SOME REACTIONS
of
POLYFLUORINATED ARYL RADICALS

by

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ABSTRACT

The thermal decomposition of perfluorobenzoyl peroxide in pentafluorobenzene, 1,2,4,5-tetrafluorobenzene, 1,3,5-trifluorobenzene and 1,4-difluorobenzene has been investigated. A reaction scheme is proposed to account for the products of this reaction, which is also applicable to the thermal decomposition of benzoyl peroxide in polyfluoroaromatic solvents and of perfluorobenzoyl peroxide in aromatic hydrocarbon solvents.

It is suggested that when the aryl radical is of very different electronegativity from that of the solvent, it can be stabilised by formation of a π-complex with the solvent. These π-complexes can collapse into σ-complexes, followed by their subsequent dimerisation and disproportionation.

It is also proposed that fluorinated σ-complexes can be defluorinated by elimination of a molecule of hydrogen fluoride between a σ-complex resulting from substitution at a fluorine bearing carbon atom and a hydrogen substituted σ-complex.

The abstraction reactions of aryl radicals of the type \( \text{P-XC}_6\text{F}_4^+ \), resulting from the reactions of polyfluorinated anilines (\( \text{P-XC}_6\text{F}_4\text{NH}_2 \), where X=F, H, MeO or Br) with amyl nitrite have been studied in polyhalogenomethane solvents and a possible explanation given for the yields of abstraction products obtained in these reactions.

The preparative usefulness of abstraction reactions by polyfluoroaryl radicals was investigated in the reactions
of pentafluoroaniline with amyl nitrite in the presence of
cumene and also with methyl mercuric iodide and in the thermal
decomposition of perfluorobenzoyl peroxide in sulphuryl
chloride. Only the last reaction gives useful yields.

The reaction of pentafluoroaniline with amyl nitrite
in the presence of iodobenzene indicated that iodine is
possibly abstracted by the aryl radical from the solvent.
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INTRODUCTION
1.1 GENERAL AND HISTORICAL

1.1.1 Heterolytic and homolytic reactions

Ingold in 1938 distinguished between two mechanisms for the fission of covalent molecules:

\[
\text{Heterolysis: } A:B \rightarrow A^- + B^+ \quad (1a) \\
\text{Homolysis: } A:B \rightarrow A^* + B^* \quad (1b)
\]

where A and B are atoms or groups of atoms. The type of reaction primarily considered in this thesis will be the latter type, homolysis, in which the covalent bond breaks to give two neutral fragments, known as free radicals, each of which contains an unpaired electron.

Since more energy would be required to separate the charged fragments in equation (1a) than the neutral fragments in (1b), it might be thought that the latter might be the more favourable reaction and in the gas phase this is usually found to be true. However, in the majority of reactions in solution, particularly in solvents of high dielectric constant, solvation of the ions produced in reaction (1a) renders heterolytic reaction energetically more favourable.

1.1.2 Free radicals

A free radical is defined as an atom or molecule containing one or more unpaired electrons. This definition includes such inorganic species as nitric oxide and halogen atoms, e.g. \( \text{Cl}^- \) and \( \text{Br}^- \), which can be produced by the
photolysis of halogen molecules.\(^2,3\)

The existence of organic free radicals was first demonstrated by Gomberg\(^4\) in his work on the dissociation of hexaaryl ethanes into triarylmethyl radicals. Organic free radicals can be conveniently divided into two categories:

(i) radicals of long life, stabilised by resonance, e.g., triarylmethyl radicals, I; oxygen radicals such as the tri-t-butyl phenoxy-radical, II;

\[
\text{Ph} \quad \text{Ph} \quad \text{C}^* \\
\text{Ph} \quad \text{Ph} \\
\text{I}
\]

\[
\text{tBu} \quad \text{tBu} \\
\text{tBu} \quad \text{tBu} \\
\text{II}
\]

and nitrogen radicals such as diphenylpicrylhydrazyl, III;

\[
\text{NO}_2 \quad \text{NO}_2 \\
\text{Ph}_2\text{N}-\text{N} \quad \text{NO}_2 \\
\text{III}
\]

which has no associated dimer and is used as a radical scavenger.\(^5\)

(ii) radicals of short life, like phenyl and methyl radicals which do not enjoy such stabilisation.

\[
\text{IV} \\
\text{CH}_3^* \\
\text{V}
\]
The difference between the two types of radical is merely one of degree of reactivity and does not imply that radicals of short life are intrinsically unstable. This thesis will be concerned with aryl radicals of short life.

1.1.3 Occurrence of short lived free radicals in reactions

The presence of short lived free radicals in solution is inferred from the kinetics of their reactions and the nature and distribution of their products. The very small concentrations in which such reactive intermediates exist often prevent their detection by the physical methods (e.g. electron spin resonance, magnetic measurements and colorimetric methods) available for the detection of such radicals as triphenylmethyl.

It was not until the work of Paneth and Hofeditz on the pyrolysis of tetramethyl lead under conditions of low pressure, that the role of radicals as transient intermediates in chemical reactions was established.

The so-called 'normal' laws of aromatic substitution developed by experiment, apply to heterolytic reactions. It was the separation of apparently anomalous substitution products from certain reactions that led Hey and Waters to interpret these reactions as being free radical processes. Among these were the reaction of aromatic nuclei with benzoyl peroxide and some decompositions of aromatic diazonium salts (e.g. Gomberg-Bachmann reaction).
1.1.4 Formation of radicals

In solution, molecules containing weak bonds with dissociation energies of 40 kcal.mole\(^{-1}\) or less, will usually dissociate at temperatures below 150°. This method of generating radicals is widely used.

Energy to break a covalent bond in a molecule can be provided by electromagnetic radiation of a suitable wavelength. The energy associated with a quantum of light, 48 kcal.mole\(^{-1}\) at 6000 Å and 96 kcal.mole\(^{-1}\) at 3000 Å, is of the same order of magnitude as that of most covalent bonds.

When one-electron transfer occurs to or from an organic species containing only paired electrons a free radical results. Metal ions are frequently used as the electron donors or acceptors and this method is of particular use in aqueous media.

1.1.5 Sources of aryl radicals

Aryl radicals in solution result either (i) directly from the cleavage of a covalent bond as in photolytic methods\(^{11}\) or (ii) from the secondary decomposition of a radical by extrusion of covalent molecules, as in (A), the cleavage of aryl-nitrogen bonds\(^{12}\) to give nitrogen and an aryl radical, and (B), the decarboxylation of aroyloxy-radicals.\(^{13}\)

(i) Photolytic methods

(a) \(\text{ArI} \xrightarrow{hv} \text{Ar}^* + \text{I}^*\) \(^{14}\)
(b) ArHgI $\xrightarrow{hv}$ Ar$^*$ + HgI$^*$ 15, 16

(ii) (A) Aryl-N fission

(a) Gomberg reaction$^{10, 17}$

\[
\text{Ar-N=N-OH} \quad \text{ArN=NOH} \quad \text{Ar}^* + N_2 + (\text{OH}^*)
\]

(b) Diazonium compounds$^{18, 19, 20}$

\[
\text{ArN=NX} \quad \text{Ar}^* + N_2 + X^*
\]

(c) Acylaryl nitrosoamines$^{21}$

\[
\text{ArN(NO)CO.R} \quad \text{ArN=N-0.C0.R} \quad \text{Ar}^* + N_2 + (\text{0.CC.R})
\]

(d) Triazens$^{22}$

\[
\text{ArN=N-NHR} \quad \text{Ar}^* + N_2 + (\text{NHR}^*)
\]

(e) Arylazotriarylmethanes$^{23, 24}$

\[
\text{ArN=NCAr}_3 \quad \text{Ar}^* + N_2 + \text{CAR}_3^*
\]

(f) Oxidation of arylhydrazines$^{25}$

\[
\text{ArNH_NH}_2 \quad \text{ArN=N}^* \quad \text{Ar}^* + N_2
\]

(g) Aromatic amines with amyl nitrite$^{26, 27, 28}$

\[
\text{ArNH}_2 + \text{AmONO} \quad \text{ArN=NOAm} \quad \text{Ar}^* + N_2 + \text{OAm}^*
\]

(ii) (B) Decarboxylation of aroyloxy-radicals

(a) Diaroyl peroxides$^{29}$

\[
\text{ArCO.O-CO.Ar} \quad 80^\circ \quad 2\text{ArCO.O}^* + \text{Ar}^* + \text{CO}_2
\]
(b) **Iodosoacylates**
\[
\text{PhI(O.CO.Ar)_2} \xrightleftharpoons{130^\circ} \text{2ArCO}^* + \text{PhI} \rightarrow \text{Ar}^* + \text{CO}_2
\]

(c) **Lead tetrasalts**
\[
\text{Pb(O.CO.Ar)_4} \xrightleftharpoons{130^\circ} \text{2ArCO}^* + \text{Pb(O.CO.Ar)_2}
\]

(d) **Silver iodide-acid complexes**
\[
\text{AgI(O.CO.Ar)_2} \xrightleftharpoons{130^\circ} \text{2ArCO}^* + \text{AgI}
\]

(iii) **Electron transfer**

(a) **Electrolysis of acids**
\[
\text{ArCO}^- \xrightarrow{-e} \text{ArCO}^*
\]

Only reactions (ii(A)g), the thermal decomposition of aromatic amines with amyl nitrite, and (ii(B)a), the thermal decomposition of diaroyl peroxides will be considered in detail in this thesis.

### 1.1.6 Types of reaction of aryl radicals in solution

The reactions of free radicals can be divided into three categories:

(i) **Radical transfer** This involves the attack of a radical on a non-radical species and can be expressed by the general equation

\[
\text{Ar}^* + \text{XR} \rightarrow \text{ArX} + \text{R}^*
\]

If \( \text{R}^* \) is the same as \( \text{Ar}^* \), or if \( \text{R}^* \) reacts further to produce
another Ar' radical, then a chain reaction is set up. There are two types of radical transfer reaction which will be dealt with in detail in this thesis, namely (A) substitution of an aryl radical into an aromatic nucleus and (B) abstraction by aryl radicals of atoms from a solvent molecule. (A) The reaction of an aryl radical with an aromatic solvent can be expressed generally by the following equation

\[ \text{Ar}^* + \text{Ar}'\text{H} \rightarrow \text{ArAr}' + [\text{H}^*] \] \hspace{1cm} (3)

The above equation is very much a simple representation of a complex reaction which will be discussed in greater detail at a later stage and is not intended to imply that free hydrogen atoms are produced in the reaction.

(B) The abstraction of an atom from a molecule by a radical can be expressed by the following equation

\[ \text{Ar}^* + \text{RY} \rightarrow \text{ArY} + \text{R}' \] \hspace{1cm} (4)

In the above equation (4) R' is usually alkyl and only rarely aryl and Y is usually halogen or hydrogen.

(C) There is a third type of radical transfer reaction involving addition of a radical to a double bond, which can be expressed by the equation

\[ \text{Ar}^* + \text{X=Y} \rightarrow \text{Ar-X-Y}' \] \hspace{1cm} (5)

where X and Y are usually both carbon. Such additions to an olefinic double bond are of immense importance in radical initiated polymerisations. As will be shown later, this reaction is analogous to
the first stage in the substitution of an aryl radical in an aromatic substrate.

(ii) **Radical combination** This is a process which can be expressed by the equation

\[ \text{Ar}^* + \text{Ar}^* \rightarrow \text{ArAr}^* \]  

(6)

and is the reverse of the dissociation of a covalent bond to give two radicals. The driving force for such reactions is large, being the energy of bond formation (which may exceed 100 kcal.mole\(^{-1}\)). Radical combination is one of the possible chain termination processes in radical chain reactions.

