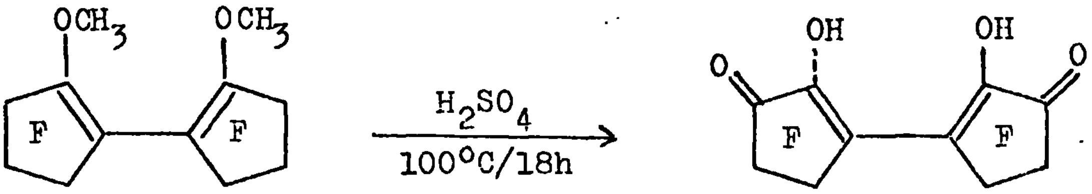


(64) (66)

(Ref:164)

(R = CH_3-, C_2H_5-)

It has also been shown that hydrolysis of 2,2'-dimethoxydodecafluorobicyclopentenyl (58) with concentrated sulphuric acid yields a diketo-dihydroxy derivative (59).[150]

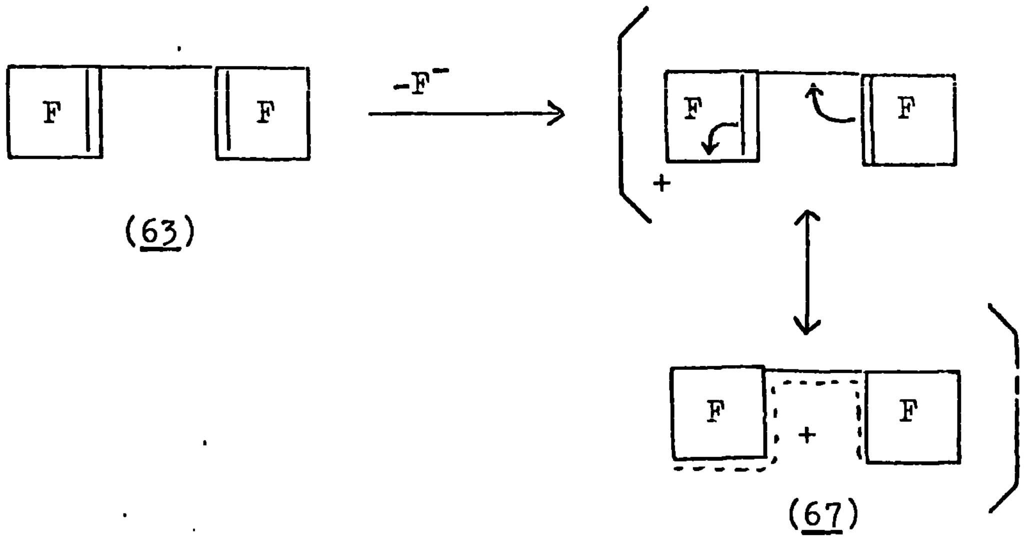


(58) (59)

4.2 Hydrolysis of Octafluorocyclopentene and Related Derivatives

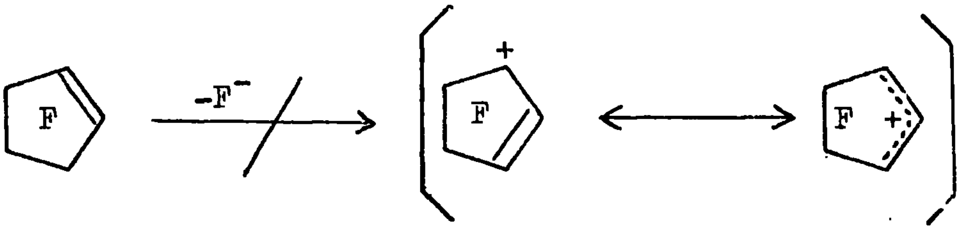
4.2.1 Octafluorocyclopentene and Perfluorobi(cyclopentylidene)

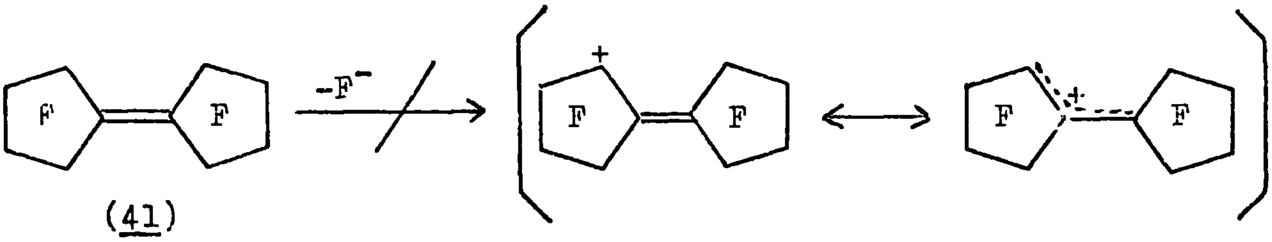
Reaction of either octafluorocyclopentene or its dimer (41) with concentrated sulphuric acid at 140-160°C for 4 to 6 days resulted only in the recovery of starting materials. Park and Frank[163] proposed a mechanism for the hydrolysis of (63), which involves loss of fluoride ion, forming a stabilised carbonium ion (67).



Presumably, the carbonium ions which would be formed by loss of a fluoride ion from both octafluorocyclopentene and (41) are uncapable of sufficient stabilisation, and hence the reactions do not proceed.

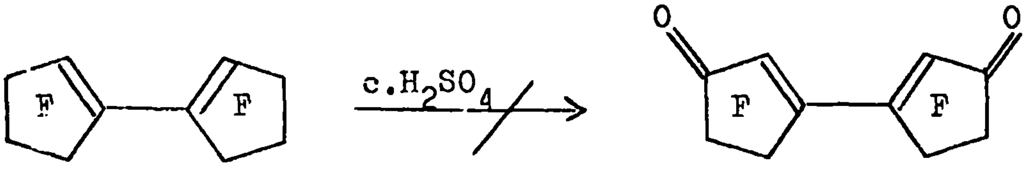
i.e.





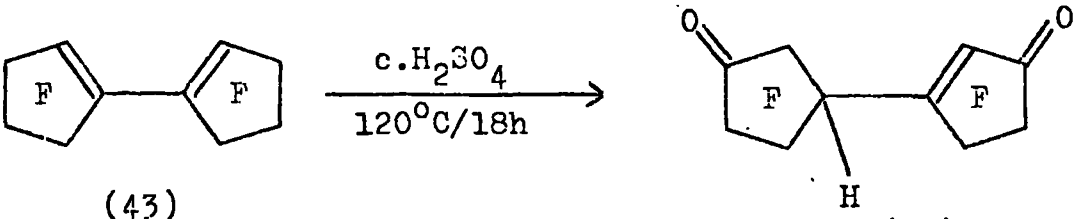
4.2.2 Perfluoro(bicyclopentenyl) (43)

Perfluoro(bicyclopentenyl) was heated with concentrated sulphuric acid, in a sealed tube for 18 hours at 120°C. After pouring into ice/water, the products were isolated by solvent extraction with ether, followed by vacuum sublimation of the resultant oil. A white crystalline solid was obtained, which mass spectrometry and analysis showed to have a molecular formula of $C_{10}HO_2F_{11}$. i.e. straightforward replacement of allylic fluorine by oxygen, as observed with decafluorobicyclobutenyl, had not occurred as expected.



(43)

Analysis of its ^{19}F n.m.r. spectrum showed that addition of HF across one double bond had occurred, along with replacement of the allylic fluorine atoms, giving (52). This was shown by the presence of only one vinylic fluorine atom, together with difluoromethylene resonances.
i.e.

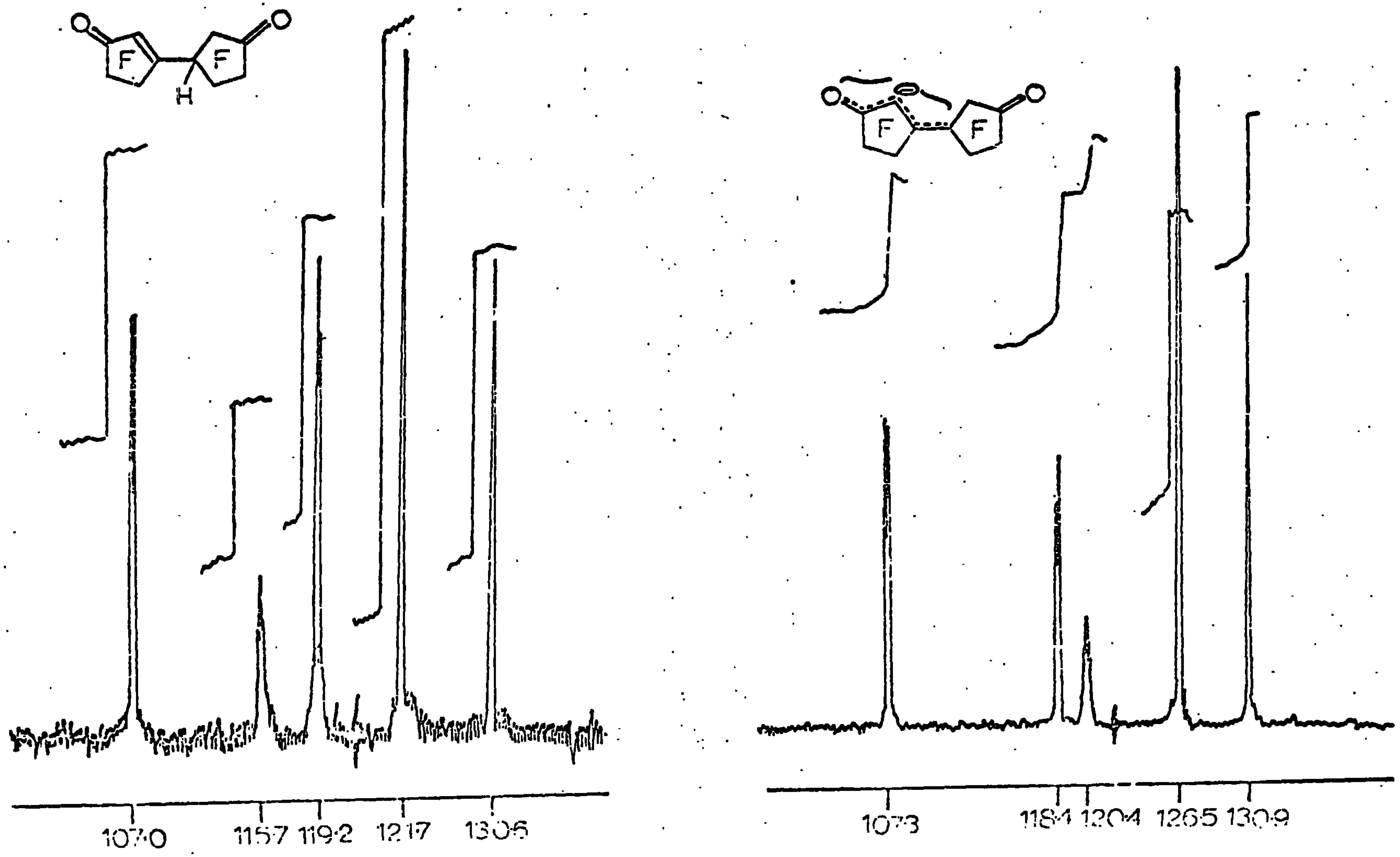


(43)

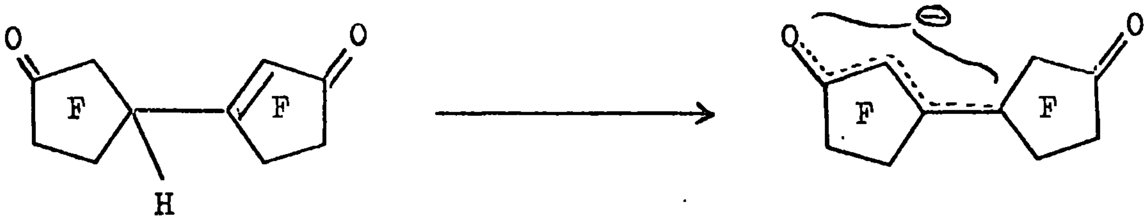
(52)

On standing. a solution of (52) in deuteroacetone developed a red colouration, which intensified with time. The chemical shift of the vinylic fluorine atom was seen to more upfield, until a situation as illustrated in fig. VIII.4 was reached. This colouration and change of chemical shift was attributed to the loss of the proton from (52), and the

Fig. VIII.4 The ^{19}F n.m.r. spectra of (52) and its anion illustrating the change in chemical shift of the vinylic fluorine atom.



formation of one the few examples of a stable anion (67).

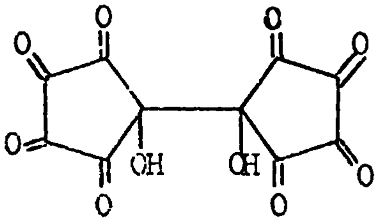


(52) (67)

As would be expected, the chemical shifts of the difluoromethylene groups moved upfield, but not so markedly. An attempt to regenerate (52) by addition of acid to the solution of (67) was unsuccessful.

4.2.3 Polymethoxyderivative of (41)

The mixture of tri- and tetra-methoxy substituted derivatives of (41) obtained from a nucleophilic substitution reaction described earlier, was heated with 50%(^{v}/v) sulphuric acid under reflux for 40 hours. After quenching with ice water and solvent extraction of the products with ether, a white crystalline solid was sublimed from the resultant oil. Its infra red spectrum showed broad intense absorptions in the hydroxyl and carbonyl regions. G.L.C./M.S. analysis of a solution in ether showed the presence of two components, the major (> 75%) one having a molecular weight of 282. Fragmentation was by losses of O, OH and OH_2 from the parent. A polyketodialcohol (68) is consistent with this data and is



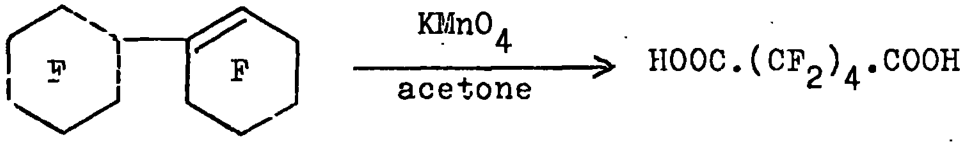
(68)

in close agreement with previously observed results.[150]

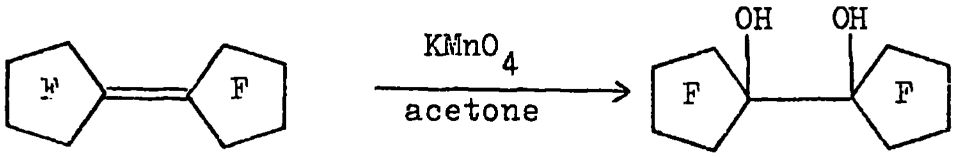
5. Oxidation Reactions

Fluoroalkenes are oxidised readily with acetone solutions of potassium permanganate, to ketones and/or carboxylic acids.[165]

When perfluoro-(1-cyclohexyl cyclohexene) was stirred with $KMnO_4$/acetone, perfluoroadipic acid was obtained, isolated as its dianilinium salt.



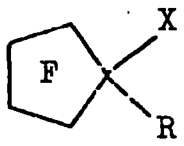
However, when (41) was oxidised under comparable conditions, a white crystalline solid melting at 63-65°C was obtained. It was shown to correspond to 1,1'-dihydroxyhexadecafluorobicyclopentyl (53). A parent peak was not observed in the mass spectrum, P-20, which corresponds to



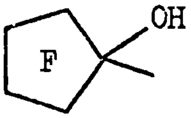
(53)

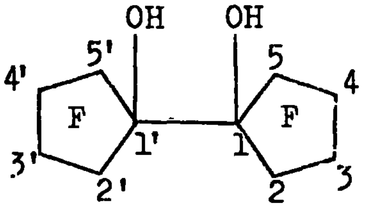
loss of HF was the highest observed mass peak, however analysis and other spectroscopic data was consistent with the structure (53). The infra red of (53) showed an intense free -OH band at approximately 3500cm^{-1}, and a proton n.m.r. spectrum showed a single resonance at δ = 7.1 p.p.m. showing only one hydroxyl environment, and as this is in the expected -OH region, the group is not attached to a fluorine containing carbon, which would deshield the proton, and move the signal downfield; i.e. the alcohol is tertiary.

A ^{19}F n.m.r. spectrum showed a symmetrical AB/AX system as previously observed for compounds of the type (60). In this



(60)

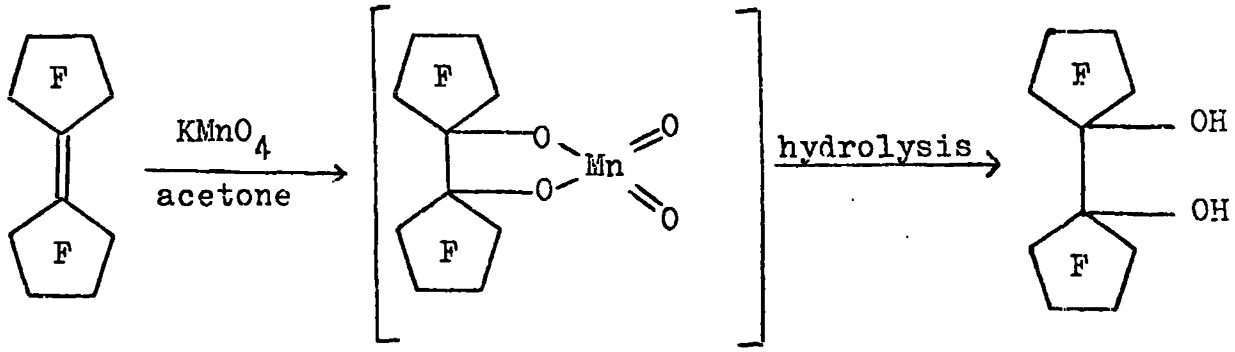
case X = OH, and as only eight signals were obtained, the molecule must be symmetrical with R =  i.e.



J_{AB} (F 2,2',5,5') = 268Hz

J_{AB} (F 3,3',4,4') = 256Hz

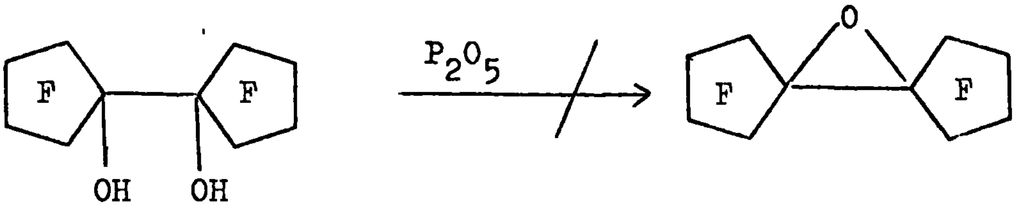
A mechanism for the formation of (53) is probably as follows:



(53)

Oxidations of this type are well established in the analogous hydrocarbon series.

An attempt to dehydrate the dialcohol (53), to form an epoxide, by heating with P_2O_5, resulted in recovery of unchanged reactant.

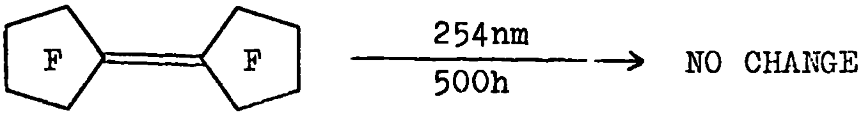


(53)

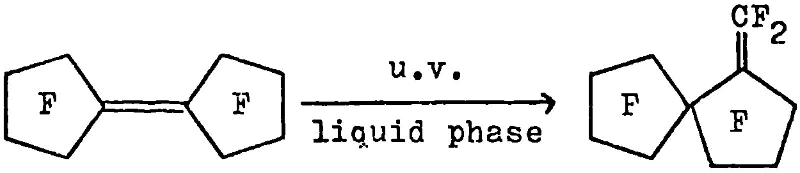
6. Photolysis and Pyrolysis Reactions

6.1 Photolysis of Perfluorobi(cyclopentylidene) (41)

When perfluorobi(cyclopentylidene) was irradiated at 254nm in the gas phase for 500 hours, unchanged starting material was recovered.



This is contrary to recent results published by Haszeldine and co-workers,[166] who report the formation of a spiro compound (69), when (41) is irradiated in the liquid phase.

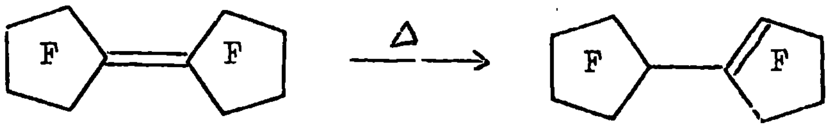


(Ref:166)

(41) (69)

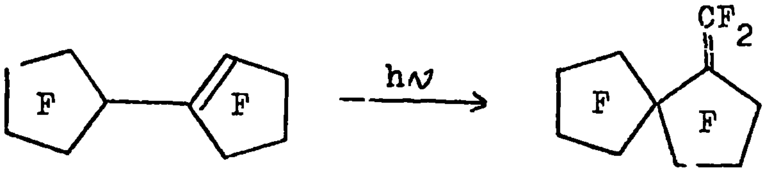
It should be noted however that the ambient temperature of the photolysis is c100°C, and as will be seen later, (Section 6.3) rearrangement of (<u>41</u>) occurs at this temperature, the double bond migrating into the ring. The spiro compound (<u>69</u>) may well be derived from irradiation of the rearranged isomer (<u>54</u>), and <u>not</u> from (<u>41</u>).

i.e.



(<u>51</u>) (<u>54</u>)

(see later)

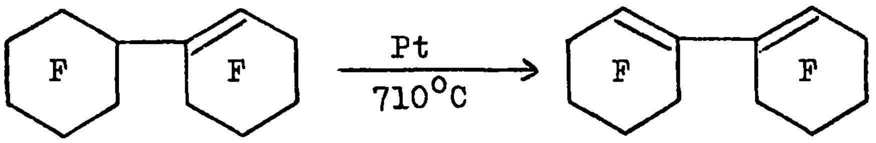


(<u>54</u>) (<u>69</u>)

6.2 <u>Pyrolysis of Perfluoro-(1-cyclohexylcyclohexene) (42)</u>

When (<u>42</u>) was passed over hot platinum foil in a stream of nitrogen, defluorination and/or degradation occurred, depending upon the temperature.

It has been shown previously,[150] that (<u>42</u>) readily defluorinates over iron at 500°C, to give perfluorobiphenyl in 45% yield. When (<u>42</u>) was passed over Pt at 710°C, removal of two fluorine atoms to give perfluorobicyclohex-1-enyl (<u>48</u>) occurred to the extent of 10% conversion. Recirculation of the mixture resulted in the formation of 25% of (<u>48</u>). Some unidentified material (approx. 10%) was also obtained, but no further defluorinated material or rearranged isomers of (42) were observed.



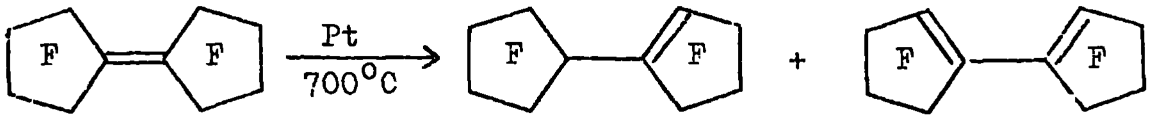
(42) (48)

10% conversion

A comparable reaction at 825°C gave low yields (50%) of a complex degraded mixture, which was not investigated further.

6.3 Pyrolysis of Perfluorobi(cyclopentylidene) (41)

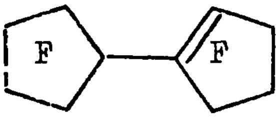
When (41) was passed over Pt at 700°C, rearrangement (40%) along with some defluorination (10%) was observed. Recirculation of the reaction product resulted in an increased proportion of defluorinated material, but the ratio of the $C_{10}F_{16}$ isomers remained constant, showing the existance of a thermal equilibrium between (41) and (54). A single tertiary fluorine atom was observed in the ^{19}F n.m.r. spectrum of (54), along with a single vinylic -CF resonance. Other difluoromethylene resonances were observed, but could only be tentatively assigned.



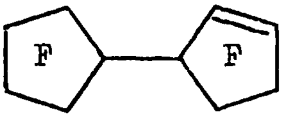
(41) (54) (43)

(40%) (10%)

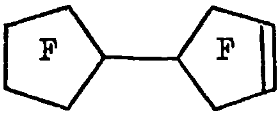
At lower temperatures, the relative proportion of (54) in the mixture increased, until at 150°C, almost complete rearrangement of (41) had occurred. However at 150°C, three isomers of (41) were observed and probably corresponded to (54), (55) and (56), the structure of (54) being confirmed, and those of (55) and (56) being the only other possibilities for migration of the double bond, without seriously rearranging the molecule. These isomers may arise from



(54)



(55)



(56)

intramolecular 1,3-fluoride ion migrations.

EXPERIMENTAL

CHAPTER IX

EXPERIMENTAL WORK

1. General

Instrumentation, reagents, and analyses were as described in Chapter VI.

Methanol was dried by distilling it from magnesium turnings, with the collection of the middle fraction.[149] Sodium methoxide and phenoxide solutions were prepared freshly, by dissolving the requisite amount of sodium in the respective solvents.

2. Preparation of Starting Materials

2.1 Octafluorocyclopentene Dimer (41)

A mixture of caesium fluoride (3.0g, 19.7m moles), sulpholan (20cm^3), and octafluorocyclopentene (8.5g, 40.0m moles) was heated at about 125°C for 20 hours in a sealed tube. The tube was then cooled, opened, and the volatile products transferred under vacuum to a cold trap. The products were distilled and the fraction boiling at 120-130°C collected. (7.3g, 86%) This was shown to be perfluorobi(cyclopentylidene) by comparison of its V.P.C. retention time (col 'A', 100°C) and its I.R. spectrum with those of an authentic sample.[150] See infra-red spectrum No.21, N.M.R. spectrum No.9.

2.2 Decafluorocyclohexene Dimer (42)

A mixture of caesium fluoride (3.0g, 19.7m moles), sulpholan (40cm^3), and decafluorocyclohexene (6.0g, 22.9m moles) was heated at about 150°C for 70 hours in a sealed tube. The tube was cooled, opened and the volatile products transferred under vacuum to a cold trap. The products were distilled and the fraction boiling at 160-165°C collected. (4.7g, 78%) This was shown to be perfluoro-(1-cyclohexylcyclohexene) by comparison of its V.P.C. retention time (col 'A', 150°C) and its I.R. spectrum with those of an authentic sample.[150] See infra-red spectrum No.22, N.M.R. spectrum No.10.

2.3 Perfluorobicyclopentenyl (43)

Perfluorocyclopentene dimer (41) (1.5g) was passed, in the vapour phase, through a silica tube containing coarse iron filings at 500°C. The average contact time was approximately 0.5 minutes. The product was collected in a cold trap, and shown to be perfluorobicyclopentenyl (0.8g, 58.6%), by comparison of V.P.C. retention time (col 'A', 50°C) and its I.R. spectrum with those of an authentic sample.[150] See infra-red spectrum No.23, N.M.R. spectrum No.11.

3. Nucleophilic Substitution Reactions

3.1 Octafluorocyclopentene Dimer (41)

3.1.1 Reaction with Sodium Methoxide in Methanol

To a stirred solution of (41) (2.12g, 5.0m moles) in methanol (30cm^3) was added, over a period of 1 hour, a solution of sodium (1.2g, 5.2m moles) in methanol (30cm^3). When addition was complete, the solution was refluxed for 24 hours. The reaction mixture was quenched with water (300cm^3), stirred well and extracted with methylene chloride (4 x 25cm^3). The extracts were bulked and dried over $MgSO_4$. Removal of $MgSO_4$ and solvent afforded a pale yellow solution, which was shown by G.L.C. (col 'O_{30}', 150°C) to comprise a mixture of 2 major and several minor components. The major products were separated by preparative G.L.C., and identified as (i) 1-(1-methoxyoctafluorocyclopentyl)-2-methoxyhexafluorocyclopent-1-ene (49) (B.p. > 200°C) (Found: C,32.42; H,1.51; F,59.7%; M^+,448. $C_{12}H_6O_2F_{14}$ requires C,32.14; H,1.34; F,59.38%; M,448). See infra-red spectrum No.24, N.M.R. spectra Nos. 12 and 13.

(ii) 1-(1-methoxyoctafluorocyclopentyl)-5-methoxyhexafluorocylopent-1-ene (50) (B.p. > 200°C) (Found: C,32.12; H,1.40; F,59.6%; M^+,448. $C_{12}H_6O_2F_{14}$ requires C,32.14; H,1.34; F,59.38%; M,448). See infra-red spectrum No.25, N.M.R. spectra Nos. 14 and 15.

The G.L.C./M.S. of the minor components corresponded to a mono-methoxy and three trimethoxy derivatives of (41).

3.1.2 Polymethoxylation of (41)

Sodium metal (0.5g, 21.8m moles), methanol (50cm^3) and (41) (3.65g, 8.62m moles) were stirred at ambient temperature for 1 week, under an atmosphere of dry nitrogen gas. The reaction mixture was quenched with water (200cm^3), stirred well and extracted with methylene chloride (4 x 25cm^3). The extracts were bulked, and dried over $MgSO_4$. Removal of $MgSO_4$ and solvent afforded a pale yellow oil (4g), which was shown by G.L.C./M.S. to comprise a mixture of tri- and tetramethoxysubstituted (41). (i.e. $^m/e$ = 460 and $^m/e$ = 472; $C_{13}H_9O_3F_{13}$ requires $^m/e$ = 460, and $C_{14}H_{12}O_4F_{12}$ requires $^m/e$ = 472.) No attempt was made to separate these derivatives; they were used, as a mixture in a later experiment, see Ch.IX, section 5.4.

3.1.3 Reaction with Sodium Phenoxide in Dimethylformamide

A mixture of (41) (6.5g, 15.3m moles), and a solution of sodium phenoxide in D.M.F. (30cm^3, 0.5m, 15m moles) were stirred together at ambient temperature for 18 hours. The reaction mixture was poured onto water ($300cm^3$) and extracted with methylene chloride ($4 \times 25cm^3$). The extracts were bulked and dried over $MgSO_4$. Removal of $MgSO_4$ and solvent left a deep yellow oil, which was distilled under reduced pressure, the fraction boiling at 45-50°C/0.04mm Hg being collected. G.L.C./M.S. (col O_{30}, 180°C) showed the fraction to comprise a minor unidentified component (P = 450) and a major component, which corresponded to a monophenoxy substituted derivative of (41), which was probably 1-(1-phenoxyoctafluorocyclopentyl) heptafluorocyclopent-1-ene (51). (i.e. M^+, 498; $C_{16}H_5OF_{15}$ requires M,498). See N.M.R. spectrum No.16.