(iii) **Disproportionation** This is the third type of reaction undergone by radicals and usually involves hydrogen transfer, e.g.

\[ 2 \text{ } \overset{\text{H}}{\equiv} \text{C} \text{C} \rightarrow \overset{\text{H}}{\equiv} \text{C} \text{C}^* + \overset{\text{H}}{\equiv} \text{C}_2 \text{C}^* \text{H} \]  

(7)

The importance of this reaction in chain terminations during the decomposition of aroyl peroxides will be discussed later.
1.2 ARYLATION WITH DIAROYL PEROXIDES

1.2.1 Reaction products and early investigations

Diaroyl peroxides provide one of the most convenient sources of aryl radicals, giving 'cleaner' products than other sources.

The products of the thermal decomposition of diaroyl peroxides in aromatic solvents, which were found to be biaryl, carbon dioxide, benzoic acid, esters and high boiling residue, were first investigated by Gelissen and Hermans\(^3\) and subsequently by Boeseken and Hermans\(^4\) who proposed the following reaction scheme for a general solvent RH.

\[
\begin{align*}
\text{(a)} & \quad (\text{Ar'}\text{CO})_2 + \text{RH} \rightarrow \text{Ar'}\text{H} + \text{CO}_2 + \text{Ar'}\text{CO.OH} \\
\text{(b)} & \quad (\text{Ar'}\text{CO})_2 + \text{RH} \rightarrow \text{Ar'}\text{R} + \text{CO}_2 + \text{Ar'}\text{CO.OH}
\end{align*}
\]

When the solvent RH is aromatic, biaryls can be formed only by route (b) and are of the form Ar'R in which one group (Ar') is derived from the peroxide and the other group (R) is derived from the substrate.

This generalisation has been confirmed by later work.\(^5,6,7\)

In 1937, Hey and Waters\(^8\) first interpreted the products of the decomposition of diaroyl peroxides in terms of a free radical process.

The first step in the thermal decomposition of diaroyl peroxides is the homolytic fission of the oxygen-oxygen bond,
which yields two aroyloxy-radicals, some of which undergo decarboxylation to yield phenyl radicals, which bring about the arylation reaction.

\[(\text{ArCO.O})_2 \rightarrow 2\text{ArCO.O}' \]  \hspace{1cm} (9a)

\[\text{ArCO.O}' \rightarrow \text{Ar}' + \text{CO}_2 \] \hspace{1cm} (9b)

It should be noted at this stage that:

(a) radicals of the type Ar' or ArCO.O' do not recombine to any appreciable extent in dilute solution and

(b) abstraction of hydrogen atoms from the substrate by either Ar' or ArCO.O' radicals is not the predominant reaction with simple benzene derivatives, since the radicals so formed (Ar') would necessarily form the symmetrical biaryl (ArAr) either by combination or by reaction with the solvent.

1.2.2 Kinetics of aroyl peroxide decomposition

There has been extensive investigation of the kinetics of the decomposition of benzoyl peroxide in a variety of solvents. Early results \(^4\,^1,^4\,^2\) indicated a first order primary dissociation of the peroxide to give two benzoyloxy-radicals, but the importance of induced, chain decompositions of benzoyl peroxide was deduced by Nozaki and Bartlett \(^4\,^3\) and by Cass. \(^4\,^4\)

In 1965 Gill and Williams \(^4\,^5\) reported a study of the kinetics and products of the thermal decomposition of benzoyl peroxide in benzene over a wide range of concentrations and
expressed their results in the rate equation

$$\frac{-d[P]}{dt} = k_1[P] + k_1'[P] + k_{1.5}[P]^{1.5} \quad (10)$$

where $P$ is the peroxide, and $k_1$ and $k_{1.5}$ are first and 1.5 order constants respectively. The first term represents a primary unimolecular decomposition of the peroxide, the second term a first-order induced decomposition of the peroxide with chain termination between dissimilar radicals. The third term represents an induced decomposition of the peroxide with chain termination between similar radicals.

In the presence of radical scavengers only the first term is observed. The variation of the observed first order rate constant with the original peroxide concentration, and the apparent first order rate constant at zero peroxide concentration gave $k_{1.5}$ and $[k_1 + k_1']$ respectively.

When benzene is the solvent, the second term is small and can be neglected giving equation (11).

$$\frac{-d[P]}{dt} = k_1[P] + k_{1.5}[P]^{1.5} \quad (11)$$

While equation (11) describes the decomposition in benzene, equation (12) accurately describes the decomposition in some other solvents.

$$\frac{-d[P]}{dt} = k_1[P] + k_1'[P] \quad (12)$$

Gill and Williams found that with chlorobenzene as solvent, equation (11) held for peroxide concentrations less
than 0.11M while at peroxide concentrations greater than this, equation (12) held. For bromobenzene as solvent it was found that equation (12) held at all concentrations.

Lewis and Williams found that equation (11) held for fluorobenzene.

1.2.3 The nature of the substitution reaction

As has been previously mentioned (1.2.1), the main reactions of radicals derived from diaroyl peroxides is nuclear substitution and it has been shown (1.2.1) that abstraction of hydrogen atoms from the substrate by aryl radicals does not take place to a large extent.

Considerable amounts of high boiling resinous materials are also formed during the reaction and any mechanistic scheme for the substitution must take this into account.

There are two ways whereby the nuclear substitution may take place:—

(i) The Addition-Abstraction Mechanism

This mechanism is a two stage process involving firstly an addition of an aryl radical to an aromatic solvent molecule, giving a fully bonded intermediate (a σ-complex), with subsequent dehydrogenation.

\[
\text{Ar}^* + \text{ArH} \rightarrow \left[ \begin{array}{c}
\text{Ar} \\
\text{H}
\end{array} \right] \xrightarrow{\text{(σ-complex VI)}} \text{Ar}^*\text{Ar} + \left[ \begin{array}{c}
\text{H}^*
\end{array} \right]
\] (13)
(ii) The Synchronous Mechanism

The second possibility is that addition of Ar' and the recession of H' occur simultaneously through a partially bonded transition state:

\[(Ar' \ldots \ldots Ar \ldots \ldots H)^*\]  \hspace{1cm} (14)

Molecular hydrogen has never been isolated from the reaction in aromatic solvents, and the formation of free hydrogen atoms in schemes (i) or (ii) is therefore ruled out.

The lack of a kinetic isotope effect in the arylation of deuterated and tritiated aromatic compounds\(^{48,49,50}\) suggested that the mechanism followed was an addition abstraction mechanism i.e. that the substitution step proceeds by the rate determining addition of an aryl radical to the substrate nucleus to give an intermediate which is dehydrogenated in the subsequent fast step.

1.2.4 The 6-complex and nature of the residue

It was originally thought that the high boiling residue formed in the reaction was a mixture of polyaryls obtained by further arylation of the biaryls originally formed.\(^{8,9,51}\) However, in 1957, Walling,\(^{52}\) and Lynch and Pausacker\(^{53}\) independently suggested an alternative scheme for the formation of the residue, which involved dimerisation and disproportionation of the 6-complexes according to the following mechanism:
The isolation of p-quaterphenyl from the reaction in benzene was attributed to the dehydrogenation of the stereoisomers of (VIII) and not to the phenylation of p-terphenyl. This postulate has been verified in work involving the phenylation of 1-\textsuperscript{14}C-benzene with benzoyl peroxide,\textsuperscript{54,55} when a residue was obtained containing much quaterphenyl labelled in two nuclei, and only a little terphenyl labelled in one nucleus, the latter being formed by further phenylation of the primary product biphenyl.

In 1958, De Tar and Long\textsuperscript{38} isolated a product of the disproportionation of σ-complexes, namely 1,4-dihydrobiphenyl (IX)

\[
\begin{align*}
\text{Ph} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{IX}
\end{align*}
\]
They also isolated one of the hydroaromatic products of the dimerisation of σ-complexes, namely an isomer of tetrahydroquaterphenyl-1',4',1''-tetrahydro-p-quaterphenyl, (VIII)

\[
\text{VIII}
\]

Later work by Hey, Perkins and Williams\textsuperscript{56} and by De Tar, Long and Rendleman\textsuperscript{57} have largely substantiated the earlier results of De Tar and Long.\textsuperscript{38} Isomers of the quaterphenyl molecule have been isolated and 1,2-dihydrobiphenyl has been recognised.

From the available experimental evidence, the formation of arylcyclohexadienyl radicals (VII) in these reactions is now firmly established.

\[
\text{VII}
\]

1.2.5 **Dehydrogenation of the σ-complex**

As has been mentioned previously, the kinetics of the decomposition of benzoyl peroxide in benzene can be represented
by equation (11)

\[-d\left[\mathcal{P}\right]/dt = k_1[\mathcal{P}] + k_{1.5}[\mathcal{P}]^{1.5}\] (11)

Kinetics of this form are given when chain termination occurs between similar radicals, such as the dimerisation and disproportionation of Σ-complexes. Termination between dissimilar radicals would lead to kinetics of the form in equation (12)

\[-d\left[\mathcal{P}\right]/dt = k_1[\mathcal{P}] + k_{1}[\mathcal{P}]\] (12)

The direct dehydrogenation of Σ-complexes by benzoyloxy-radicals (16)

\[
\text{Ar'ArH}^* + \text{Ar'CO.O}^* \longrightarrow \text{Ar'Ar} + \text{Ar'CO.OH} \] (16)

is a termination of the latter type and cannot therefore occur to a significant extent if the kinetics are of the form represented by equation (11).

Recent determination of the values of the rate constants in equation (11) by kinetic experiments in the presence and absence of radical scavengers and correlations of these results with the variation in yield of the various products, biaryls, esters, aroic acids, dihydrobiphenyls and the residue, have shown that the Σ-complex is the most important chain carrier. Reaction (17f) is thus the main transfer stage and is one of the reactions in which biaryls and aroic acids are formed.
1.2.6 Mechanism of the decomposition of benzoyl peroxide

The following scheme, proposed by Gill and Williams, is in agreement with the kinetics and with the formation of the products mentioned above:

\[
\begin{align*}
P & \rightarrow 2R' \quad \text{(a)} \\
R' & \rightarrow R'' + \text{CO}_2 \quad \text{(b)} \\
R' + \text{PhX} & \rightarrow \sigma^* \quad \text{(c)} \\
R'' + \text{PhX} & \rightarrow \sigma^{''} \quad \text{(d)} \\
\sigma^* + P & \rightarrow R' + \text{PhR} + \text{PhCO}_2\text{H}^* \quad \text{(e)} \\
\sigma^{''} + P & \rightarrow R' + \text{PhR'} + \text{PhCO}_2\text{H} \quad \text{(f)} \\
2 \sigma^{''} \text{ or } 2 \sigma^* & \rightarrow \text{Dimerisation and disproportionation products} \quad \text{(g)} \\
\sigma^* + \sigma^{''} & \rightarrow \text{Products} \quad \text{(h)} \\
R' + P & \rightarrow R'' + \text{CO}_2 + \text{ester} \quad \text{(i)} \\
R'' + P & \rightarrow R' + \text{ester} \quad \text{(j)} \\
\end{align*}
\]

Equation (17)

where \(P\) is the peroxide, \(R'\) is a benzoyloxy-radical, \(R''\) is an aryl radical and \(\sigma^*\) and \(\sigma^{''}\) are the corresponding complexes derived from \(R'\) and \(R''\) and a solvent molecule.

The reaction of benzoyl peroxide in benzene, alkyl benzene, fluorobenzene and chlorobenzene at low peroxide concentrations follows the kinetic equation (11).

1.2.7 Decomposition of benzoyl peroxide in bromobenzene

The reaction in bromobenzene has quite different characteristics from the reaction in the previously mentioned
solvents. The kinetics are characterised by equation (12) indicating chain termination between dissimilar radicals and the yields of biaryl and benzoic acid are very high while the yields of dihydrobiphenyl and high boiling residue are very small. In this solvent and also in chlorobenzene at high peroxide concentrations, the chains are thought to be terminated by reaction (16).