(N.B. all attempts to separate the monophenoxy derivative (51) and purify it for analytical purposes resulted in the formation of resinous materials.)

4. Addition Reactions

4.1 Attempted Addition of Bromine to (41), (42) and (43)

When (41), (42) or (43) was heated with either bromine water or bromine in carbon tetrachloride, no decolourisation was observed. i.e. NO REACTION.

4.2 Attempted Difluorocarbene Addition to (41)

Octafluorocyclopentene dimer (41) (3g, 7.1m moles) and sodium chlorodifluoroacetate (2.1g, 14m moles) were sealed into a carius tube and heated at 250°C for 48 hours. When cool, volatile material was vacuum transferred from the tube. This was shown to be recovered starting material (2.9g) i.e. NO REACTION.

4.3 Free Radical Reaction (γ-ray Irradiation) of Methanol with (41)

Dry methanol ($1cm^3$, 24.7m moles) and (41) (5g, 11.8m moles) were transferred to a carius tube. The mixture was thoroughly degassed, the tube evacuated, sealed and then subjected to γ-irradiation for 30 days.

The tube was opened. and volatile material was vacuum transferred to a cold trap (5.5g). V.P.C. analysis of the volatile mixture (col 'A', 120°C) showed it to be a complex mixture of at least eleven components. Further investigation of the mixture was not pursued at this stage.

5. Hydrolysis Reactions

5.1 Reaction of (41) with Concentrated H_2SO_4

Concentrated sulphuric acid (3g) and (41) (1.5g, 3.5m moles) were introduced into a carius tube, which was then evacuated and sealed. The tube and contents were heated at 140°C for 6 days. Only starting material (1.45g) was recovered, when the tube was opened.

5.2 Reaction of Octafluorocyclopentene with Concentrated H_2SO_4

Concentrated sulphuric acid (5g) and octafluorocyclopentene were sealed into a carius tube. The tube and contents were heated at 150°C for 4 days. Only starting material (5g) was recovered when the tube was opened.

5.3 Reaction of (43) with Concentrated Sulphuric Acid

Perfluorobicyclopentenyl (43) (1g, 2.6m moles) and concentrated H_2SO_4 ($5cm^3$) were sealed into a carius tube. The tube and contents were heated at 120°C for 18 hours. The tube was opened and the contents poured onto crushed ice (50g), diluted to 250cm^3 with water, and extracted with ether (4 x 50cm^3). The extracts were bulked and dried over $MgSO_4$. Removal of $MgSO_4$ and solvent afforded a brown tar, from which a white solid (0.5g, 53.3%) was sublimed (50°C/0.005mm Hg), identified as <u>1-(3-oxo-1H-hexafluorocyclopentyl)-3-oxopentafluorocyclopent-1-ene</u> (<u>52</u>) (M.p. 120-122°C) (Found: C,33.6; H,0.4; F,57.3%; M$^+$,362. $C_{10}HO_2F_{11}$ requires C,33.2; H,0.3; F,57.7%; M,362). See infra-red spectrum No.26, N.M.R. spectrum No.17.

The ^{19}F n.m.r. spectrum of (<u>52</u>) was recorded as a solution in D6-acetone. After standing for two days, the initially colourless solution was seen to have turned deep red. This colouration was thought to be due to the formation of an anion, which resulted from the loss of the proton from (<u>52</u>). See N.M.R. spectrum No.18.

5.4 Reaction of Polymethoxy Derivative from Section 3.1.2 with Sulphuric Acid

Polymethoxylated (<u>41</u>) from section 3.1.2 (3.5g) was stirred under reflux with dilute sulphuric acid (30cm^3 of 50% (^{v}/v)) for 40 hours. The reaction mixture was cooled, poured onto iced water (200cm^3) and extracted with ether (4 x 20cm^3). The extracts were bulked and dried ($MgSO_4$). Removal of $MgSO_4$ and solvent afforded a deep brown oil, which was heated under vacuum (100°C/0.005mm Hg) to yield a white crystalline solid. M.S./G.L.C. analysis (col O, 125°C) of a solution of this solid in ether indicated the presence of two components, the major ($>$75%) one corresponded to a hydrocarbon with a molecular weight of 282 and showed principal fragmentation by losses of O, OH and OH_2. An infra-red spectrum showed broad absorptions in the -O-H and $>C=O$ regions.

6. Oxidation Reactions

6.1 Reaction of (41) with Potassium Permanganate in Acetone

To a stirred solution of $KMnO_4$ (4g) in dry acetone (150cm^3), was added, dropwise, (41) (4g, 9.3m moles). The mixture was stirred at ambient temperature for 18 hours, and then quenched with water (400cm^3). The solution was decolourised by passing sulphur dioxide, the acetone removed (rotavap), and the aqueous phase extracted with ether (4 x 25cm^3). The extracts were bulked and dried ($MgSO_4$). Removal of $MgSO_4$ and solvent afforded an oily residue, from which a white crystalline solid (2.5g, 58.4%) was sublimed (0.001mm Hg/75°C), identified as 1,1'-dihydroxyhexadecafluorobicyclopentyl (53) (M.p. 63-65°C) (Found: C,25.85; H,0.43; F,66.71%; M^+,438 (Parent minus HF). $C_{10}H_2O_2F_{16}$ requires C,26.20; H,0.44; F,66.38%; M,458.) See infra-red spectrum No.27, N.M.R. spectra Nos. 19 and 20.

An attempt to dehydrate the dihydroxy derivative (53) by heating it with P_2O_5, resulted in the recovery of starting material.

6.2 Reaction of (42) with Potassium Permanganate in Acetone

To a stirred solution of $KMnO_4$ (2g) in dry acetone (75cm^3), was added, dropwise, (42) (2.3g, 4.38m moles). The mixture was refluxed for 2 hours, cooled and poured onto water (200cm^3). The solution was decolourised by passing sulphur dioxide, the acetone removed (rotavap), and the aqueous phase extracted with ether (4 x 25cm^3). The extracts were bulked and dried ($MgSO_4$). The $MgSO_4$ was filtered off and aniline was added dropwise to the ether solution. A white solid separated (2.34g, 56%), which was filtered off and identified as the dianilinium salt of perfluoro adipic acid, by analysis and comparison of its I.R. spectrum with that of an authentic sample. (Found: C,45.22; H,3.60; N.5.98%. Calc. for $C_{18}H_{16}O_4N_2F_8$ C,45.38; H,3.36; N,5.88%.) See infra-red spectrum No.28, N.M.R. spectrum No.21.

7. Photolysis and Pyrolysis Reactions

7.1 Photolysis of (41)

Perfluorocyclopentene dimer (3.0g, 7m moles) was introduced into a silica vessel. The contents were deoxygenated, the vessel evacuated, sealed and then irradiated at 253.7nm for 500 hours. Only starting material was recovered (2.9g).

7.2 Pyrolysis of (42) over Pt.

Perfluoro-(1-cyclohexylcyclohexene) (2.1g,4.0m moles) was passed over Pt at 710°C in a stream of nitrogen gas. (The flow rate of N_2 was 60-80cm^3 min^{-1} which gave an approximate contact time of 20 secs.). A pale yellow liquid (1.3g) was collected, and was shown to be (G.L.C./M.S.) starting material (80.7%), perfluorobicyclohex-1-enyl[150] (10.2%) and unidentified material (9.1%). Recirculation of this mixture gave a second mixture of composition: perfluoro-(1-cyclohexylcyclohexene) (63.5%), perfluorobicyclohex-1-enyl (24.9%) and unidentified material (11.6%).

A comparable reaction at 825°C gave low yields (50%) of a complex mixture, which was unworthy of further investigation.

7.3 Pyrolysis of (41) over Pt.

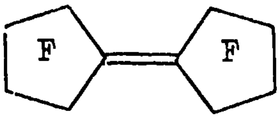
Perfluorocyclopentene dimer (2g, 4.7m moles) was passed over Pt at 700°C in a stream of N_2 gas. (approx. 20 secs. contact time). A colourless liquid (1.9g) was collected and G.L.C. analysis (col 'A', 35°C) showed it to comprise starting material (approx. 50%), perfluorobicyclopentylidene (approx. 10%), and a third component (approx. 40%) identified as perfluoro-(1-cyclopentylcyclopentene). The structure of the rearranged third product was determined from its mass spectrum (M^+,424. $C_{10}F_{16}$ requires M,424) and analysis of its ^{19}F n.m.r. spectrum. See N.M.R. spectrum No.22.

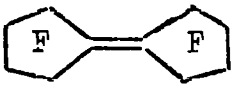
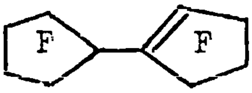
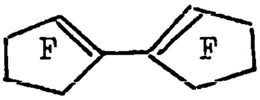
Recirculation of this mixture gave a second mixture containing an increased proportion of defluorinated material. The ratio of the $C_{10}F_{16}$ isomers remained constant.

The reaction was repeated at different temperatures, and the results are summarised in Table IX.1.

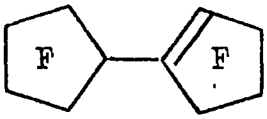
Table IX.1

Summary of Products of Pyrolysis

of  over Pt

Temperature	Products (approx. %)		
			
700°C	50	40	10
560°C	45	50	5
450°C	40	> 55	< 5
150°C	< 10	‡ See below	< 5

‡ A mixture containing three components of molecular weight 424 (i.e. isomers of octafluorocyclopentene dimer) was obtained as the major product ($>$ 80%). Presumably, these correspond to the three rearranged isomers (54), (55) and (56).



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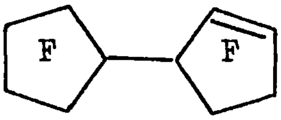

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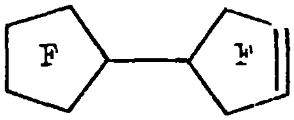


(56)

APPENDIX I

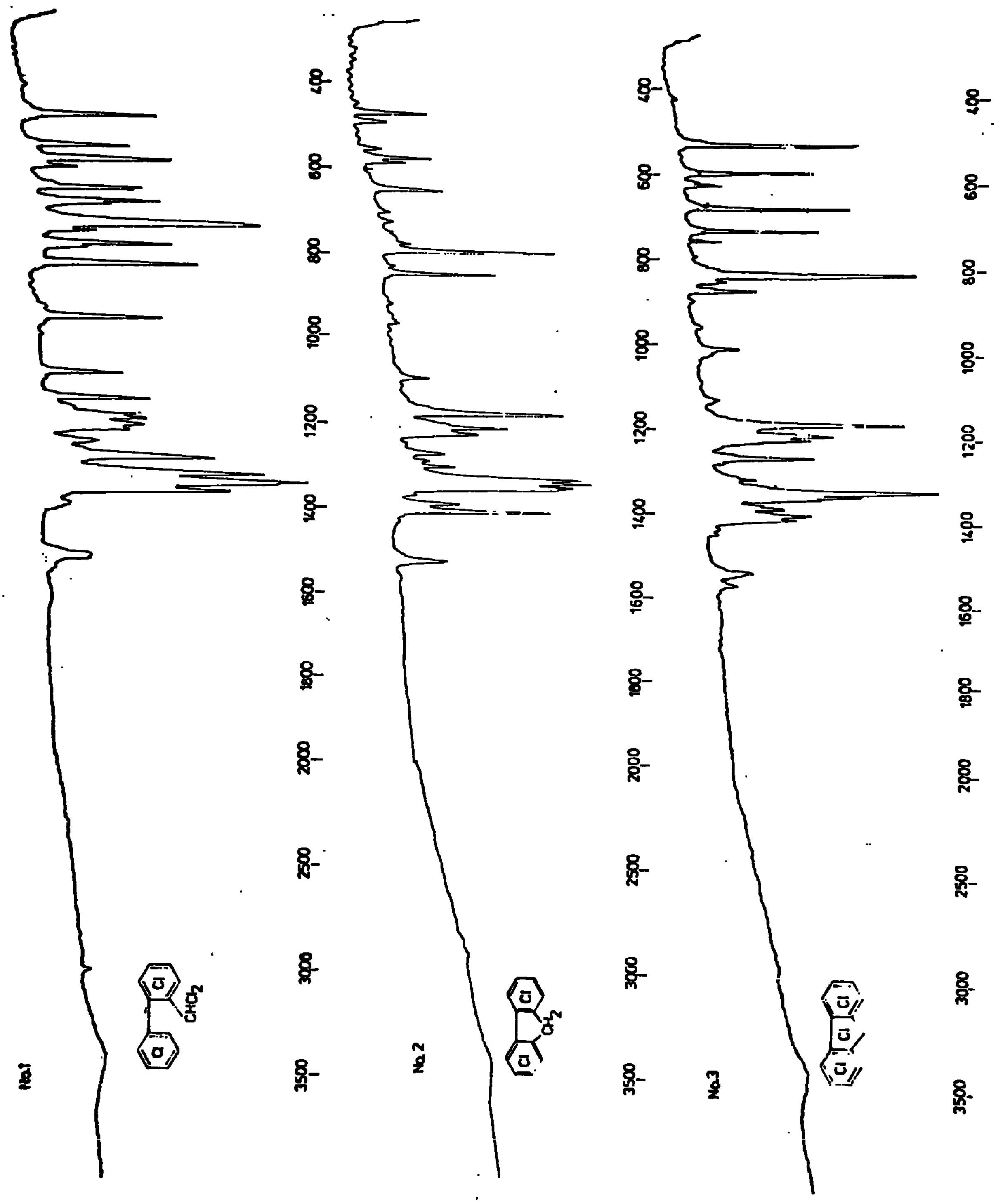
INFRA-RED SPECTRA

APPENDIX I

Infra-red Spectra

Spectrum No.	Compound	State
1	2-Dichloromethyl-2',3,3',4,4',5,5',6,6'-nonachlorobiphenyl	KBr Disc
2	1,2,3,4,5,6,7,8,-Octachlorofluorene	KBr Disc
3	Perchlorofluorene	KBr Disc
4	Decachlorobiphenyl	KBr Disc
5	4,4'-Dichlorobiphenyl	KBr Disc
6	Octachlorodibenzo(b,d)thiophen	KBr Disc
7	Octachlorodibenzo(b,d)furan	KBr Disc
8	Octachlorofluoren-9-one	KBr Disc
9	Octachlorothianthrene	KBr Disc
10	Octachloronaphthalene	KBr Disc
11	1-Methyl-2,3,4,5,6-pentachlorobenzene	KBr Disc
12	Hexachlorobenzene	KBr Disc
13	2,3,4,6,7,8-Hexachloro-1,9-epidithiodibenzo(b,d)thiophen	KBr Disc
14	2,3,4,6,7,8-Hexachlorodibenzo (b,d)-thiophen	KBr Disc
15	Perfluoro-(bis-(p-phenylphenylene)) sulphide	KBr Disc
16	Perfluoro-(4,4'-bisisopropylbiphenyl)	KBr Disc
17	Methoxy perfluoro-(4,4'-bisisopropylbiphenyl)	KBr Disc
18	1,8-Dichloro-3,6-dioxaoctane	Contact Film
19	18-crown-6 polyether	Contact Film
20	Tetrafluoropyrazine	Contact Film

Spectrum No.	Compound	State
21	Perfluoro-bi(cyclopentylidene)	Contact Film
22	Perfluoro-(1-cyclohexylcyclohexene)	Contact Film
23	Perfluorobicyclopentenyl	Contact Film
24	1-(1-Methoxyoctafluorocyclopentyl)-2-methoxy-hexafluorocyclopent-1-ene	Contact Film
25	1-(1-Methoxyoctafluorocyclopentyl)-5-methoxy-hexafluorocyclopent-1-ene	Contact Film
26	1-(3-oxo-1H-hexafluorocyclopentyl)-3-oxopentafluorocyclopent-1-ene	KBr Disc
27	1,1'-dihydroxyhexadecafluoro-bicyclopentyl	Contact Film
28	Dianiline salt of perfluoroadipic acid	KBr Disc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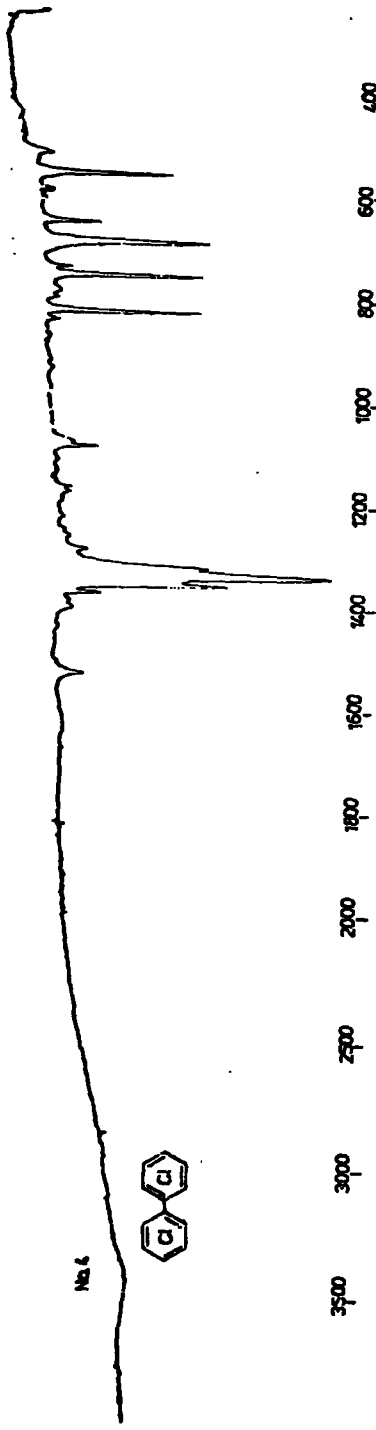
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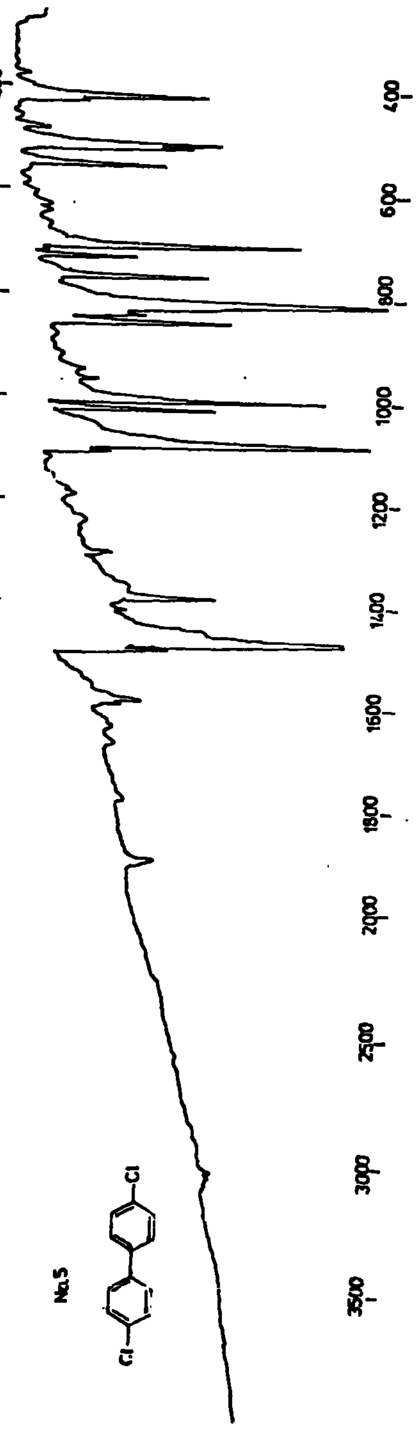
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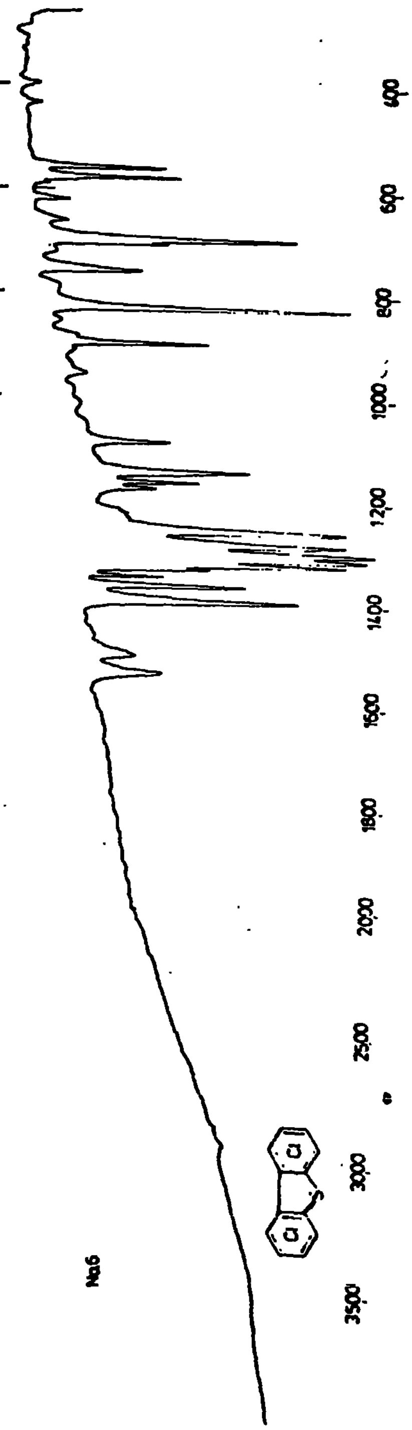
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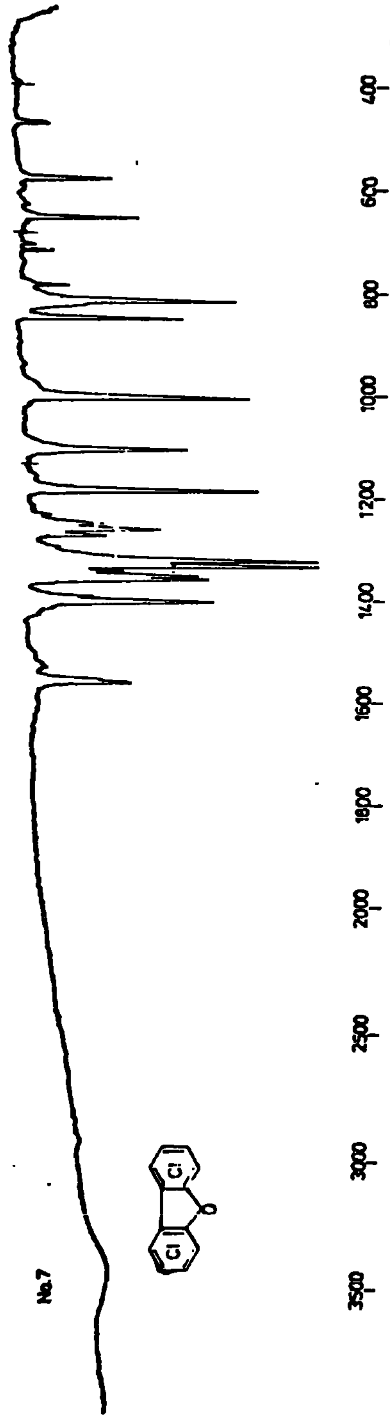
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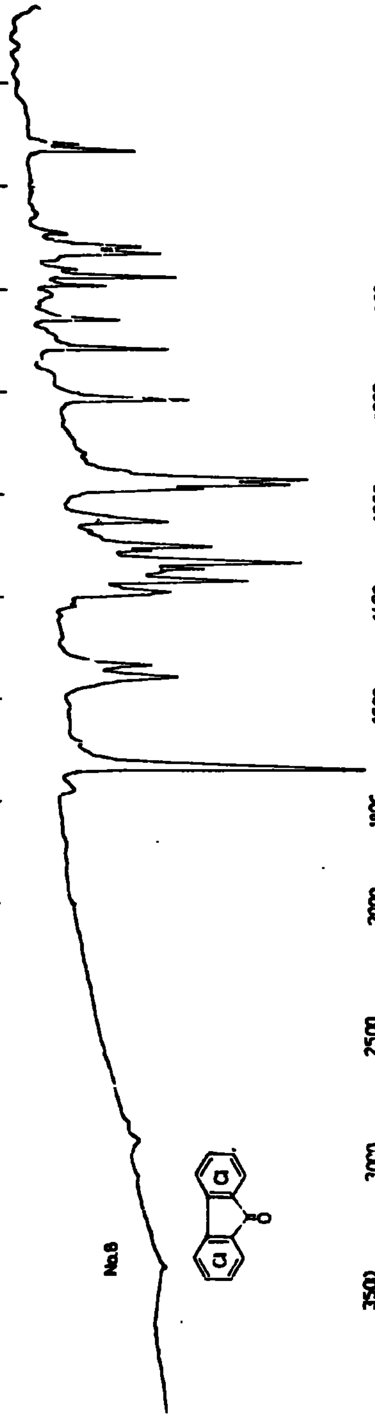
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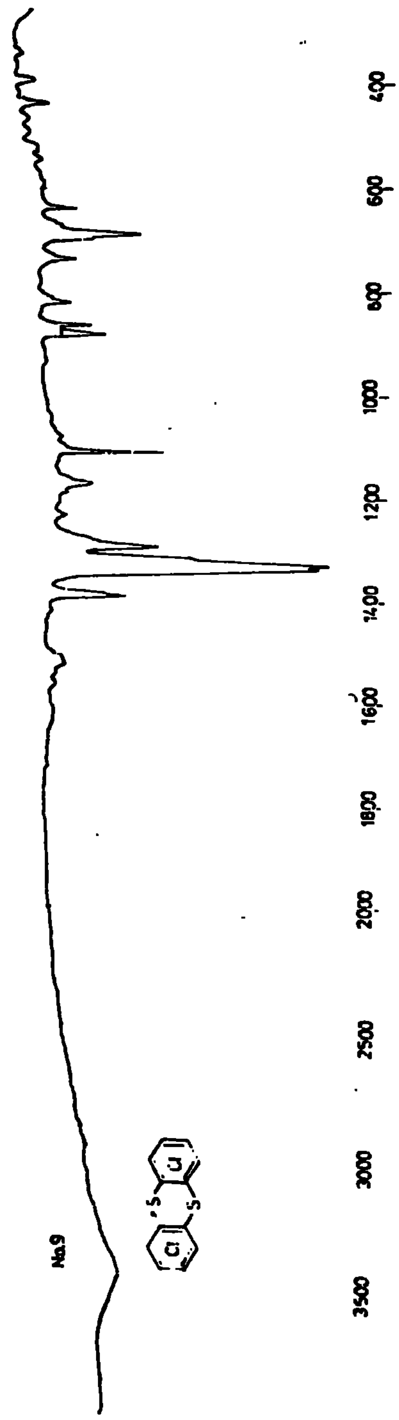
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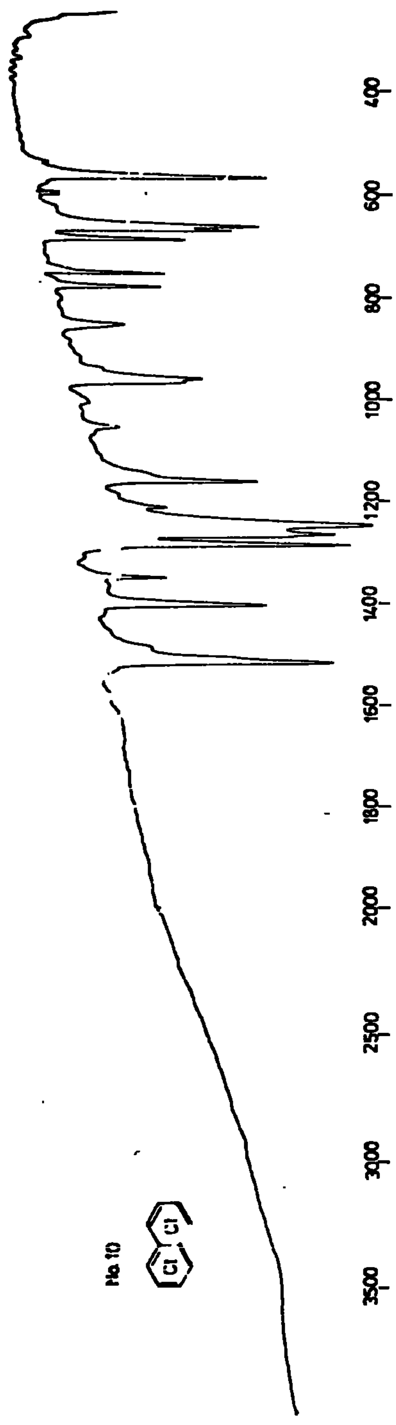
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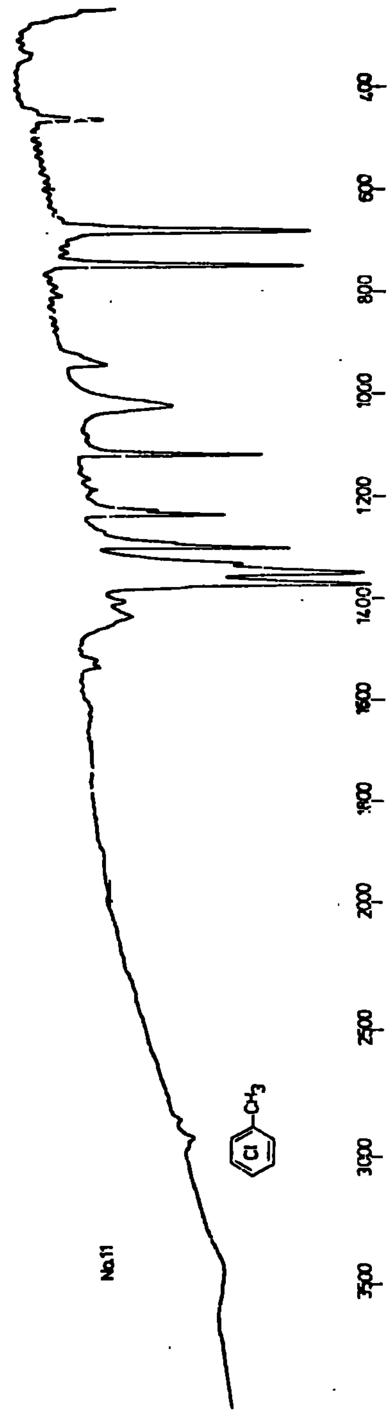
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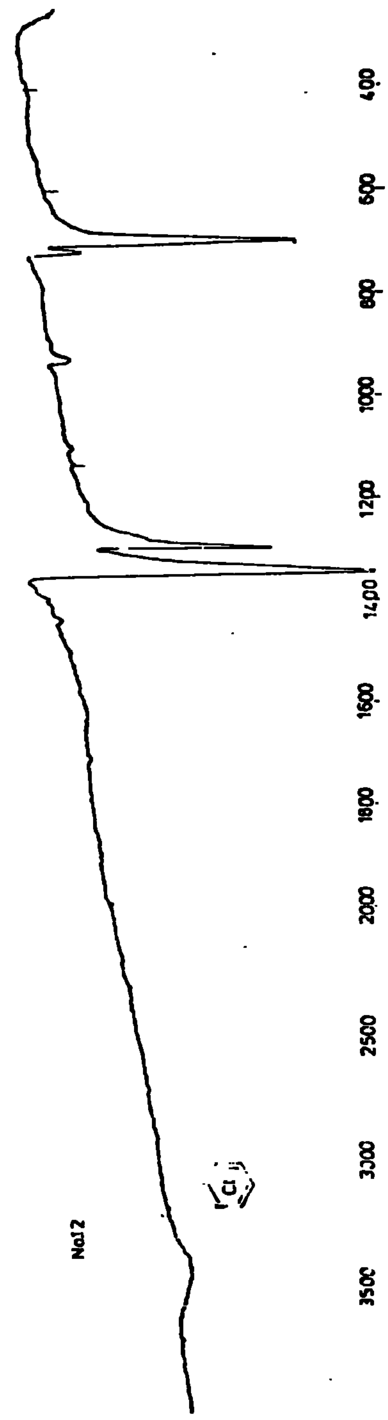
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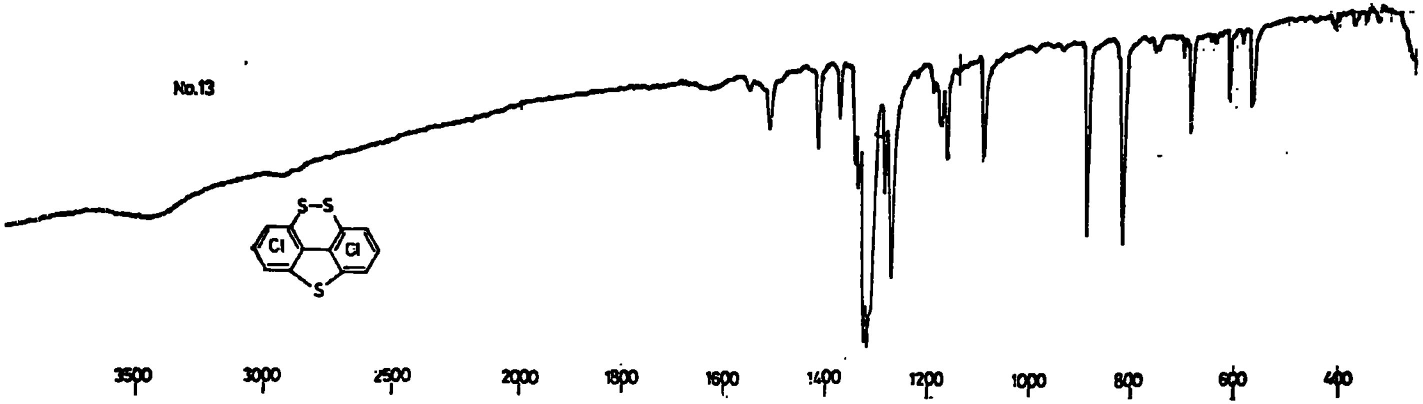