This contrast in behaviour is thought to be due to the greater stabilisation of the benzoyloxy-radical in bromobenzene by formation of π-type charge transfer complexes between the radical and the solvent, which may or may not involve the actual transfer of one electron to the acceptor radical.

\[
\begin{aligned}
\text{H} & \quad \text{O.CO. Ph} \\
\text{O.CO. Ph} & \quad \text{H} \\
\text{Br} & \quad \text{O.CO. Ph} \\
\text{Br} & \quad \text{O.CO. Ph}
\end{aligned}
\]

The result would be a higher stationary concentration of benzoyloxy-radicals and a lower stationary concentration of σ-complexes than in benzene.

1.2.8 The effect of oxidising agents

(1) Oxygen

Eberhardt and Eliel\(^6\) have studied the effect of oxygen on the product distribution from the decomposition of benzoyl
peroxide in benzene. They found that both in dilute and in concentrated solutions the yield of biphenyl was greatly increased with an accompanying decrease in the yields of quaterphenyl and dihydrobiphenyl. It was suggested that oxygen facilitated the dehydrogenation of \( \sigma \)-complexes, thus suppressing the formation of dimers and disproportionation products. Morrison, Cazes, Samkoff and Howe also reported increased biphenyl yields, while the isomer ratios remained constant.

(ii) Nitro compounds and their derivatives.

Small quantities of nitrobenzene, \( m \)-dinitrobenzene, nitrosobenzene and phenylhydroxylamine have been found by Hey, Perkins and Williams to increase the yields of biaryl and benzoic acid and decrease the yield of residue in the decomposition of benzoyl peroxide in benzene and in fluoro-benzene. It has now been shown that the effective catalyst in these reactions is nitrosobenzene.

(iii) Transition metal compounds

Transition metal compounds such as copper salts and other electron acceptors also catalyse the oxidation of \( \sigma \)-complexes. Dailly and Williams have shown that addition of ferric benzoate causes great increase in biaryl yields. It was suggested that biaryl and benzoic acid were formed in the following scheme:
\[
\begin{align*}
\text{PhArH}^* + \text{Fe}^{3+} & \rightarrow \text{PhAr} + \text{H}^+ + \text{Fe}^{2+} \\
\text{PhCO.O}^- + \text{Fe}^{2+} & \rightarrow \text{PhCO.O}^- + \text{Fe}^{3+} \quad (19) \\
\text{PhCO.O}^- + \text{H}^+ & \rightarrow \text{PhCO.OH}
\end{align*}
\]
1.3 THE REACTION OF PRIMARY AROMATIC AMINES WITH ALKYL NITRITES

1.3.1 Aromatic solvents

As mentioned earlier (1.1.5) aryl radicals can be obtained from azo and diazo derivatives of primary amines. Probably the best known experimental use is in the Gomberg-Hey arylation of aromatic compounds, in which aqueous diazotised amine is allowed to decompose at pH > 8, in the presence of the aromatic compound to be arylated. This reaction, and other similar processes, has the disadvantage that yields of biaryls are low and that large quantities of tarry side products are formed.

The use of amyl nitrite as an 'in situ' diazotising agent has been reported in connection with the formation of benzene from anthranilic acid and the deamination of aromatic amines in the presence of dimethyl formamide. In particular, the formation of diazonium salts from protonated amines using alkyl nitrites was well known. However, little had been reported about the reaction of amyl nitrite with free amines. It had been found that such reactions lead to the formation of N-diazo-amino-compounds. The thermal decomposition of such compounds had been shown to give aryl radicals.

Huang Shu in 1959 and later Cadogan in 1962 have shown that treatment of aromatic primary amines with amyl nitrite in aromatic solvents at 80° or above gave good yields.
of the corresponding biaryl.

Both Huang Shu and Cadogan suggested that the decomposition of aromatic amines with amyl nitrite was a free radical reaction.

In view of the formation and free radical decomposition of \( N \)-diazo-amino- compounds mentioned above, it seemed possible that the reaction of primary aromatic amines with amyl nitrite in aromatic solvents could proceed through this route. However, this appeared unlikely from the low temperatures at which the decomposition occurred (ca. 80°) compared with those necessary to induce the decomposition of the corresponding diazoamino benzenes (150°).

Also, no products resulting from the reaction of aryl-amino radicals, \( \text{ArNH}^+ \) (20), which are formed from \( N \)-diazo-amino- compounds, were detected in this particular reaction.

\[
\text{ArN}=\text{N}-\text{NHAr} \longrightarrow \text{Ar}^* + \text{N}_2 + \text{HNHAr} \quad (20)
\]

The free radical nature of the Huang Shu-Cadogan reaction was confirmed by the work of Ray, who used a competitive technique to investigate the activating or deactivating influence of different substituents in the aromatic nucleus towards phenylation with phenyl radicals formed from aniline and amyl nitrite. It was found that the aromatic nucleus was activated towards attack by phenyl radicals in the formation of biaryls, irrespective of the polarity of the aromatic substituents. It has also been found that the ratio of isomers formed in the decomposition of aniline with amyl
nitrite in chlorobenzene is the same as the ratio of isomers formed by phenylation of chlorobenzene using other standard sources of phenyl radicals.\textsuperscript{76}

The following mechanism was proposed:\textsuperscript{75}

\begin{align*}
\text{PhNH}_2 + \text{AmONO} & \rightarrow \text{PhN=NOAm} + \text{H}_2\text{O} \quad (a) \\
\text{PhN=NOAm} & \rightarrow \text{Ph}^* + \text{N}_2 + \cdot\text{OAm} \quad (b) \\
\text{ArH} + \text{Ph}^* & \rightarrow \text{PhArH}^* \quad (c) \\
\text{PhArH}^* + \cdot\text{AmO}^* & \rightarrow \text{PhAr} + \text{AmOH} \quad (d)
\end{align*}

Equation (21)

(a) the aromatic amine reacts with amyl nitrite to form amyl aryldiazo ethers which then (b) undergo homolysis to give an aryl radical, an amyloxy-radical, and nitrogen. The aryl radical reacts (c) with the aromatic substrate to give an intermediate arylcyclohexadienyl radical

\[
\begin{array}{c}
\text{Ph} \\
\text{H} \\
\text{VII}
\end{array}
\]

which reacts (d) with the amyloxy-radical to give the biaryl and amyl alcohol.

1.3.2 The reaction of primary aromatic amines with amyl nitrite in polyhalogenomethane solvents

Following Shu's demonstration that the reaction of
aniline with butyl nitrite in carbon tetrachloride gave a low yield of chlorobenzene, Cadogan investigated the reaction of primary aromatic amines with amyl nitrite in other polyhalogenomethane solvents at their boiling points. An investigation of the abstraction reactions of aryl radicals derived from the corresponding diaroyl peroxides or from arylazotriphenylmethanes, with chloroform, carbon tetrachloride and bromotrichloromethane under nitrogen had shown that (i) the selectivity of an aryl radical is independent of the nature of the substituent (p-Cl, p-CH₃, p-NO₂), (ii) the aryl radical abstracts hydrogen or bromine almost exclusively from chloroform and bromotrichloromethane respectively and (iii) hydrogen is abstracted more readily from chloroform than chlorine is from carbon tetrachloride.

Cadogan found that using amyl nitrite and aniline as a source of phenyl radicals, again hydrogen and bromine were abstracted in preference to chlorine from chloroform and bromotrichloromethane respectively. With substituted anilines, however, there was more variation in the amount of abstraction product with change in substituent then found when using substituted radicals from other sources.

Cadogan suggested that in some cases the reaction of aromatic amines with amyl nitrite in the presence of, for example, bromoform, could provide a useful preparative alternative to the Sandmeyer bromination the yields from which may vary considerably (20 -90%) with different substituents.
1.4 PREPARATION OF OTHER SUBSTITUTED BENZENES BY HOMOLYTIC PROCESSES

1.4.1 Reaction of benzoyl peroxide with sulphuryl chloride

In 1939, Kharasch and Brown found that in the presence of certain catalysts (such as organic peroxides) sulphuryl chloride served as a source of chlorine atoms. They found that benzoyl peroxide was the most effective catalyst, and while investigating the mechanism of the reaction, they found that on refluxing benzoyl peroxide itself in sulphuryl chloride an 80% yield of chlorobenzene was obtained.

1.4.2 Methylmercuric iodide as a source of methyl radicals

Corbett and Williams found that methyl radicals were formed in solution by photolysis of methylmercuric iodide with light of wavelength 3130 Å (equivalent to 90 kcal.mole⁻¹). Several aromatic solvents were methylated in good yield and the composition of the high boiling mixture was also investigated.

The results are consistent with a mechanism in which methyl radicals formed by direct photodissociation of methylmercuric iodide, add to the aromatic nucleus to give σ-complexes, some of which are dehydrogenated by methyl radicals to give methane and products of methylation.

\[
\begin{align*}
\text{MeHgI} & \rightarrow \text{Me}^+ + \text{HgI}^- \quad (a) \\
2\text{Me}^+ & \rightarrow \text{C}_2\text{H}_6 \quad (b)
\end{align*}
\]
1.4.3 Organomercury compounds

The reaction of unsymmetrical mercury compounds of the type $RHgR'$ with carbon tetrachloride in the presence of benzoyl peroxide has been investigated\(^7^9\) and the following scheme proposed:-

\[ (C_6H_5CO)_2 \rightarrow C_6H_5^* + CO_2 \]  
(a)

\[ C_6H_5^* + CCl_4 \rightarrow C_6H_5Cl + CCl_3^* \]  
(b)

\[ CCl_3^* + RHgR' \rightarrow R'CCl_3 + RHg^* \]  
(c)

\[ RHg^* + CCl_4 \rightarrow RHgCl + CCl_3^* \]  
(d)

Equation (23)

1.4.4 Abstraction of hydrogen atoms from aromatic side chains

(i) Cumene as a source of hydrogen atoms

Corbett and Williams\(^8^0\) investigated the reaction of methyl radicals, produced from methylmercuric iodide, with
aromatic side chain compounds and found that the order of reactivity of α-hydrogen atoms to abstraction by methyl radicals was primary < secondary < tertiary, i.e. the α-hydrogen atom in cumene was most susceptible to abstraction.

(ii) Abstraction by aryl radicals

The decomposition of benzoyl peroxide in alkylbenzenes was investigated by Foster and Williams\textsuperscript{58} and it was found that using benzene, isopropylbenzene and p-xylene as solvents, large yields of dimerisation products of radicals resulting from abstraction of hydrogen atoms from the side chain were obtained, as compared with yields of biphenyls resulting from nuclear substitution.

1.4.5 Abstraction of iodine from aromatic iodides

In the following series of experiments\textsuperscript{81} Cadogan obtained the products given

(i) \( o-, m- \) or \( p- \)-Iodo-\( N \)-nitrosoacetanilide in excess benzene under conditions which precluded photolysis, gave \( o-, m- \) or \( p \)-diiodobenzene together with \( o-, m- \) and \( p \)-terphenyl and \( 2-, 3- \) and \( 4 \)-iodobiphenyl, the expected products of the reaction.

(ii) Di-\( p \)-iodobenzoyl peroxide in benzene gave \( p \)-di-iodobenzene and \( p \)-terphenyl together with \( 4 \)-iodobiphenyl.

(iii) \( p \)-Chloro-\( N \)-nitrosoacetanilide in iodobenzene gave \( p \)-chloroiodobenzene together with products resulting from the radical phenylation of iodobenzene, whereas only
traces of 4-chloro, 2', 3', or 4'-iodobiphenyls were found.

(iv) Decomposition of aroyl peroxides not containing iodine, in iodobenzene, gave significant yields of the corresponding aryl iodides together with 2, 3, and 4-iodobiphenyls resulting from the radical phenylation of iodobenzene. These latter biphenyls were found to occur in the normal ratios found for the radical phenylation of aromatic solvents.

(v) p-Di-iodobenzene was found in the reaction of p-iodoaniline with amyl nitrite in benzene.