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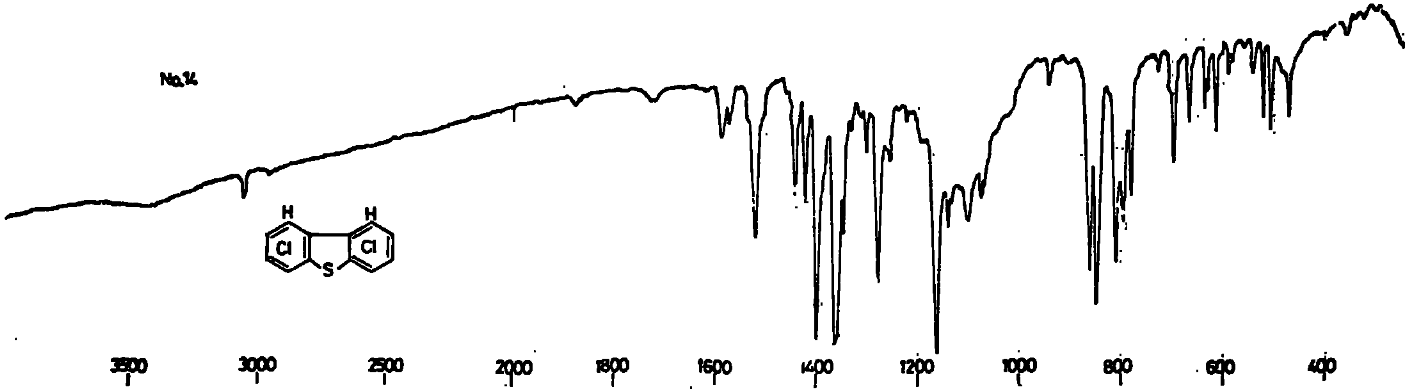

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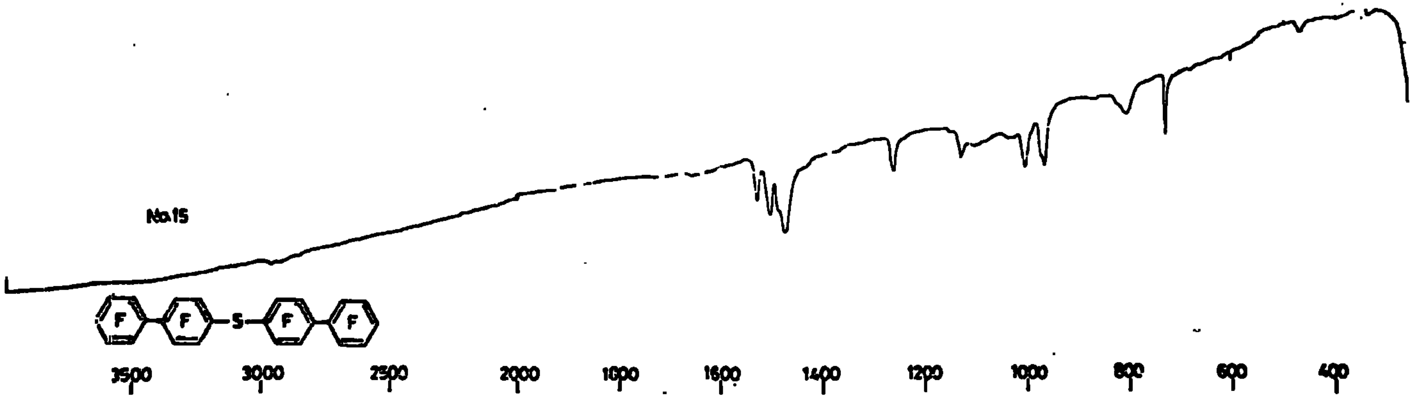

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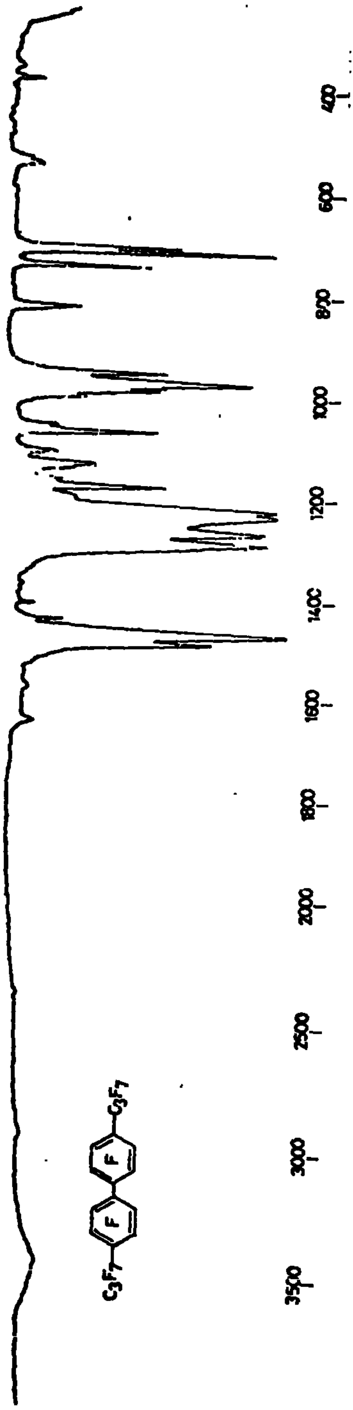
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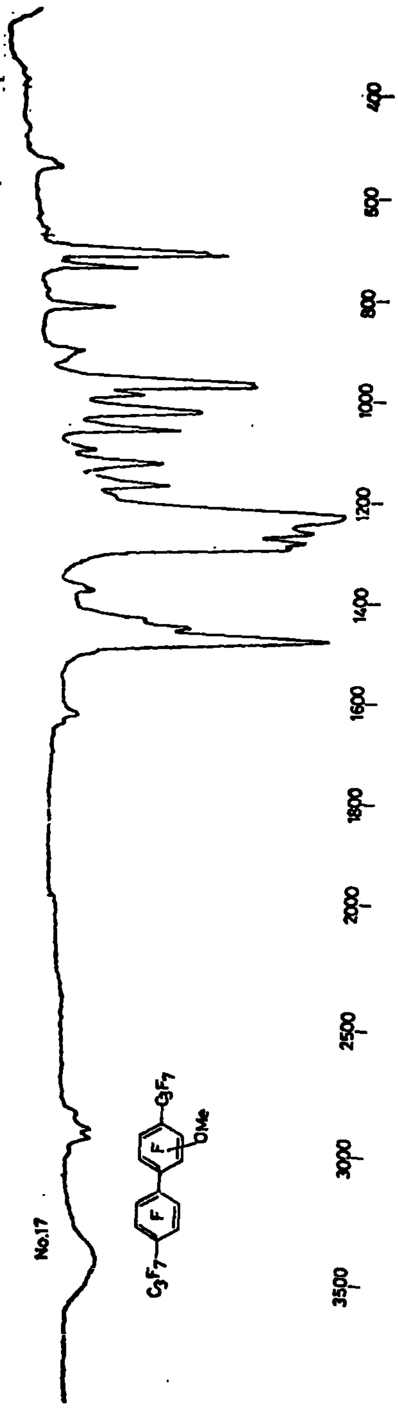
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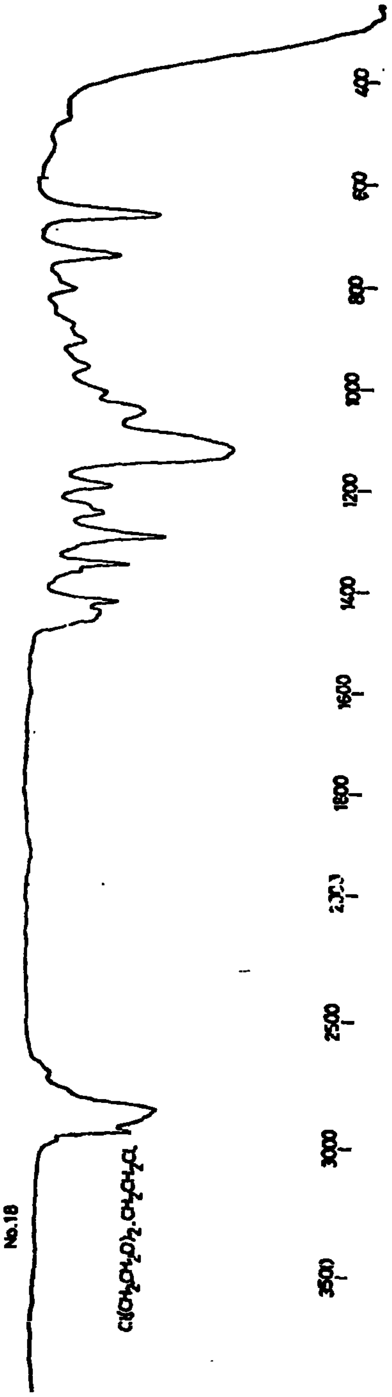
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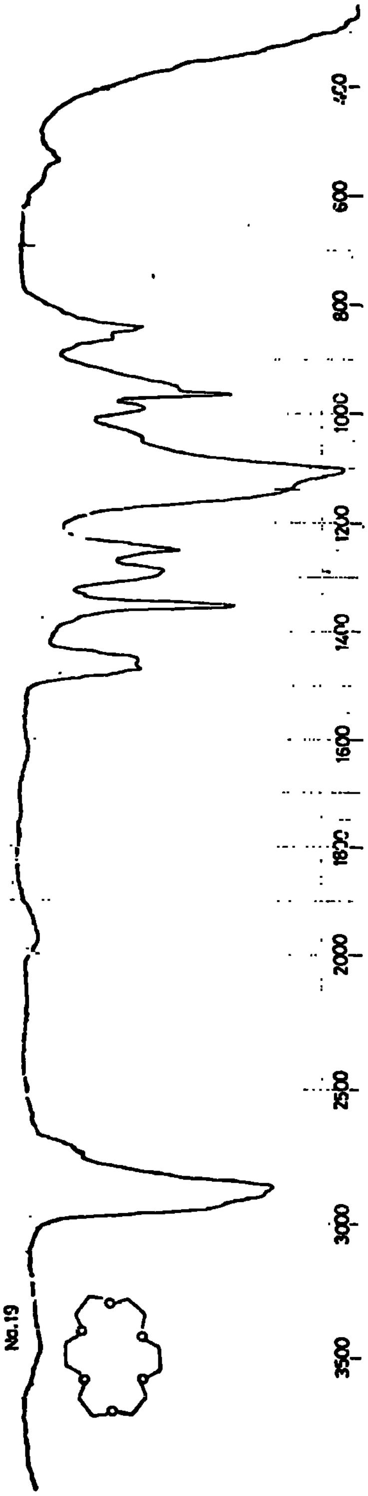
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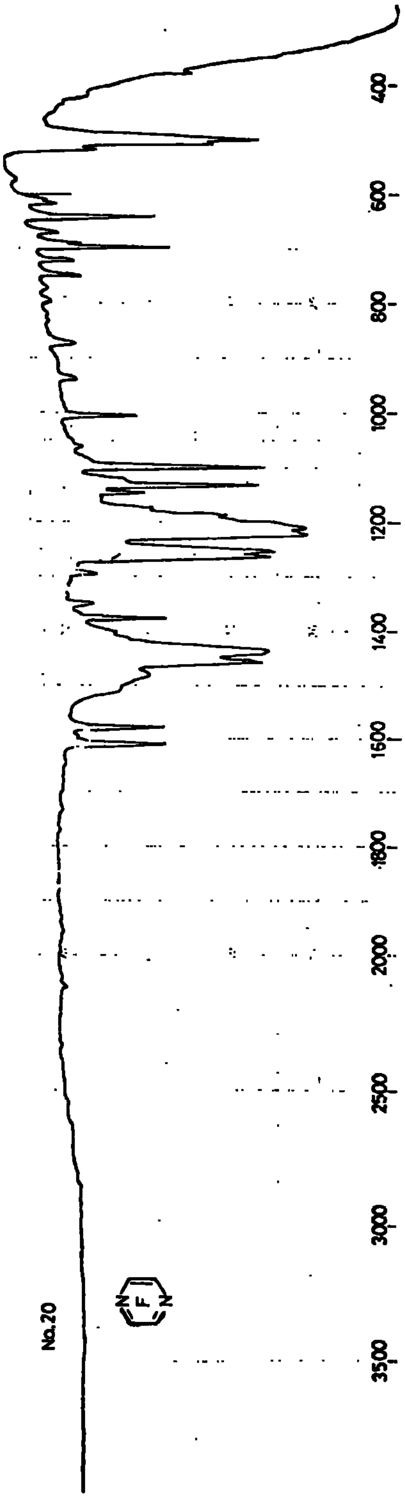
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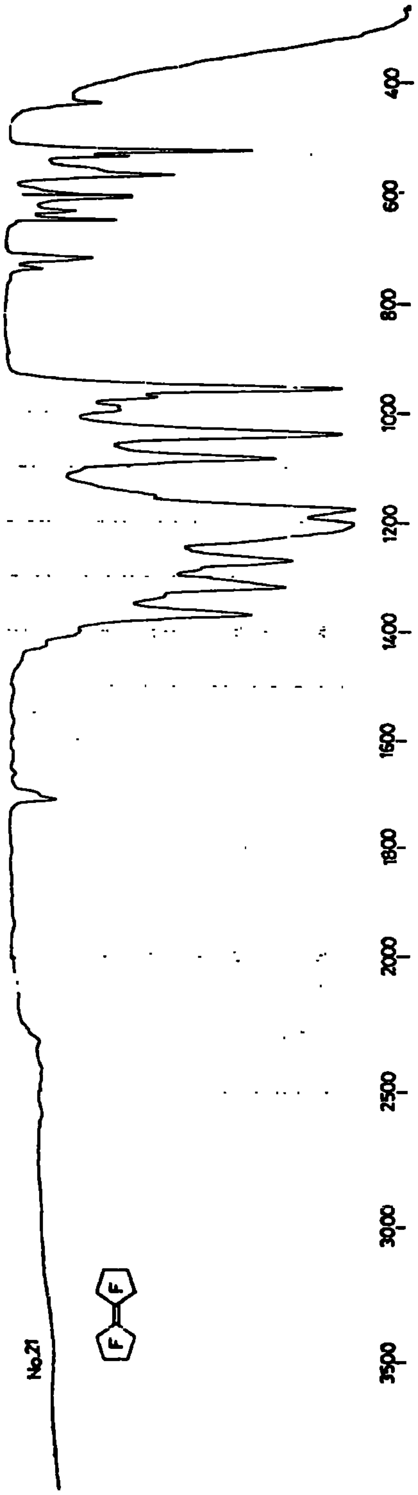
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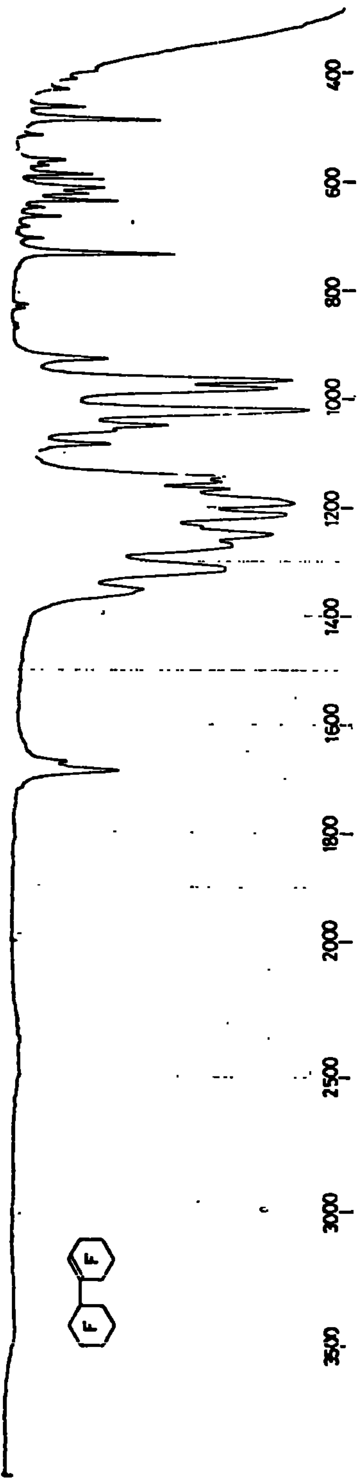