Cadogan suggested the following reaction scheme (24) for the decomposition of diaroyl peroxides in iodobenzene.

\[
(ArCO_2)_2 \rightarrow Ar^* + ArCO_2^* + CO_2 \quad \text{(a)}
\]

\[
Ar^* + PhI \rightarrow ArI + Ph^* \quad \text{(b)}
\]

\[
Ph^* + PhI \rightarrow (PhC_6H_5I)
\]

\[
\frac{(ArCO_2)_2}{PhC_6H_4I + ArCO_2H + ArCO_2} \quad \text{(c)}
\]

Equation (24)

In support of this proposed mechanism, it was found that 4-bromobiphenyl is not formed in the reaction of di-p-bromo-benzoyl peroxide in iodobenzene. This would preclude such reactions as
Ar* + PhI $\rightarrow$ Ar\textsuperscript{+} \rightarrow ArI + ArPh \quad (24(d))
1.5 POLYFLUOROAROMATIC COMPOUNDS

1.5.1 Historical

Until 1947, polyfluoroaromatic compounds were prepared by the Schiemann reaction, in which fluorine was introduced into the aromatic ring by decomposition of the corresponding aryldiazonium tetrafluoroborate, up to four fluorine atoms being introduced into the aromatic ring by this method.

However, in 1947, McBee, Lingren and Ligett reported the first synthesis of hexafluorobenzene. Hexachlorobenzene was treated with bromine trifluoride to give a mixture of average composition C_6Br_2Cl_4F_6, which on treatment with antimony pentafluoride gave a mixture of average composition C_6BrCl_4F_7. On dehalogenation with zinc dust, small amounts of hexafluorobenzene were obtained together with other products such as perfluorocyclohexanes, polyfluorocyclohexadienes and chlorofluoro compounds.

Several methods for the synthesis of hexafluorobenzene have since been developed, one of the most successful of which, for application on a large scale, involves the direct fluorination of hexachlorobenzene. A mixture of chlorofluorocyclohexanes is obtained, which, on dehalogenation with iron filings packed in a cobalt fluoride reactor, gives high yields of hexafluorobenzene and chlorofluorobenzenes.

With the advent of hexafluorobenzene a large range of polyfluoroaromatic compounds have been synthesised and these have given rise to a new branch of organic chemistry.
1.5.2 Complex formation

Complex formation has been observed between aromatic hydrocarbons and aromatic polyfluorocarbons. For example, a 1:1 molar mixture of benzene (m.p. 5.4°) and hexafluorobenzene (m.p. 5.0°) gives a solid complex melting at 23.7° and appreciable association has been observed between pentafluoriodobenzene and both benzene and toluene. These complexes are presumably similar to the π-type charge transfer complexes formed with certain aromatic hydrocarbons, for example benzene and 1,3,5-trinitrobenzene form a complex of similar character.

1.5.3 Heterolytic reactions of polyfluoroaromatic compounds

The strong inductive effect of the highly electronegative fluorine atoms would be expected to render the nuclear carbon atoms highly electropositive and in agreement with this postulate, hexafluorobenzene has not, to date, been reported to react with electrophilic reagents. But in pentafluorobenzene and the tetrafluorobenzenes, replacement of hydrogen by electrophilic reagents has been shown to take place, for example, halogenation, sulphonation and nitration have been effected.

However, strong nucleophilic reagents displace fluorine as fluoride. If X is a nucleophile, then displacement of fluorine from hexafluorobenzene yields pentafluorophenyl derivatives of the type C₆F₅X. The functional groups so
introduced can be treated to give many other pentafluorophenyl derivatives by employing the standard reactions of organic chemistry. The pentafluorophenyl derivative can be subjected to further nucleophilic attack resulting in the formation of a tetrafluorophenyl derivative. The displacement of fluorine from hexafluorobenzene by nucleophilic reagents has been reviewed by Tatlow\textsuperscript{93} and by Wall, Pummer, Fearn and Antonucci.\textsuperscript{94}
1.6 HOMOLYTIC REACTIONS OF POLYFLUOROAROMATIC COMPOUNDS

1.6.1 Free radical addition

While hexafluorobenzene has been shown to be relatively stable to ultraviolet light, photochemical addition reactions do take place. In 1965, Godsell, Stacey and Tatlow found that when a mixture of hexafluorobenzene and chlorine was irradiated with ultraviolet light, hexachlorohexafluorocyclohexane was formed. Similarly, pentafluorobenzene was found to give hexachloropentafluorocyclohexane.

1.6.2 Thermolysis of benzoyl peroxide in polyfluoroaromatic solvents

(i) Products

Claret, Coulson and Williams investigated the thermal decomposition of benzoyl peroxide in hexafluorobenzene and obtained a 76% yield of 2,3,4,5,6-pentafluorobiphenyl. Similar reactions were carried out with p-nitro, m-methyl, m-chloro, and m-bromo-benzoyl peroxide to give the expected biaryls, although in lower yields when the peroxide contained an electron withdrawing substituent (m-Br, m-Cl, p-NO₂). Low yields (~30%) of the appropriate substituted benzoic acids were obtained.

This work was continued by Oldham who investigated the thermal decomposition of benzoyl peroxide in hexafluorobenzene, chloropentafluorobenzene, bromopentafluorobenzene and nitropentafluorobenzene. In the case of hexafluoro-
benzene, Oldham was unable to reproduce the yield of 76% of biaryl obtained by Claret et al. He found that the yield of biaryl obtained varied with isolation conditions from 34% to 46% (when the reaction mixture was distilled under extreme conditions - at 760 mm, 300°). He also found that addition of ferric benzoate, oxygen or nitrobenzene had no effect on the total yield of biaryl, although the isomer distribution varied somewhat.

(ii) Mechanism

By analogy with arylation reactions of aromatic hydrocarbons with benzoyl peroxide, it was suggested that arylation of aromatic fluorocarbons proceeds by the following mechanism:

\[(\text{PhCO}_2\text{O})_2 \rightarrow 2\text{PhCO}_2\text{O}^*\]  \hspace{1cm} (a)

\[\text{PhCO}_2\text{O}^* \rightarrow \text{Ph}^* + \text{CO}_2\]  \hspace{1cm} (b)

\[\text{Ph}^* + \text{C}_6\text{F}_6 \rightarrow  \text{(6-complex XI)}\]  \hspace{1cm} (c)

Equation (25)

Benzoyl peroxide decomposes to give phenyl radicals in the manner described previously (1.2.1). The phenyl radical is then thought to add to the aromatic nucleus to give a phenylcyclohexadienyl radical or 6-complex (XI). Formation of a biaryl from a 6-complex differs in the case of a fluorinated substrate (from the formation of a biaryl in the
case of an aromatic hydrocarbon) in that aromatisation involves defluorination rather than dehydrogenation. The method of defluorination has not been previously fully explained. No products which might result from the abstraction of a fluorine atom from the $\mathcal{S}$-complex by a phenyl radical, such as fluoro-benzene, have been found among the reaction products.

The following methods of defluorination have previously been suggested (26):

(a) A fluorine molecule could be eliminated between two $\mathcal{S}$-complexes, to give two molecules of biaryl

$$
\begin{align*}
\begin{array}{c}
\text{Ph} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{F}
\end{array}
\end{align*}
\xrightarrow{2} \begin{array}{c}
\text{F}_2 \\
2\text{C}_6\text{H}_5\text{C}_6\text{F}_9
\end{array}
\quad(26a)
$$

(b) Complexes can disproportionate to give a molecule of biaryl and a heptafluorodihydrobiphenyl molecule (1.2.5)

$$
\begin{align*}
\begin{array}{c}
\text{Ph} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{F}
\end{array}
\end{align*}
\xrightarrow{2} \begin{array}{c}
\text{C}_6\text{H}_5\text{C}_6\text{F}_9
\end{array} + \begin{array}{c}
\text{Ph} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{F}
\end{array}
\quad(26b)
$$

(c) A fluorine atom could be removed from the complex by a benzoyloxy-radical to give benzoyl hypofluorite in a manner analogous to the removal of hydrogen from a hydrocarbon complex to give benzoic acid. During the work up of
the reaction mixture, benzoyl hypofluorite would be hydrolysed to give benzoic acid and ultimately hydrofluoric acid (27).

\[ \text{Ph} \quad F \quad F \quad F \quad F \quad F \quad F \quad F \quad F \quad F \quad F \quad \hto \quad (\text{C}_6\text{H}_5\text{CO}_2)_2 \quad \hto \quad \text{C}_6\text{H}_5\text{C}_6\text{F}_5 \quad + \quad \text{C}_6\text{H}_5\text{CO.OF} \quad + \quad \text{C}_6\text{H}_5\text{CO.O}^* \quad (27) \]

\begin{center}
\text{XI}
\end{center}

(d) During distillation, heptafluorodihydrobiphenyl (XII) and dodecafluorotetrahydroquaterphenyl (XIII) molecules (resulting from the dimerisation of 6-complexes) could decompose with loss of fluorine to yield further molecules of biaryl (28a and b)

\[ \text{Ph} \quad F \quad F \quad F \quad F \quad F \quad F \quad F \quad F \quad F \quad F \quad \hto \quad 2\text{C}_6\text{H}_5\text{C}_6\text{F}_5 \quad + \quad \text{F}_2 \quad (28a) \]

\begin{center}
\text{XIII}
\end{center}

\[ \text{Ph} \quad F \quad F \quad F \quad F \quad F \quad F \quad F \quad F \quad F \quad F \quad \hto \quad \text{C}_6\text{F}_5\text{C}_6\text{H}_5 \quad + \quad \text{F}_2 \quad (28b) \]

\begin{center}
\text{XII}
\end{center}

This was also suggested by Oldham to account for the increase in biaryl yields during vigorous distillation.
(iii) Kinetics

Coleman\textsuperscript{100} investigated the kinetics of the decomposition of benzoyl peroxide in hexafluorobenzene and found that the kinetics could be represented by equation (11)

\[ -\frac{d[P]}{dt} = k_1[P] + k_{1.5}[P]^{1.5} \]  \hspace{1cm} (11)

These results suggested that the decomposition of benzoyl peroxide in hexafluorobenzene was analogous to the decomposition in benzene, i.e. that the first order term represented a unimolecular decomposition of the peroxide and the 1.5 order indicated an induced decomposition of the peroxide. Also this form of kinetic equation indicated chain termination between similar radicals, for example chain termination by dimerisation and disproportionation of \(\delta\)-complexes as suggested by Claret et al.\textsuperscript{98}

The isolation in small yields of 2,2',3,4,5,6-hexafluorobiphenyl XIV\textsuperscript{100} and of benzoic acid shows one route (29) whereby an induced decomposition of the peroxide occurs.

\[
\text{Ph} \quad \text{F} \\
\text{F} \quad \text{F} \quad \text{F} \\
\text{F} \quad \text{F} \\
\text{F} \\
\text{F} \\
+ \ (C_6H_5CO.O)_2 \rightarrow \text{Ph} \quad \text{F} \\
\text{F} \quad \text{F} \\
\text{F} \quad \text{F} \\
\text{F} \\
\text{F} \\
+ \ C_6H_5CO.OH \\
+ \ C_6H_5CO.O^- \hspace{1cm} \text{(29)}
\]
Wilson investigated the thermal decomposition of the peroxide in pentafluorobenzene and in 1,2,4,5-tetrafluorobenzene. It was found that the substitution at fluorine-bearing atoms was predominant for pentafluorobenzene while for 1,2,4,5-tetrafluorobenzene, substitution at hydrogen-bearing carbon atoms predominated. An explanation for this substitution pattern was given in terms of electron densities at various ring positions.