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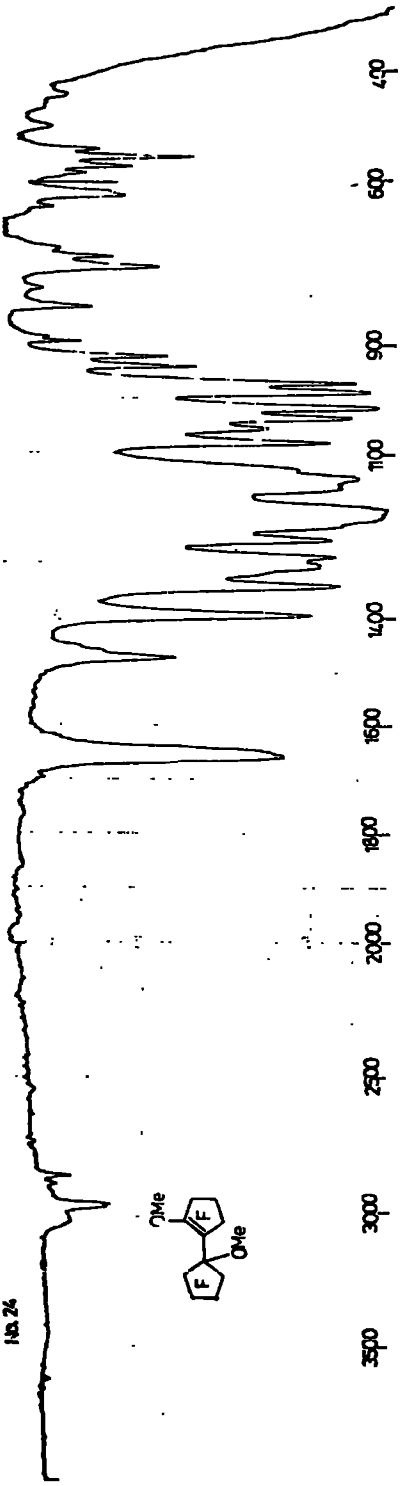
No.24



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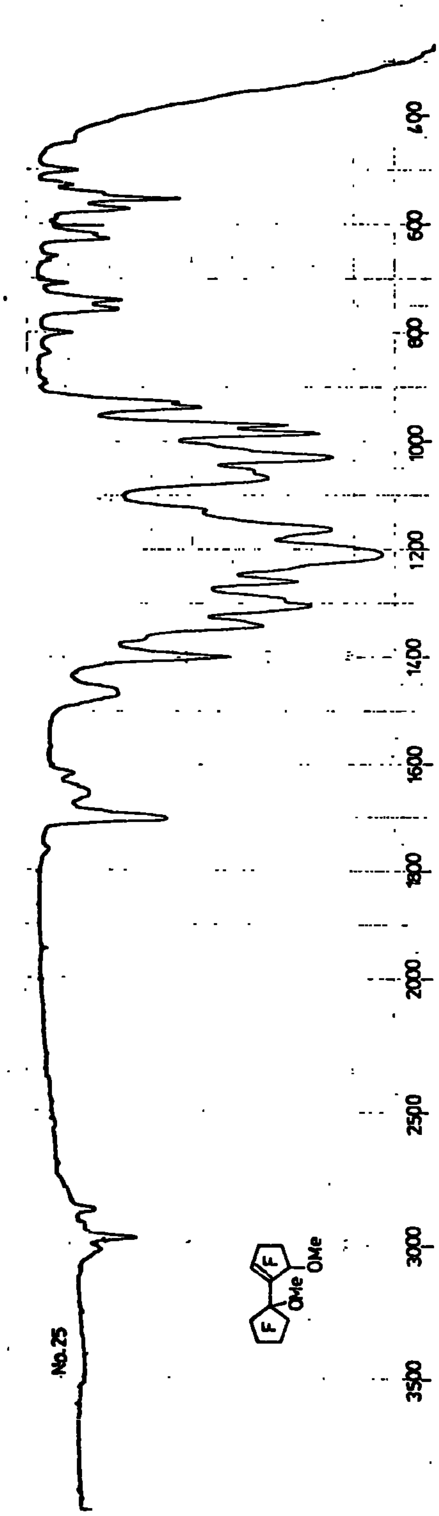
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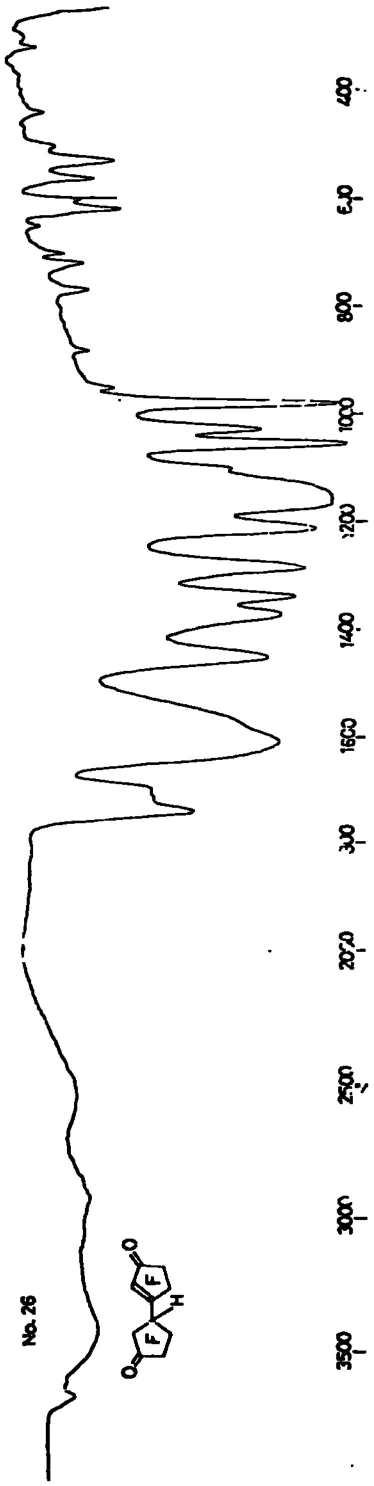
600
800
1000
1200
1400
1600
1800
2000
2500
3000
3500
F
F
OMe
OMe

No. 26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600
800
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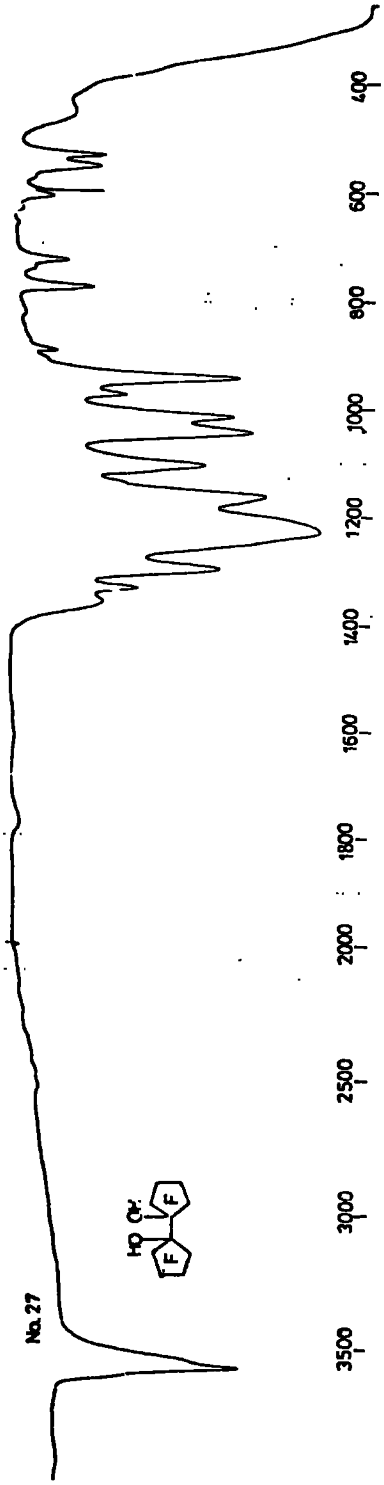
1200
1400
1600
1800
2000
2500
3000
3500
O
F
F
O
H


No. 27
HO CH
F
F
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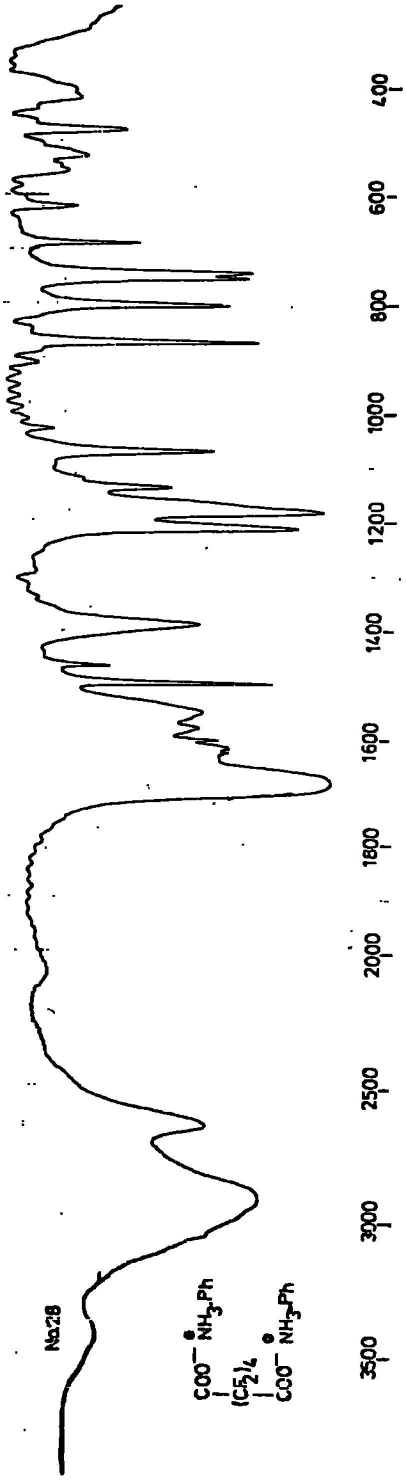
600
800
1000
1200
1400
1600
1800
2000
2500
3000
3500


No.28
COO⁻ NH₃-Ph
(CF₂)₄
COO⁻ NH₃-Ph
400
600
800
1000
1200
1400
1600
1800
2000
2500
3000
3500

APPENDIX II

^{19}F and ^{1}H N.M.R. SPECTRA

APPENDIX II

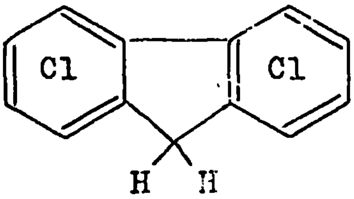
^{19}F and ^{1}H N.M.R. Data

Spectrum No.	Compound	Nucleus
1.	1,2,3,4,5,6,7,8-octachlorofluorene	^{1}H
2.	Perfluoro-(bis(p-phenylphenylene)) sulphide	^{19}F
2(a).	Perfluorobiphenyl	^{19}F
3.	Methoxy perfluoro-(4,4'-bisisopropyl biphenyl)	^{19}F
3(a).	Perfluoro-(4,4'-bisisopropyl biphenyl)	^{19}F
4.	Methoxy perfluoro-(4,4'-bisisopropyl biphenyl)	^{1}H
5.	1,8-Dichloro-3,6-dioxaoctane	^{1}H
6.	18-Crown-6 polyether	^{1}H
7.	1-Methyl-2,3,4,5,6-pentachlorobenzene	^{1}H
8.	2,3,4,6,7,8-Hexachlorodibenzo(b,d) thiophen	^{1}H
9.	Perfluoro-bi(cyclopentylidene)	^{19}F
10.	Perfluoro-(1-cyclohexylcyclohexene)	^{19}F
11.	Perfluorobicyclopentenyl	^{19}F
12.	1-(1-Methoxyoctafluorocyclopentyl)-2-methoxy-hexafluorocyclopent-1-ene	^{19}F
13.	As 12.	^{1}H
14.	1-(1-Methoxyoctafluorocyclopentyl)-5-methoxy-hexafluorocyclopent-1-ene	^{19}F

15.	As 14.	^{1}H
16.	1-(1-Phenoxyoctafluorocyclopentyl)-heptafluorocyclopent-1-ene	^{19}F
17.	1-(3-oxo-1H-hexafluorocyclopentyl)-3-oxopentafluorocylopent-1-ene (52)	^{19}F
18.	Anion of (52)	^{19}F
19.	1,1'-Dihydroxyhexadecafluoro-bicyclopentyl	^{19}F
20.	As 19.	^{1}H
21.	Dianiline Salt of Perfluoroadipic acid	^{19}F
22.	Perfluoro-(1-cyclopentylcyclopentene)	^{19}F

The following abbreviations have been used in describing spectra:- S-singlet; D-doublet; T-triplet; Q-quartet; M-multiplet; B-broad. All shifts are given in p.p.m. and coupling constants are in Hz. Tentative assignments are in brackets.