1.6.3 The reaction of aniline with amyl nitrite in hexafluorobenzene as solvent

Oldham investigated the reaction of aniline with amyl nitrite in hexafluorobenzene as solvent and obtained a low yield (10%) of 2,3,4,5,6-pentafluorobiphenyl together with a trace of biphenyl. A mechanism was suggested (equation 30) similar to that suggested by Ray.

\[
\begin{align*}
C_6H_5NH_2 + AmONO & \rightarrow C_6H_5N=NOAm + H_2O \quad (a) \\
C_6H_5N=NOAm & \rightarrow C_6H_5^* + N_2 + ^*OAm \quad (b) \\
C_6H_5^* + C_6F_6 & \rightarrow C_6H_5F + C_6H_5C_6F_5 \quad (c)
\end{align*}
\]

Equation (30)
The presence of fluorobenzene in the reaction mixture suggests that a fluorine atom was abstracted from the $\sigma$-complex by a phenyl radical.
1.7 THE PENTAFLUOROPHENYL RADICAL

1.7.1 General methods for the formation of pentafluorophenyl radicals

Several methods are available for the generation of polyfluorophenyl radicals, all of which have counterparts in the chemistry of hydrocarbon radicals (section 1.1.5). The main methods which have been used to date are:

(i) Oxidation of pentafluorophenylhydrazine

(ii) Thermolysis of perfluorobenzoyl peroxide

(iii) Reaction of pentafluoroaniline with amyl nitrite

(iv) Photolysis of pentafluoriodobenzene

(v) Thermolysis of pentafluorohalobenzenes

(vi) Photolysis and thermolysis of polyfluoroarylmercury compounds

(vii) Decomposition of pentafluorobenzenesulphonyl chloride

Only reactions (i), (ii) and (iii) will be discussed in detail in this thesis.

1.7.2 Formation from pentafluorophenylhydrazine

Oxidation of arylhydrazines by a number of reagents in aromatic solvents gives rise to biaryls, probably by a process of homolytic arylation. Birchall, Haszeldine and Parkinson have reported that when pentafluorophenylhydrazine is treated with silver oxide in a large excess of benzene at 0-10°, almost quantitative evolution of nitrogen
occurs and 2,3,4,5,6-pentafluorobiphenyl is formed in a 63% yield. The authors postulated that a pentafluorophenyl radical was formed through the diazo-compound C₆F₅N:NH and that arylation of the aromatic nucleus took place through the formation of a Σ-complex, XV, (31)

\[
\text{C}_6\text{F}_5^\cdot + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{F}_5^\cdot \begin{array}{c}
\cdot \\
\cdot
\end{array} \quad (31)
\]

XV

Removal of the hydrogen atom from the Σ-complex was effected either by the oxidising agent or by another radical. The absence of pentafluorobenzene from the reaction products ruled out the abstraction of hydrogen by a pentafluorophenyl radical either from the aromatic solvent or from a Σ-complex.

Birchall, Haszeldine and Parkinson also investigated the reaction of the pentafluorophenyl radical with hexafluorobenzene. Oxidation of pentafluorophenylhydrazine with silver oxide in the presence of hexafluorobenzene gave a little pentafluorobenzene (6.4%) together with a little decafluorobiphenyl (2%). Pentafluorobenzene was thought by these authors to be formed by hydrogen abstraction from unreacted pentafluorophenylhydrazine,

\[
\text{C}_6\text{F}_5^\cdot + \text{C}_6\text{F}_5\text{NH.NH}_2 \rightarrow \text{C}_6\text{F}_5\text{H} + \text{C}_6\text{F}_5\text{N.NH}_2 \quad (32a)
\]

It may also possibly arise from ArN=NH, the first oxidation product of phenyl hydrazine.
while decafluorobiphenyl was thought to be formed by the
dimerisation of perfluorophenyl radicals in solution.

1.7.3 The thermal decomposition of perfluorobenzoyl peroxide
in aromatic solvents

(i) Benzene

The thermal decomposition of perfluorobenzoyl peroxide
in benzene was first investigated by Oldham and Williams \(^{104}\)
and subsequently by Burdon, Campbell and Tatlow, \(^{109}\) and
Coleman \(^{100}\) who also investigated the kinetics of the reaction.

The products were found to be pentafluorobenzoic acid
(0.82 mole per mole peroxide) and biaryl (0.61 mole per mole
peroxide) together with phenylpentafluorobenzoate (0.13 mole
per mole peroxide) and a trace of pentafluorophenyl penta-
fluorobenzoate (0.04 mole per mole peroxide).

It was found \(^ {100}\) that for peroxide concentrations less
than 0.028M, the kinetics of the decomposition could be
represented by equation (11)

\[
-d[P]/dt = k_1[P] + k_{1.5}[P]^{1.5}
\]  \hspace{1cm} (11)

whilst at concentrations greater than this, equation (12)
was obeyed

\[
-d[P]/dt = k_1[P] + k'_1[P]
\]  \hspace{1cm} (12)
It has been suggested that the reaction proceeds by a mechanism similar to that of the decomposition of benzoyl peroxide in benzene. Decomposition of the peroxide gives pentafluorophenyl and pentafluorobenzoyloxy-radicals; attack of these on the aromatic nuclei gives the 6-complexes (XV) and (XVI) respectively.

\[
\text{C}_6\text{F}_5\text{C}^\text{O.} \quad \text{C}_6\text{F}_5\text{CO.O}
\]

\[
\begin{align*}
\text{XV} & \quad \text{XVI} \\
\text{H} & \quad \text{H}
\end{align*}
\]

Dehydrogenation of the 6-complexes by reaction with a further molecule of peroxide gives an ester or biaryl together with pentafluorobenzoic acid.

\[
(\text{XV}) + (\text{C}_6\text{F}_5\text{CO.O})_2 \rightarrow \text{C}_6\text{F}_5\text{C}_6\text{H}_5 + \text{C}_6\text{F}_5\text{CO.OH} + \text{C}_6\text{F}_5\text{CO.O}^* \quad (33a)
\]

\[
(\text{XVI}) + (\text{C}_6\text{F}_5\text{CO.O})_2 \rightarrow \text{C}_6\text{F}_5\text{CO.OC}_6\text{H}_5 + \text{C}_6\text{F}_5\text{CO.OH} + \text{C}_6\text{F}_5\text{CO.O}^* \quad (33b)
\]

Dimerisation of (XV) gives tetranuclear products (XVII) which were thought to be the main constituents of the residue whilst disproportionation of (XV) gives a further molecule of biaryl and a dihydro-derivative (XVIII)

\[
2\text{G}^* \rightarrow \text{C}_6\text{F}_5\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{C}_6\text{F}_5 \quad (34a)
\]

\[
\begin{align*}
\text{XVII} & \quad \text{XVII} \\
\text{H} & \quad \text{H}
\end{align*}
\]
The contribution of disproportionation to the reaction was not thought to be large however, as the yields of biaryl did not greatly exceed that of pentafluorobenzoic acid. (cf. equation (17e) in section 1.2.6).

(ii) Halogenobenzenes

The thermal decomposition of perfluorobenzoyl peroxide in chlorobenzene and bromobenzene has also been reported and the kinetics investigated. The products were found to be mainly pentafluorobenzoic acid and phenyl pentafluorobenzoate, with negligible yields of biaryl. Coleman found that the kinetics were represented by the rate equation,

\[-d[F]/dt = k_1[F] + k'_1[F]\]  

(12)

indicating first order induced decomposition of the peroxide, which is characteristic of chain termination between dissimilar radicals. Traces of isomeric chlorophenyl and bromophenyl pentafluorobenzoates were also found.

Pentafluorophenyl benzoate can only arise in the reaction with halogenated solvents by replacement of the halogen. It was suggested that owing to their electrophilicity, pentafluorobenzoyloxy-radicals are stabilised by the formation of...
charge transfer complexes such as (XIX) with the halobenzenes. The formation of such complexes has already been postulated in the reaction of benzoyl peroxide with bromobenzene (section 1.2.7., equation (18)).

\[
\begin{align*}
C_6F_5COO^+ &+ \text{X} \quad \xrightarrow{} \quad C_6F_5COO^- + \text{X} \quad \text{XIX} \\
\end{align*}
\]

It was also postulated that the halogen was removed from the resulting 6-complex by a benzoyloxy-radical to give a hypohalite in the manner suggested for the removal of a fluorine atom from a 6-complex (section 1.6.2 (iii)). This hypohalite would also be hydrolysed during work-up of the reaction mixture.

(iii) Hexafluorobenzene and pentafluorobenzene

With hexafluorobenzene as solvent, Eurdon, Campbell and Tatlow \(^ {109} \) found that the reaction products were decafluorobiphenyl (2%), pentafluorophenyl pentafluorobenzoate (7%) and much tarry material.

Kobrina \(^ {110} \) found for the same reaction that the products
were decafluorobiphenyl (10%), pentafluorophenyl pentafluorobenzoate (3-5%) and \( p,p'-\text{bis(pentafluorobenzoyloxy)-1,1',4,4'} \)-tetrahydroperfluorobiphenyl (50%).

The reaction has also been carried out in pentafluorobenzene and the products found to be biaryl (7% fluorine replacement and 3% hydrogen replacement) and pentafluorophenyl pentafluorobenzoate (12%).

1.7.4 The reaction of pentafluoroaniline with amyl nitrite in aromatic solvents

Oldham investigated the reaction of pentafluoroaniline with amyl nitrite in benzene, bromobenzene, chlorobenzene and nitrobenzene, and obtained yields of fluorinated biaryls comparable to those yields obtained using aniline and aromatic solvents. He postulated that the pentafluorophenyl radical could be considered an electrophilic species on the evidence of the isomer ratios of biaryls obtained and of competitive reactions. When the pentafluorophenyl radical was allowed to react with a compound containing a group that was deactivating and \( m \)-directing towards electrophilic substitution, the proportion of \( m \)-product to \( o \)- and \( p \)-product was increased, as compared with the isomer ratios obtained with pentafluorophenylation of such compounds as chlorobenzene. The proportion of \( m \)-product obtained from nitrobenzene was also increased as compared with the ratio for the phenylation of nitrobenzene, the phenyl radical being nearly neutral.

A study of electromeric effects provides further
evidence of the electrophilic nature of the pentafluorophenyl radical.

An electrophilic radical should be able to call into play the electromeric effect of the halogens in such compounds as chlorobenzene, thus increasing the electron density at the o- and p- positions. The increased proportion of o- and p- to m- substituted products in the pentafluorophenylination of chlorobenzene as compared with the phenylation of chlorobenzene, seemed to verify this.

The mechanism of the decomposition of pentafluoroaniline with amyl nitrite and the subsequent arylation of the solvent was thought to be analogous to that postulated for the reaction of aniline with amyl nitrite in aromatic solvents (section 1.3.1., equation (21)).

The reaction of pentafluoroaniline with amyl nitrite in hexafluorobenzene was also investigated and it was found that the main reaction product consisted of a high boiling residue, with only a trace of decafluorobiphenyl formed.

1.7.5 Comparison between $\text{C}_6\text{F}_5^-$ and $\text{C}_6\text{H}_5^-$

It was suggested that the pentafluorophenyl radical can be considered to be a more electrophilic species than the phenyl radical. Their reaction with benzene give comparable yields of biaryls (1.7.3 i) and the kinetics are similar. However in the reactions of the respective peroxides with chlorobenzene (1.7.3 ii) although the kinetics are again
similar in the case of the fluorinated analogue, the precursor of the pentafluorophenyl radical, (i.e. the pentafluoro-benzoyloxy radical-) appears to be stabilised to such an extent that ester is formed to the exclusion of biaryl.

The most noticeable difference appears in their reaction with hexafluorobenzene. The phenyl radical gives good yields of biaryl whereas very little biaryl is formed in the reaction of the pentafluorophenyl radical with hexafluorobenzene, whatever the source of pentafluorophenyl radical.
EXPERIMENTAL
2.1 PREPARATION AND PURIFICATION OF REAGENTS

2.1.1 Purification of reagents

Melting and boiling points quoted are uncorrected. Infra-
red spectra were recorded either on a Perkin-Elmer 457 or
a Unicam S.P. 200 instrument.