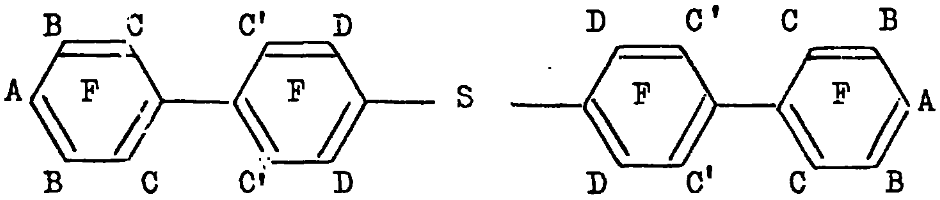
1. 1,2,3,4,5,6,7,8-Octachlorofluorene



Recorded as a solution in carbon tetrachloride.

^{1}H	Shift	Assignment
	4.05(B,S)	$>CH_2$

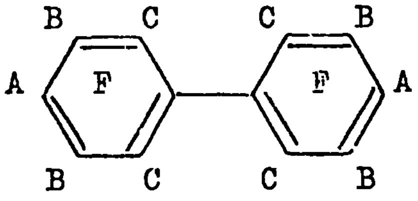
2. Perfluoro-(bis-(p-phenylphenylene)) sulphide



Recorded as a solution in deutero acetone.

^{19}F	Shift	Assignment
	132.4	F_D
	137.8 138.5	F_C and $F_{C'}$
	151.3	F_A
	162.2	F_B

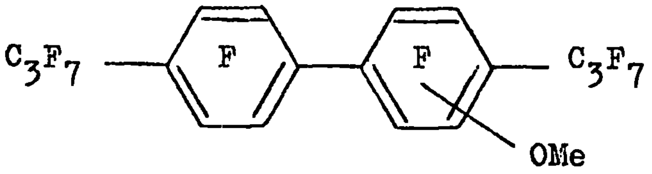
2(a). Perfluorobiphenyl



Recorded as a solution in acetone.

^{19}F	Shift	Assignment
	141.2 (D)	F_C
	156 (T)	F_A
	164.5 (M)	F_B

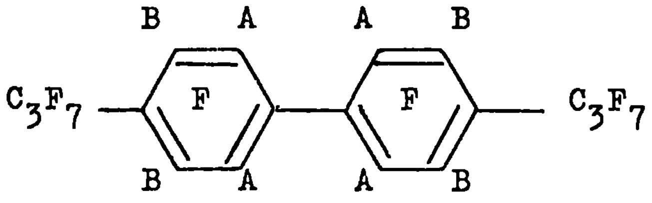
3. Methoxy perfluro-(4,4'-bisisopropyl biphenyl)



Recorded as a solution in deutero acetone.

^{19}F	Shift	Assignment
	180.1	tertiary F
	77.04	- CF_3 groups
	138.1	Aromatic F
	139.4	
	140.9	
	130.2	

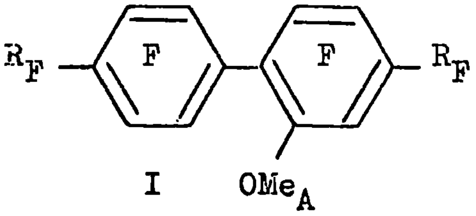
3(a). Perfluoro-(4,4'-bisisopropylbiphenyl)



Recorded as a neat liquid at 155°C.

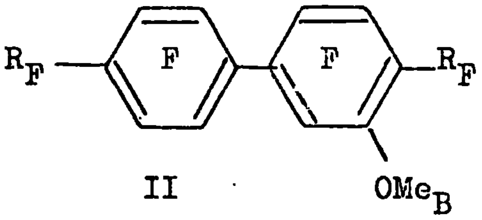
^{19}F	Shift	Assignment
	77.57 (S)	$-CF_3$ groups
	180.0 (T)	tertiary F
	138.8 (S)	F_A
	136.7 (B,S)	F_B

4. Methoxy perfluoro-(4,4'-bisisopropylbiphenyl)



I

and



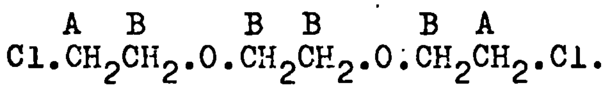
II

Recorded as a solution in deuterochloroform.

^1H	Shift	Assignment
	3.7 (S)	$-O\ CH_3$ A
	4.0 (D) ($J_{(H-t_F)}=3$)	$-O\ CH_3$ B

Ratio I : II = 1 : 3

5. 1,8-Dichloro-3,6-dioxaoctane

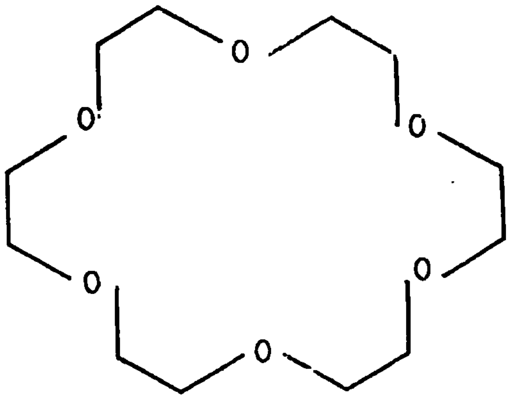


$Cl.\overset{A}{CH_2}\overset{B}{CH_2}.O.\overset{B}{CH_2}\overset{B}{CH_2}.O.\overset{B}{CH_2}\overset{A}{CH_2}.Cl.$

Recorded as a neat liquid.

^1H	Shift	Assignment
	3.51 (S)	$(-CH_2-)A$
	3.56 (S)	$(-CH_2-)B$

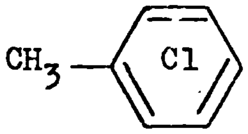
6. 18-Crown-6 Polyether



Recorded as a solution in carbon tetrachloride.

^1H	Shift	Assignment
	3.57 (S)	$-OCH_2-$

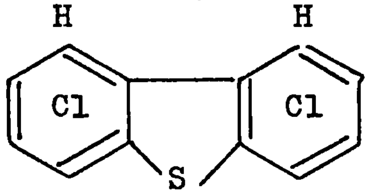
7. 1-Methyl-2,3,4,5,6-pentachlorobenzene



Recorded as a solution in deutero chloroform.

^1H	Shift	Assignment
	3.15 (S)	$-CH_3$ group

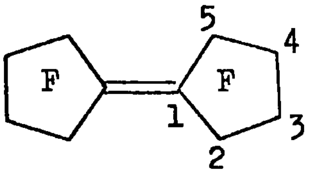
8. 2,3,4,6,7,8-Hexachlorodibenzo(b,d)thiophen



Recorded as a solution in deutero chloroform.

^1H	Shift	Assignment
	9.1 (S)	$H_{1,9}$.

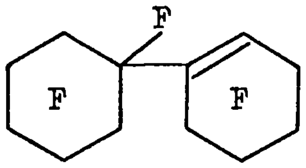
9. Perfluoro-bi(cyclopentylidene)



Recorded as a neat liquid.

^{19}F	Shift	Assignment
	110.1 (S)	$F_{2;5}$
	136.1 (S)	$F_{3,4}$

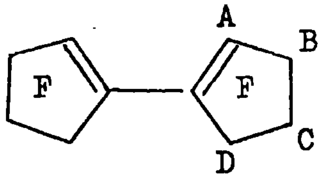
10. Perfluoro-(1-cyclohexylcyclohexene)



Recorded as a neat liquid.

^{19}F	Shift	Assignment
	98.3	Vinylic-F
	181.9	Tertiary-F
	105.6, 113.1, 114.5, 118.6, 120.0, 123.7, 125.4, 128.2, 133.6, 135.8, 140.0, 141.1, 144.7.	Unassigned

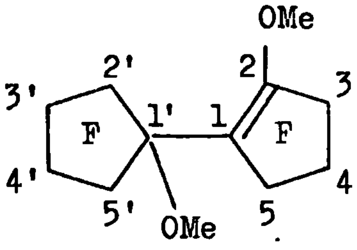
11. Perfluorobicyclopentenyl



Recorded as a neat liquid.

^{19}F	Shift	Assignment
	101.9 (DxD) J_{A-D} 15 Hz	F_D
	105.3 (M)	F_A
	114.4 (D) J_{A-B} 12Hz	F_B
	125.0 (S)	F_C

12. 1-(1-Methoxyoctafluorocyclopentyl)-2-methoxyhexafluorocyclopent-1-ene



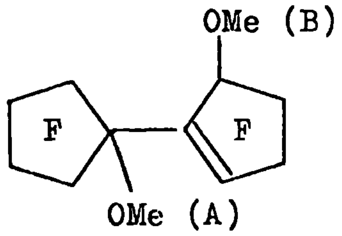
Recorded as a neat liquid.

^{19}F	Shift		Assignment
	108.3 (S)		$-CF_2-$ 5
	116.7 (S)		$-CF_2-$ 3
	134.2 (S)		$-CF_2$ 4
	114.2	(D) J_{AX} 262Hz	$-CF_2-$ 2',5'
	118.8		
	132.5	(D) J_{AX} 262Hz	$-CF_2-$ 2',5'
	137.2		
	122.2	(D) J_{AB} 251Hz	$-CF_2-$ 3',4'
	126.6		
	131.3	(D) J_{AB} 251Hz	$-CF_2-$ 3',4'
	135.8		

13. See 12 for Name and Structure

^{1}H	Shift	Assignment
	3.09 (S)	tertiary $-OCH_3$
	3.80 (S)	vinylic $-OCH_3$

14. 1-(1-Methoxyoctafluorocyclopentyl)-5-methoxyhexafluorocyclopent-1-ene



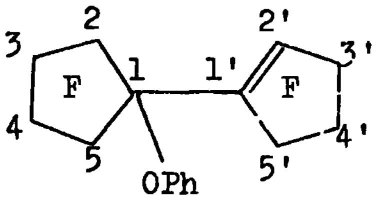
Recorded as a neat liquid.

^{19}F	Shift	Assignment
	Very complex showing many peaks in the $-CF_2-$ Fluorine region.	

15. See 14 for Name and Structure

^{1}H	Shift	Assignment
	3.10 (S)	$-OCH_3$ (A)
	3.35 (S)	$-OCH_3$ (B)

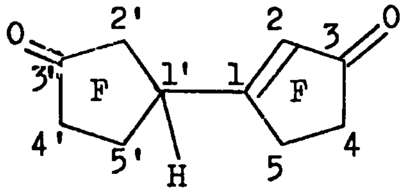
16. 1-(1-Phenoxyoctafluorocyclopentyl)heptafluoro cyclopent-1-ene



Recorded as a solution in deuterochloroform.

^{19}F	Shift		Assignment
	100.4		Vinylic -CF 2'
	105.3		$-CF_2-$ 5'
	112.1		$-CF_2-$ 3'
	131.4		$-CF_2-$ 4'
	117.2 120.2	(D)J_{AX} 260Hz	$-CF_2-$ 2,5
	130.6 133.7	(D)J_{AX} 260Hz	$-CF_2-$ 2,5
	123.5 126.5	(D)J_{AB} 254Hz	$-CF_2-$ 3,4
	129.2 132.2	(D)J_{AB} 254Hz	$-CF_2-$ 3,4

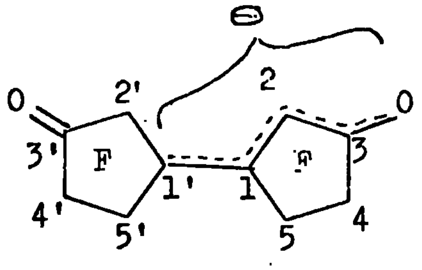
17. 1-(3-oxo-1H-hexafluorocyclopentyl)-3-oxopentafluorocyclopent-1-ene (52)



Recorded as a solution in deuteroacetone.

^{19}F	Shift	Assignment
	107.0 (D)	$-CF_2-$ (5')
	115.7 (B,S)	vinylic -CF 2
	119.2 (M)	$-CF_2-$ (2')
	124.7 (S)	$-CF_2-$ (4,4')
	130.6 (S)	$-CF_2-$ (5)

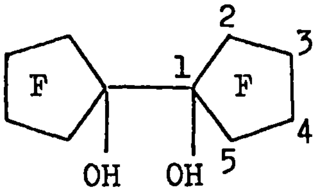
18. Anion of (52)



Recorded as a solution in deuteroacetone.

^{19}F	Shift	Assignment
	107.3	$-CF_2-$ (5')
	118.4	$-CF_2-$ (2')
	120.4	"vinylic" -CF 2
	126.5	$-CF_2-$ (4,4')
	130.9	$-CF_2-$ (5)

19. 1,1'-Dihydroxyhexadecafluorobicyclopentenyl



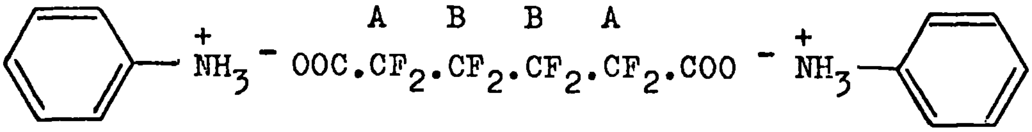
Recorded as a solution in carbon tetrachloride.

^{19}F	Shift		Assignment	
	114.6	(D) J_{AB} = 268Hz	$-CF_2-$	(2,5)
	119.3			
	128.8	(D) J_{AB} = 268Hz	$-CF_2-$	(2,5)
	133.7			
	118.1	(D) J_{AB} = 256Hz	$-CF_2-$	(3,4)
	122.5			
	127.2	(D) J_{AB} = 256Hz	$-CF_2-$	(3,4)
	131.8			

20. See 19 for Name and Structure

^1H	Shift	Assignment
	7.1 (S)	-OH

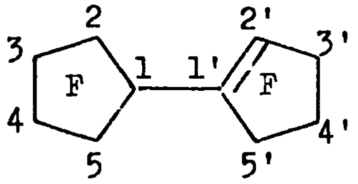
21. Dianiline Salt of Perfluoroadipic Acid



Recorded as a solution in Ether.

^{19}F	Shift	Assignment
	118.9	$-CF_2-$ B
	122.6	$-CF_2-$ A

22. Perfluoro-(1-cyclopentylcyclopentene)



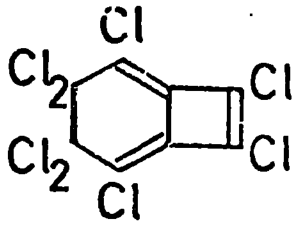
Recorded as a neat liquid.

^{19}F	Shift	Assignment
	107.7 (B,S)	$-CF_2-$ (2,5)
	118.1 (M)	vinylic -CF 2'
	123.01 (D)	$-CF_2-$ (3')
	128.51 (S)	$-CF_2-$ (5')
	130.73 (S)	$-CF_2-$ (4')
	133.30 (S)	$-CF_2-$ (3,4)
	181.26 (B,S)	tertiary-F 1

APPENDIX III

FORMULA INDEX

(1)



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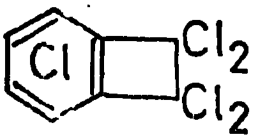

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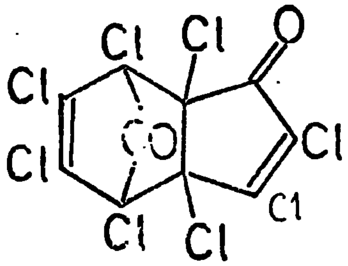

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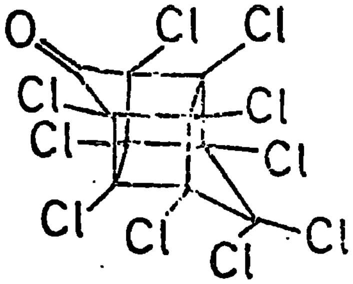

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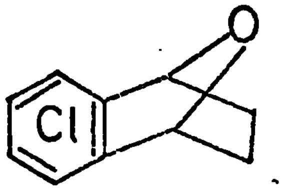

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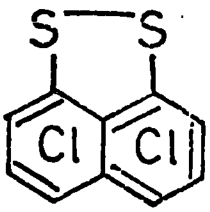

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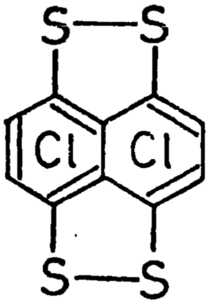

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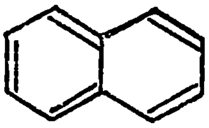

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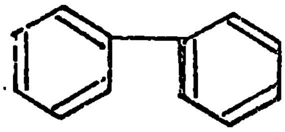

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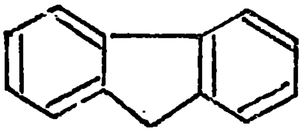

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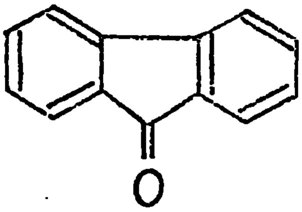

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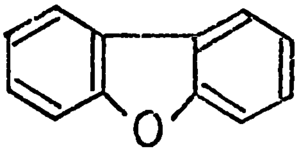

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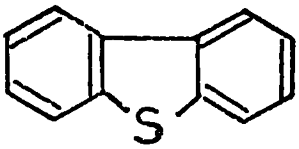

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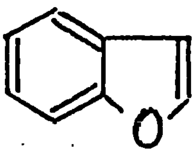

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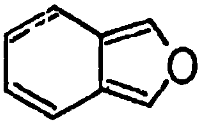

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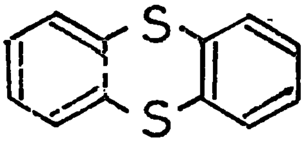

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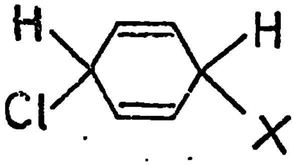

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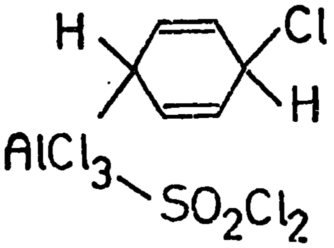

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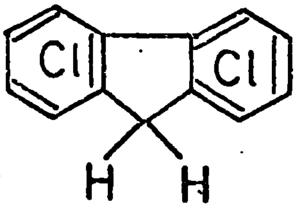

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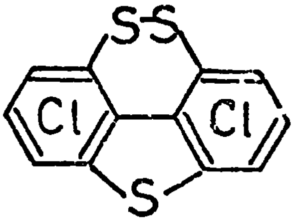

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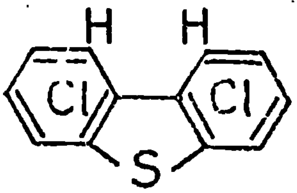

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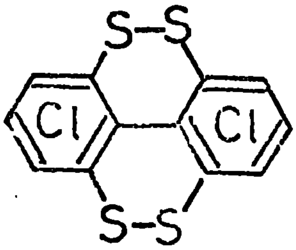

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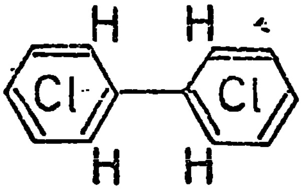

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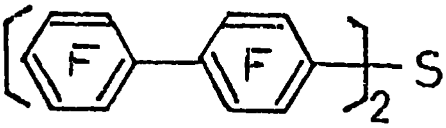

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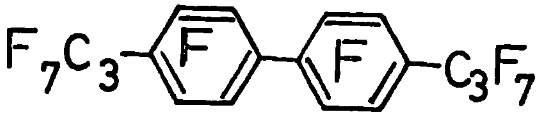

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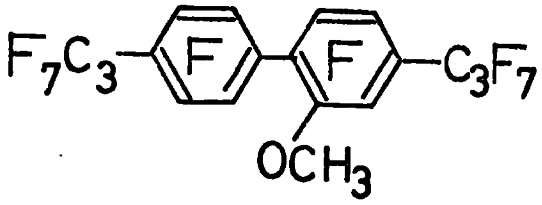

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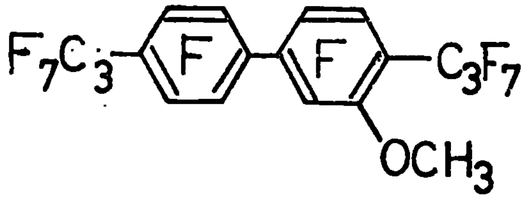

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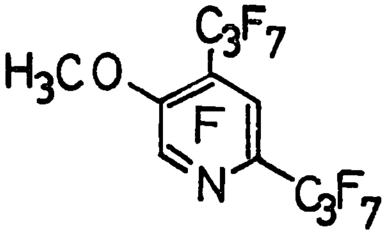
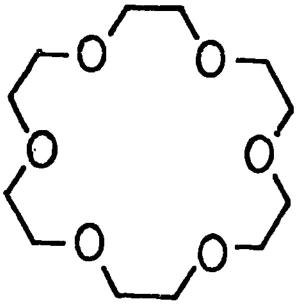


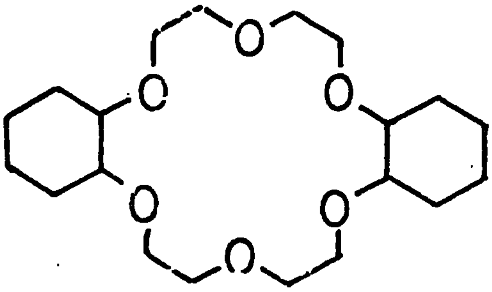
(31) $Cl(CH_2CH_2O)CH_2CH_2Cl$

(32)



(33) $Cl(CH_2CH_2O)_5CH_2CH_2OH$

(34)



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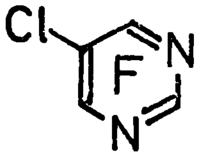

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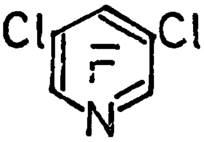
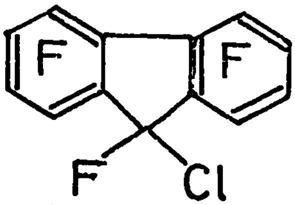


(37)

(38)



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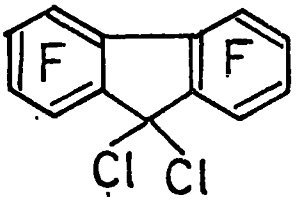

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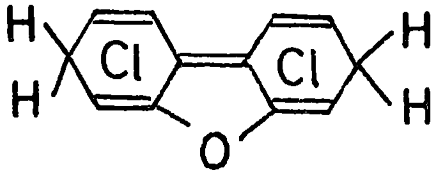

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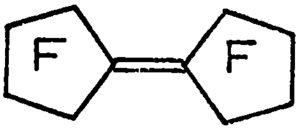

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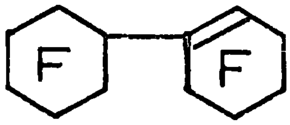

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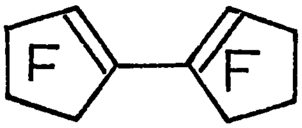

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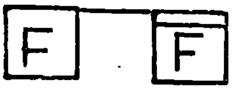

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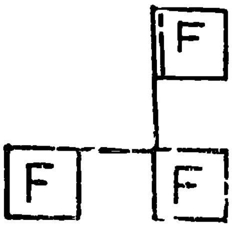

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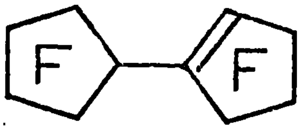

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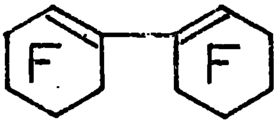

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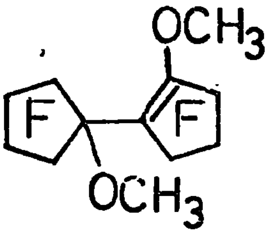

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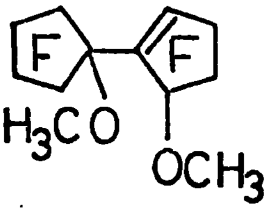

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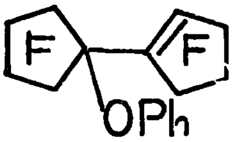

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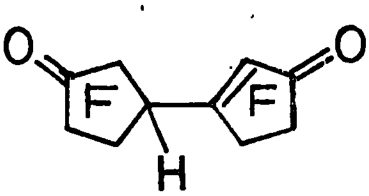

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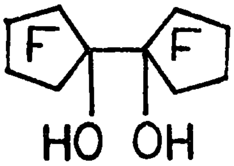

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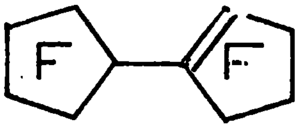

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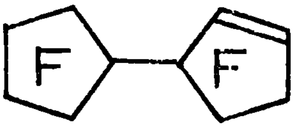

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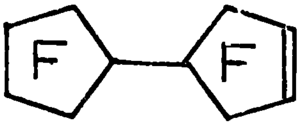

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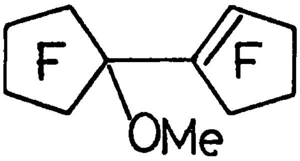

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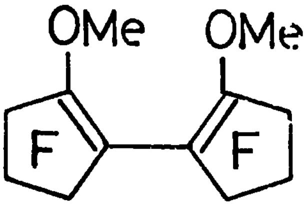

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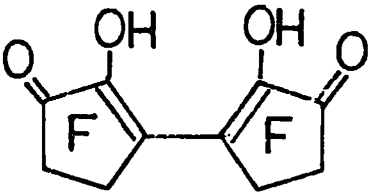

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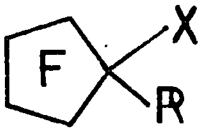

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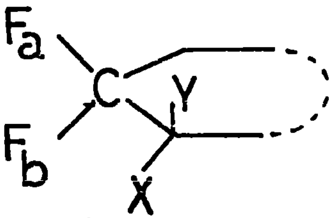

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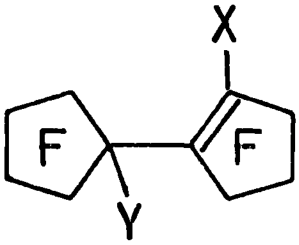

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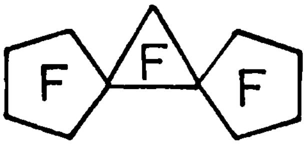

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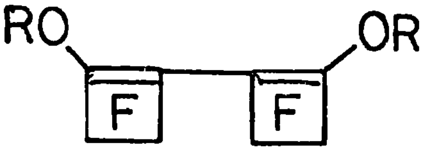

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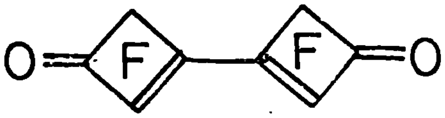

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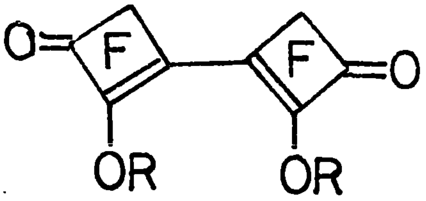

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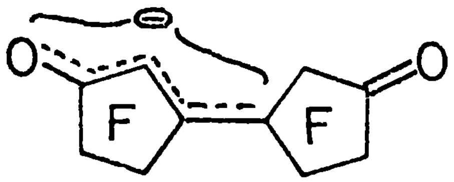

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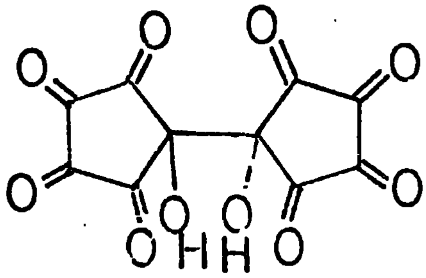

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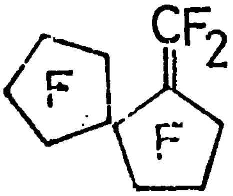

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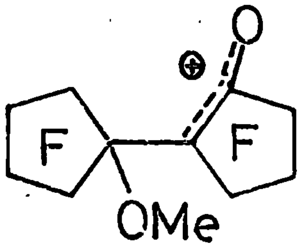

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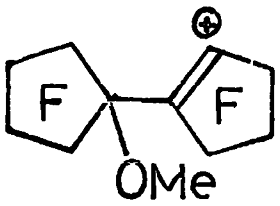

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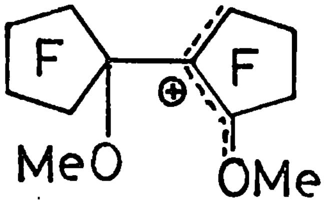

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