Unless otherwise stated, solvents were dried for twenty
four hours at room temperature. Fractional distillations
were carried out on a helix packed column with an electrically
heated jacket, the distillates being protected against
moisture by attaching calcium chloride guard tubes to the
head of the distillation column. The purity of solvents was
checked, after distillation, on a Perkin Elmer F 21 Prepar-
ative Gas Liquid Chromatograph, varying the column temperature
from 50-100° and the gas pressure readings from 0.8-1.4 kp/cm²
(units as shown on the instrument).

Pentafluoroaniline: A sample of commercial reagent (I.S.C.)
was recrystallised to constant m.p. (34-35°) from light
petroleum (b.p. 40-60°). Lit. m.p. 33.5-35°.111

Amyl nitrite: AnalAr grade reagent was distilled under
reduced pressure (b.p. 32-34°/20 mm). Lit. b.p. 104°/760 mm.112
After distillation, g.l.c. showed only one peak.

Carbon tetrachloride: The commercial reagent (M&B) was dried
(CaSO₄) and fractionally distilled (b.p. 77°/760 mm). Lit.
b.p. 76.7°/760 mm.112
Chloroform: The commercial product (M&B) was washed with concentrated sulphuric acid, until the washings were colorless to remove ethanol. After drying (CaSO\(_4\)), the solvent was fractionally distilled (b.p. 61\(^\circ\)/760 mm). Lit. b.p. 61-2\(^\circ\)/760 mm.\(^{112}\)

Bromotrichloromethane: The commercial material (Fluka) was dried, then fractionally distilled in the dark (b.p. 104\(^\circ\)/760 mm). Lit. b.p. 104.3\(^\circ\)/760 mm.\(^{112}\)

Cumene: Commercial isopropylbenzene was washed first with concentrated sulphuric acid until the washings (originally bright yellow) were colorless and then with sodium carbonate. After drying (MgSO\(_4\)), it was fractionally distilled (b.p. 150\(^\circ\)/760 mm). Lit. b.p. 152-3\(^\circ\)/760 mm.\(^{112}\)

Sulphuryl chloride: Commercial reagent (B.D.H.) was distilled using a Dufton column, collecting the fraction boiling at 69\(^\circ\). Lit b.p. 69-70\(^\circ\)/760 mm.\(^{113}\)

Fluorinated aromatic compounds: The following compounds were dried (MgSO\(_4\)) and fractionally distilled under an atmosphere of nitrogen:

- Pentafluorobenzene (I.S.C.) 85\(^\circ\). Lit. b.p. 88-89\(^\circ\)/760 mm.\(^{114}\)
- 1,2,4,5-tetrafluorobenzene (I.S.C.) 90\(^\circ\). Lit. b.p. 88\(^\circ\)/760 mm.\(^{115}\)
- 1,3,5-trifluorobenzene (Bristol Organics) 75.5\(^\circ\). Lit. b.p.75.5\(^\circ\)/760 mm.\(^{115}\)
- 1,4-difluorobenzene (Koch-Light) 83\(^\circ\). Lit. b.p. 82\(^\circ\)/760 mm.\(^{112}\)
Iodobenzene: Commercial reagent (Hopkin and Williams) was distilled under reduced pressure, rejecting the high boiling impurities. The distillate was then shaken with sodium hydroxide solution to remove iodine. After drying (MgSO₄) it was redistilled under atmospheric pressure (b.p. 188-89°). Lit. b.p. 188.5⁰/760 mm.¹¹²

2.1.2 Preparation of compounds

(i) Perfluorobenzoyl peroxide

This was prepared by a modification of the method of Price and Krebs¹¹⁶ for preparing benzoyl peroxide. Pentafluorobenzoic acid (50 g, 0.24 mole) was refluxed with thionyl chloride (250 ml) for 48 hours. Excess of thionyl chloride was removed by distillation (77⁰/760 mm) and pentafluorobenzoyl chloride was distilled under reduced pressure (100⁰/20 mm). Yield 50 g (92%).

The pentafluorobenzoyl chloride was dissolved in chloroform (35 ml) and added at a rate of one ml per minute to a well-shaken, ice-cold solution of aqueous hydrogen peroxide (30%, 100 volume: 56 ml) and sodium hydroxide (14 g in 25 ml of water). The flask was then shaken at 0⁰ for 90 minutes. Solid peroxide which had precipitated was filtered. The chloroform layer was treated with twice its own volume of ice cold methanol. More peroxide precipitated and was filtered. The perfluorobenzoyl peroxide was recrystallised by dissolving in a minimum of chloroform, filtering rapidly,
and adding twice the volume of ice cold methanol to precipitate it. A further crop of crystals was obtained by cooling the methanolic solution in an acetone-DriKold mixture. The peroxide obtained was dried in vacuo for 48 hours to remove all traces of solvent. (m.p. 76-77°, Lit. m.p. 79-79.5°,104 72°.109)

The purity of the peroxide prepared in this manner was checked iodometrically by the method of Nozaki.117 Using potassium iodide in acetic anhydride as solvent, the liberated iodine was titrated against sodium thiosulphate, using starch as indicator.

(ii) 4-Bromo-2,3,5,6-tetrafluoroaniline

This was prepared by the method of Castellano, Green and Kauffman.118 Bromine (8 ml, 0.3 mole) dissolved in glacial acetic acid (20 ml) was added drop by drop to a solution of 2,3,5,6-tetrafluoroaniline (20 g, 0.12 mole) in glacial acetic acid (100 ml) at room temperature. After addition, the solution was stirred at room temperature for two hours.

The solution was then poured onto ice (ca. 500 g) and the yellow solid which precipitated was washed, filtered and dried. After recrystallisation from petroleum ether (b.p. 40-60°) a white crystalline solid was obtained in 70% yield (20.5 g), (m.p. 57-59°, Lit. m.p. 58-59°).118

(iii) 4-Chloro-2,3,5,6-tetrafluorobenzene

This was prepared by a modification of the method of
Tamborski and Soloski. Chloropentafluorobenzene (25 g) and hydrazine hydrate (15 ml) were refluxed in 1,4-dioxan for one hour. Water (500 ml) was then added to the solution and the resulting precipitate filtered and washed thoroughly with water. The crude product obtained, 4-chloro-2,3,5,6-tetrafluorophenyl hydrazine (8.5 g), was used for the next stage of the reaction.

The prepared hydrazine was suspended in water and copper sulphate solution (25 g in 100 ml water) was added. The mixture was refluxed for several hours, the organic fraction being collected in a Dean-Stark trap. The aqueous layer from the Dean-Stark trap was extracted with ether and the combined organic fractions dried (MgSO₄). Excess of ether was distilled off and the remaining fraction distilled, collecting the fraction which boiled at 120-25° (Lit. b.p. 123-125°). Yield 4.2 g (18.4%).

(iv) 4-Bromo-2,3,5,6-tetrafluorobenzene

This was also prepared by the above method, starting with bromopentafluorobenzene (25 g) and obtaining 4 g (17.4%) of the desired product (b.p. 140-45°, Lit. b.p. 143°).

(v) Preparation and standardisation of sodium methoxide

Pellets of sodium were dropped into dry methanol and the solution was boiled for several hours. Samples of the methoxide were diluted with water and titrated against 0.1N sulphuric acid, using phenolphthalein as indicator.
(vi) 4-Chloro-2,3,5,6-tetrafluoroanisole

This was prepared by the method of Burdon, Coe, Marsh and Tatlow. Chloropentafluorobenzene (20 g) was boiled with 0.95N sodium methoxide (104 ml) in dry methanol (100 ml) for four hours. The solution was then poured into water and the organic products removed by extraction with ether. The solution was dried (CaCl₂), ether was removed under pressure and the remaining products were fractionally distilled, collecting the fraction boiling at 170-76°/760 mm. (Lit. b.p. 174°/760 mm). This fraction was redistilled until the impurity shown to be present by g.l.c. was present to less than 1%. Yield 12 g (57%).

(vii) 4-Bromo-2,3,5,6-tetrafluoroanisole

This was prepared in a similar manner to (vi). B.p. 190-96°/769 mm (Lit. b.p. 194-5°/760 mm). Yield 10 g (48%). G.l.c. again showed the presence of about 1% impurity.

(viii) 4-Methoxy-2,3,5,6-tetrafluoroaniline

This compound was prepared by the method of Burdon, Morton and Thomas. The preparation was in three stages:

(1) Decafluoroazobenzene:
Pentafluoroaniline (50 g, 0.27 mole) and aqueous sodium hypochlorite (1500 ml, 10-14% w/v Cl₂) were stirred vigorously for four hours at room temperature. A red solid separated from the red solution and was filtered. The solution was extracted with ether (4x100 ml) which was washed
with water to remove sodium chloride, the ether removed by distillation and a further crop of red solid obtained. After recrystallisation from ethanol, 9 g of decafluoroazobenzene, a red crystalline solid, were obtained. M.p. 139-40°, Lit m.p. 142-43°.121

(2) Octafluoro-4,4'‑dimethoxyazobenzene:
Sodium methoxide (102 ml, 0.5N) in dry methanol was dripped slowly into a well stirred solution of decafluoroazobenzene (9 g, 0.025 mole) in sodium dried ether at room temperature. The crude solid after removal of solvent was recrystallised from petroleum ether (b.p. 60-80°), m.p. 164-66°, Lit. m.p. 164-65°.121 Yield 4.5 g.

(3) 4-methoxy-2,3,5,6-tetrafluoroaniline:
The above product was boiled with hydrochloric acid (11N, 151 ml), glacial acetic acid (15 ml) and tin (60 g) for five hours. The mixture was then neutralised with sodium hydroxide (10N, 750 ml). The solution was extracted with ether, the ether removed and the resulting crude product steam distilled. After recrystallisation from petroleum ether (b.p. 60-68°), 2.5 g (4.8% overall yield) of the desired product were obtained, m.p. 70-72°, Lit. m.p. 73-75°.121

(ix) 1-Bromo-4-chloro-2,3,5,6-tetrafluorobenzene

4-Chloro-2,3,5,6-tetrafluorobenzene was prepared as described in (iii) above. This compound was then brominated using the 'hot' bromination method of Crawford and Stewart122 other methods of bromination having proved unsuccessful.90,123
4-Chloro-2,3,5,6-tetrafluorobenzene (6.5 g, 0.035 mole) was added to concentrated sulphuric acid (31 ml), containing water (3 ml) and bromine (1.82 ml, 0.035 mole). To this mixture was added silver sulphate (5.5 g, 0.035 mole). The mixture was shaken until the bromine colour had disappeared and silver bromide was precipitated. The reaction mixture was then poured into a solution of sodium sulphite and the mixture filtered. The solid was boiled with ether for one hour and the ether washings were combined with the ether washings of the aqueous extract. The ethereal solution was dried and the ether removed under reduced pressure. The reddish brown liquid from this was then separated on an alumina column which was then eluted with ether and then with benzene. The first colorless extract was collected. The solvent was removed from this extract and the remaining liquid distilled, collecting the fraction which boiled at 178°.

A solid collected at the end of the condenser and this was found to be a pure compound, by g.l.c. inspection. A further crop of pure solid was obtained by distilling the liquid collected in the receiving vessel. Yield 0.5 g (5.4%) m.p. 40-42°, b.p. 178-80°.

This compound was found to be extremely volatile. This volatility caused difficulty in recording the mass spectrum of the compound, however, a main peak of 262 (M.Wt. of desired compound) was found and the isotope pattern was correct for bromine and chlorine. However, no mass measure-
ment was made.

(x) **2,3,5,6-tetrafluorophenol**

This was prepared by the method of Burdon, Aroskar, Campbell and Stephens. Pentafluorobenzene (2.5 g), and KOH (5 g) were refluxed in t-butyl alcohol (15 ml) for six hours. The solution was diluted with water and t-butanol removed by distillation. The aqueous solution was extracted with ether. The aqueous extract was acidified and the phenol removed by extraction with ether. The ether was removed by distillation under reduced pressure and the product collected by distillation b.p. 60° at 30 mm, 144-48° at 760 mm (by the capillary method), (Lit. b.p. 144-45°). Yield, 0.3 g pK\textsubscript{a} value (see 2.4) 5.7.

(xi) **2,4,5-Trifluorophenol**

This was prepared from 1,2,4,6-tetrafluorobenzene by the method described in (ix), the mixture being refluxed for a total of sixteen hours. 0.2 g of a phenol were obtained, b.p. 50° at 30 mm, 170° at 760 mm.

Determination of the molecular weight by the method of pH titration in aqueous solution (see 2.4) gave a value of 152.5 (molecular weight of trifluorophenol, 148). pK\textsubscript{a} value 7.7.

2.1.3 **Other compounds used**

The following compounds, supplied by the Imperial
Smelting Corporation were used without further purification: bromopentafluorobenzene, chloropentafluorobenzene, iodo-
pentafluorobenzene, 1,4-dibromotetrafluorobenzene, penta-
fluorotoluene, pentafluorobenzoic acid, pentafluorophenol,
2,3,5,6-tetrafluoromethoxybenzene, 2,3,5,6-tetrafluoroaniline.
2.2 GAS LIQUID CHROMATOGRAPHY

All g.l.c. investigations were carried out on a Perkin Elmer F21 Preparative Gas Chromatograph. The carrier gas in this instrument was nitrogen and the detector was of the flame ionisation type.

Two U-shaped 90 cm columns were used containing either Apiezon L, Carbowax 20M/TPA or OV 17, packed on Chromosorb P(30-60 mesh). The carrier gas flow rate, column temperature, detector sensitivity and size of sample injection were varied as required. Sample injection was made using a microlitre syringe.

2.2.1 Quantitative chromatographic analysis

It was found that using a gas flow pressure of about 0.8 kp/cm² and column temperatures of about 80°, wide chromatographic separation of the components of a mixture was obtained, the speed of elution of the components resulting in broad peaks on the chromatogram. However, it was found that for the mixtures being investigated, by increasing the gas pressure and column temperature to 1.0-1.6 kp/cm² and 100-150° respectively, depending on the column type, a similar good resolution could be obtained, the resulting chromatogram consisting of sharp peaks.

(i) Internal standard

As a chromatogram could be obtained consisting of sharp peaks, a quantitative estimation of identified products in
a reaction could be made by measuring the relative peak height of that component to that of an added 'internal standard'. An internal standard is a reagent which is added in a known weight to a known weight of reaction mixture. It is not involved in the reaction and must be one selected whose retention time does not coincide with that of any of the reaction products. Two internal standards used in the present investigation were toluene and cyclohexane.

The peak height of the internal standard relative to that of the product could be measured and, the number of moles of internal standard being known, the yield of product could be determined using calibration graphs obtained by a method to be described. It was found that the relative peak heights did not vary with the size of the sample injection.

(ii) Calibration of the instrument for different products

Mixtures of pure samples of product and internal standard were weighed in known mole ratios. At least five successive injections of each mixture were performed on the instrument, the relative peak height of internal standard to product measured and the average value for each mixture plotted against the mole ratio for that mixture. This calibration graph holds for a given column at a given column temperature and a given carrier gas pressure.

Fig. 1 shows the different slopes obtained for a given product and internal standard, varying the column conditions.
Calibration graphs for Chloropentafluorobenzene, using cyclonexane as internal standard with varying column conditions.

Column - Carbowax
Column Temp. (1) 150° (3) 100°
Gas Pressure (1) 1.6 kp/cm² (3) 1.0 kp/cm²
Calibration graphs for Chloroventafluorobenzene
using different internal standards

- Column - carbowax
- Column Temp 150\°C
- Column gas pressure 1.6kpa/cm²

Internal Standards
- (1) cyclohexane
- (2) toluene

Relative Peak Heights (R.P.H.)

<table>
<thead>
<tr>
<th>Standard</th>
<th>2.4</th>
<th>2.2</th>
<th>2.0</th>
<th>1.8</th>
<th>1.6</th>
<th>1.4</th>
<th>1.2</th>
<th>1.0</th>
<th>0.8</th>
<th>0.6</th>
<th>0.4</th>
<th>0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆F₅Cl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Mole Ratio (M.R.) Standard

\[
\frac{C₆F₅Cl}{C₆F₅Cl}
\]
Fig. 2 shows the variation in slope for a given product with different internal standards.

(iii) Assignment of peaks

Because of the proximity of the peaks on the chromatogram and the small fluctuations in the retention times on the instrument used, identification of compounds could not be made by comparison of retention times. Instead, a sample of the suspected product was added to a sample of the reaction mixture and a sample of this injected into the instrument. If one of the peaks already present increased in height compared to the other peaks and no other peaks appeared, then that peak was assigned to the suspected product.

(iv) Preparative gas liquid chromatography

The biaryl products resulting from the thermal decomposition of perfluorobenzoyl peroxide in polyfluoroaromatic solvents were isolated by means of preparative g.l.c. Injections were made using an automatic dosing system. The complexity of the mixtures being separated, together with instrumental limitations, necessitated the manual operation of the instrument rather than automatic programming of the instrument.

The collecting traps were cooled in an acetone-DriKold mixture contained in a Dewar flask. The carrier gas passed through a closely meshed gauze in the traps to facilitate the condensation of the products. By collecting compounds
whose weights were originally known, it was found that under the optimum collecting conditions, only 10% of each compound was collected. The weights of compounds collected were therefore adjusted accordingly to determine the yields of products formed during the reactions.

All preparative separations were carried out using columns containing Apiezon L as stationary phase.
2.3 MASS SPECTROMETRY

Because the yields of biaryls separated by preparative means were very small, the most suitable means of identification of the various biaryls was by mass spectrometry. All spectra were recorded at the Physico-Chemical Measurements Unit at the Atomic Energy Establishment at Harwell.
2.4 pH MEASUREMENTS

All pH titrations were carried out using a Pye 'Dynacap' pH meter, with a Pye combined glass and reference electrode. Solutions were made up using boiled carbon dioxide-free distilled water and titrations were carried out under nitrogen at room temperature using a 10 ml burette.

Graphs were plotted of pH against volume and of d(pH)/dV against volume and from the graphs the quantities and pK's of acids present in the solution determined. (Figs. 3 and 4 respectively).

The number of moles of acid present in solution could be determined from the end point $V'$ (Fig. 4).

The pK of an acid could be determined using the Henderson equation:

$$pH = pK + \log\left(\frac{[\text{salt}]}{[\text{acid}]}\right)$$

At the half neutralisation point of a titration, $[\text{salt}] = [\text{acid}]$, hence $pH = pK$ and pK could be read from $V'/2$ in Fig. 3.

2.4.1 Titrations of mixtures of acids

pH Titrations were carried out on alkaline solutions containing mixtures of salts of carboxylic acids and phenols. pH curves and differential graphs were obtained as in Figs. 5 and 6 respectively.

The number of moles of acid 1 can be obtained from $v_2 - v_1$, acid 2 from $v_3 - v_1$ and acid 3 from $v_{\text{end point}} - v_3$
(Fig. 6). Hence the pK's of acids 1, 2, 3 can be obtained from the points

\[
\frac{v_2 - v_1}{2}, \quad \frac{v_3 - v_2}{2} \quad \text{and} \quad \frac{v_{\text{end}} - v_3}{2}
\]

respectively (Fig. 5).
2.5 ESTIMATION OF FLUORIDE ION PRESENT IN SOLUTION

The fluoride ion content of solutions was determined by titration with thorium nitrate solution, using Alizarin red S as indicator. When thorium nitrate solution is present in excess in solution, a red lake is formed with the indicator. The pH of the solution must be controlled and the following procedure was used:

Reagents: Standard sodium fluoride solution (approx. 0.01N). Thorium nitrate solution (approx. 0.01N, Th(NO₃)₂·6H₂O), standardised against sodium fluoride. Buffer, monochloroacetic acid (9.45 g) and sodium hydroxide (2.0 g) dissolved in water (100 ml). Alizarin red S indicator.

To adjust the pH of the solution to about 3.0, several drops of indicator were added, followed by dilute sodium hydroxide where necessary, until a pink colour was obtained. N/100 hydrochloric acid was then added until the pink colour was just discharged, the solution then being acid. Addition of 1.0 ml of chloroacetic acid buffer gave a solution of pH approximately 3.0.

The solution was then titrated with thorium nitrate until a permanent pink colour was obtained. A blank titration was carried out and this titre subtracted from the sample titre.
2.6 The Thermal Decomposition of Perfluorobenzoyl Peroxide in Polyfluoroaromatic Solvents

In these experiments, except where otherwise stated, a solution of perfluorobenzoyl peroxide in a given solvent was refluxed under nitrogen for 72 hours (98-100% decomposition). The solutions were protected from atmospheric moisture by fitting the reflux condensers with calcium chloride drying tubes. At the end of this time, a sample was removed for g.l.c. analysis.

The solutions were analysed by the following means:

Stage 1 Acidic material was removed from the reaction mixture by thorough washing with saturated aqueous sodium bicarbonate. The aqueous layer was extracted with ether and the original organic solution was washed with water.

The combined aqueous solution was acidified with concentrated hydrochloric acid and was exhaustively extracted with methylene chloride. The dried (MgSO₄) methylene chloride extract was evaporated to dryness to give a white solid which in all cases was identified as pentafluorobenzoic acid. M.p. 103-4° (Lit. m.p. 103-4°).¹³⁴

i.r. spectrum: Strong: 1720, 1495, 1315, 1260, 1115, 1050
Medium: 1650, 1530, 1150, 990, 915 cm⁻¹.

The aqueous layer was analysed for fluoride ion arising from hydrofluoric acid and easily hydrolysable precursors.

Stage 2 The combined organic extracts from stage 1 were dried (MgSO₄) and concentrated to remove ether. A sample was removed for g.l.c. inspection and sufficient standard
N/10 sodium hydroxide solution added to the organic solution to hydrolyse any esters formed in solution (on the basis that one mole of perfluorobenzoyl peroxide will yield two moles of ester, four moles of sodium hydroxide are required to hydrolyse the products resulting from one mole of peroxide). 20% (by volume) of methanol was added to the mixture to obtain a homogeneous solution, which was then boiled under nitrogen for 30 minutes (investigation having shown that fluorinated aromatic esters were hydrolysed by N/10 sodium hydroxide solution within 10-15 minutes).

On cooling, carbon dioxide-free water was added to the solution and organic products removed from the solution by ether extraction. The remaining aqueous solution was then made up to a standard volume with carbon dioxide-free distilled water.

As preliminary tests suggested the presence of improbably large amounts of weak acids, potentiometric titration of the original solution was abandoned. Instead aliquots were acidified (hydrochloric acid) and then were saturated with sodium bicarbonate. Ether extraction of such solutions removed acids of pK > 8. Reacidification (hydrochloric acid) of the aqueous layer allowed stronger acids to be extracted (methylene chloride). In each case the solvent was removed from the dried (MgSO₄) organic solution after exhaustive extraction and the residue was weighed, dissolved in carbon dioxide-free water, and titrated potentiometrically to allow the estimation of organic acids formed during hydrolysis (2.4).
On treatment of a further aliquot of solution as described, the i.r. spectra of the isolated solids were recorded.

Direct titration of aliquots of the aqueous hydrolysate gave a measure of fluoride ion formed from the hydrolysis (2.5).

Stage 3  Organic layer The organic solution of extracts from the hydrolysed reaction mixture was dried (MgSO$_4$) and the ether removed by distillation. Biaryls present in solution were separated by g.l.c. as described (2.2.1 iv).

The suspected structures of the biaryls obtained were confirmed by mass spectroscopy, and the m.p.s. and i.r. spectra of the separated compounds were recorded where possible.
2.6.1 *Decomposition of perfluorobenzoyl peroxide in 1,2,4,5-tetrafluorobenzene*

Experiments 1, 2 and 3 were carried out at 80° in a thermostat, instead of at the boiling point of the solvent. In each experiment considerable tarry material formed round the edges of the dark red solution which was obtained.

**Experiment 1** Perfluorobenzoyl peroxide (0.41 g, $0.097 \times 10^{-2}$ mole) was allowed to decompose in 1,2,4,5-tetrafluorobenzene (5 ml). In stage 1 of the work up, no measurements of fluoride ion were made, but the experiment was otherwise carried out in the usual manner.

G.l.c. analysis of the reaction mixture before hydrolysis showed the presence of many components, but only seven peaks were resolvable after hydrolysis.

**Experiment 2** Perfluorobenzoyl peroxide (1.134 g, $0.318 \times 10^{-2}$ mole) was allowed to decompose in 1,2,4,5-tetrafluorobenzene (5 ml). Extraction of the sodium bicarbonate solution with ether resulted in the formation of a tarry layer which was sparingly soluble in methanol only.

**Experiment 3** Perfluorobenzoyl peroxide (0.975 g, $0.231 \times 10^{-2}$ mole) was dissolved in 1,2,4,5-tetrafluorobenzene (4.5 ml). In this experiment, the reaction mixture was not hydrolysed, an attempt being made to separate esters present in solution by preparative g.l.c. analysis. This experiment, however, proved unsuccessful as resolution of the many peaks could not be obtained.
The results for experiments 1, 2 and 3 are summarised in Table 1. Attempts to separate the biaryl fraction by preparative g.l.c. were unsuccessful in each case.

The following decompositions of perfluorobenzoyl peroxide in 1,2,4,5-tetrafluorobenzene were carried out at the boiling point of the solvent, following the described procedure (2.7).

**Experiment 4** Perfluorobenzoyl peroxide (0.962 g, 0.228×10⁻² mole) was allowed to decompose in 1,2,4,5-tetrafluorobenzene (6 ml) and stages 1 and 2 of the reaction work-up procedure (2.6) followed. 100 ml of 0.1001N sodium hydroxide solution were employed for the alkaline hydrolysis (stage 2). The organic residue from stage 2 was then steam distilled. Ether extraction of the distillate gave a white material which could not be resolved by g.l.c. analysis.

**Experiment 5** Perfluorobenzoyl peroxide (2.014 g, 0.48×10⁻² mole) was allowed to decompose in 1,2,4,5-tetrafluorobenzene (10 ml) and the reaction mixture worked up as described (2.6). 200 ml of 0.1001N sodium hydroxide solution were used in stage 2. Attempts to separate the organic fraction by g.l.c. (stage 3) were unsuccessful.

The results obtained for experiments 4 and 5 are summarised in Table 1.

**Experiment 6** Perfluorobenzoyl peroxide (1.43 g, 0.34×10⁻² mole) was dissolved in 1,2,4,5-tetrafluorobenzene (10 ml)
and the reaction carried out as described (2.6). 150 ml of 0.1001N sodium hydroxide solution were used in stage 2 of the work-up.

In stage 3, g.l.c. separation was carried out on an Apiezon L column, with injection block and manifold oven at 250°. One biaryl was isolated with the column temperature at 130° and the gas pressure at 1.6 kp/cm². 0.012 g of this biaryl were collected and this yield was extrapolated as described (2.2.1 iv) to give the total yield formed during the experiment as 0.12 g. The properties of this biaryl are as follows:-

(a) Mass Spectrum

Mass Peak: Calculated for C_{12}HF_9, 315.9934

Measured 315.9937

(b) m.p. 77-78°. (Lit. m.p. 4-H-nonafluorobiphenyl 77°).126

These properties indicated that the compound isolated was 4-H-nonafluorobiphenyl.

Experiment 7 Perfluorobenzoyl peroxide (2.113 g, 0.501x10⁻² mole) was allowed to decompose in 1,2,4,5-tetrafluorobenzene (6.5 ml) and the reaction worked up as described (2.6). 200 ml of 0.1001N sodium hydroxide solution were used in stage 2. Figure 7 shows the chromatograph of the organic fraction before alkaline hydrolysis and Figure 8 shows the chromatograph of the organic fraction after hydrolysis. The column type used for g.l.c. analysis was Apiezon L and the
injection block and manifold oven temperatures were maintained at 250°. Figure 8 shows the resolution of the mixture and the biaryl components isolated with a column temperature of 130° and a gas pressure of 1.6 kp/cm². As can also be seen, the high boiling components resolved by raising the column temperature to 180° and the gas pressure to 1.8 kp/cm² gave a very complex chromatograph.

The properties and yields of the two biaryls isolated are as follows:

**Biaryl 1**

Extrapolated yield (2.2.1 iv) 0.22 g.

(a) Mass spectrum

Mass Peak Calculated for C₁₂H₉F₉ 315.9934

Measured 315.9936

(b) m.p. 77-78° (Lit. m.p. 4-H-nonafluorobiphenyl 77°). ¹²⁷

These properties indicated that biaryl 1 is 4-H-nonafluorobiphenyl.

**Biaryl 2**

Extrapolated yield (2.2.1 iv) 0.02 g.

(a) Mass spectrum

Mass Peak Calculated for C₁₂H₂F₈ 298.0029

Measured 298.0032

(b) m.p. 44-45°.
The mass spectrum indicated that biaryl 2 is a biaryl resulting from substitution in a fluorine carrying position.

The results for experiment 6 and 7 are summarised in Table 1.
EXPERIMENT 7

solvent - C_{6} F_{4}H_{2}

Before hydrolysis.

Column Temp. 150°

Gas Pressure 1.6kp/cm²

FIGURE 7

Disappears after hydrolysis
EXPERIMENT 7

solvent- $C_6F_4H_2$

Separation of Components after hydrolysis:

<table>
<thead>
<tr>
<th>Column Temp.</th>
<th>Gas Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>180°</td>
<td>1.8 kp/cm²</td>
</tr>
</tbody>
</table>

Biaryl components collected.

<table>
<thead>
<tr>
<th>Column Temp</th>
<th>Gas Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>130°</td>
<td>1.6 kp/cm²</td>
</tr>
</tbody>
</table>

Retention Time.
<table>
<thead>
<tr>
<th>Ex. Peroxide No. (mole/litre)</th>
<th>Free $\text{C}_6\text{H}_5\text{CO}_2\text{H}$</th>
<th>Free HF</th>
<th>Phenol (1)</th>
<th>Phenol (2)</th>
<th>Total acid from esters</th>
<th>Acid isolated</th>
<th>Saponifiable fluoride</th>
<th>Biaryl (1)</th>
<th>Biaryl (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7. 0.77</td>
<td>0.076</td>
<td>0.51</td>
<td>0.20</td>
<td>0.88</td>
<td>0.21</td>
<td>0.56</td>
<td>0.11</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>5. 0.48</td>
<td>0.10</td>
<td>0.24</td>
<td>0.05</td>
<td>0.44</td>
<td>0.18</td>
<td>0.31</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4. 0.38</td>
<td>0.23</td>
<td>0.17</td>
<td>0.09</td>
<td>0.88</td>
<td>0.40*</td>
<td>0.48</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6. 0.34</td>
<td>0.06</td>
<td>0.15</td>
<td>0.03</td>
<td>0.58</td>
<td>0.24</td>
<td>0.32</td>
<td>0.11</td>
<td>not isolated</td>
<td></td>
</tr>
</tbody>
</table>

2. 0.64                       | 0.68                          | 0.55   | 0.08       | 0.43       | 1.38                  | 0.36*        | 0.94                 | -         | -         |
3. 0.51                       | 0.37                          | 0.39   | -          | -          | -                     | -            | -                    | -         | -         |
1. 0.195                      | 0.35                          | -      | 0.19       | 0.41       | 2.89                  | 0.81         | 2.08                 | -         | -         |

* Indicates acid from esters estimated by difference between total acid and fluoride ion.

- Indicates species not isolated or measured.

Biaryl (1) identified as $\text{C}_6\text{F}_5\text{C}_6\text{F}_4\text{H}$. Biaryl (2) identified as $\text{C}_6\text{F}_5\text{C}_6\text{F}_3\text{H}_2$.

Phenol (1) identified by $pK_a$ measurements as a trifluoro phenol, phenol (2) similarly identified as either a tetrafluoro- or pentafluoro-phenol.
2.6.2 Thermal decomposition of perfluorobenzoyl peroxide in 1,3,5-trifluorobenzene

The following reactions were carried out as previously described (2.6). For the g.l.c. analysis in stage 3 an Apiezon L column was used with injection block and manifold oven temperatures at 250°. For the elution of biaryls, the temperature of the column was 100° and the gas pressure 1.8 kp/cm². For the elution of high boiling components, the column temperature was raised to 180°.

**Experiment 8** Perfluorobenzoyl peroxide (1.11 g, 0.26x10⁻² mole) was allowed to decompose in 1,3,5-trifluorobenzene (5 ml) and the reaction worked up as described (2.6). 125 ml of 0.1N sodium hydroxide solution were used for the alkaline hydrolysis in stage 2.

A single component was collected during the g.l.c. analysis (stage 3) with an extrapolated yield (2.2.1 iv) of 0.1 g. The properties of this component will be described after experiment 10.

**Experiment 9** Perfluorobenzoyl peroxide (1.98 g, 0.468x10⁻² mole) was allowed to decompose in 1,3,5-trifluorobenzene (15 ml) and the reaction worked up as described (2.6). 200 ml of 0.1N sodium hydroxide solution were employed for alkaline hydrolysis in stage 2.

A single component was collected during g.l.c. analysis (stage 3) with an extrapolated yield of 0.66 g. The properties of this component will be described after experiment 10.
Experiment 10 Perfluorobenzoyl peroxide (0.93 g, $0.221 \times 10^{-2}$ mole) were allowed to decompose in 1,3,5-trifluorobenzene (5 ml) and the reaction worked up as described (2.6). 100 ml of 0.1N sodium hydroxide were used for the alkaline hydrolysis in stage 2.

A single component was isolated by g.l.c. analysis (stage 3) with an extrapolated yield of 0.38 g.

In each of the above experiments (8, 9 and 10) a single component was isolated by g.l.c. analysis (stage 3) and these compounds were found to have the same properties as described below:

(a) Mass Spectrum

The mass spectrum of one of the components was recorded

Mass Peak Calculated for $C_{12}H_{2}F_{8}$ 298.0028
Measured 298.0038

This suggests that the product is a biaryl resulting from substitution at a hydrogen carrying position.

(b) i.r. Spectrum (solvent - carbon tetrachloride)

Strong: triplet(1525, 1510, 1500), 1210, 1000 cm$^{-1}$.
Medium: 1650, 1600, 1420, 1260 cm$^{-1}$.

(c) m.p. 43-44°.

A summary of the results for experiments 8, 9 and 10 is given in Table 2.
TABLE 2

Yields (mole/mole) peroxide of species identified from reaction of perfluorobenzoyl peroxide with 1,3,5-trifluorobenzene

<table>
<thead>
<tr>
<th>Ex. No.</th>
<th>Peroxide (mole/litre)</th>
<th>Free ( \text{C}_6\text{F}_5\text{CO}_2\text{H} )</th>
<th>Free HF</th>
<th>Phenol</th>
<th>Total acid from esters</th>
<th>Acid isolated</th>
<th>Saponifiable fluoride</th>
<th>Biaryl</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.</td>
<td>0.53</td>
<td>0.84</td>
<td>0.63</td>
<td>0.17</td>
<td>0.48</td>
<td>0.22</td>
<td>0.06</td>
<td>0.13</td>
</tr>
<tr>
<td>10.</td>
<td>0.44</td>
<td>0.85</td>
<td>0.07</td>
<td>0.27</td>
<td>0.29</td>
<td>0.23</td>
<td>0.10</td>
<td>0.58</td>
</tr>
<tr>
<td>9.</td>
<td>0.31</td>
<td>0.89</td>
<td>0.07</td>
<td>0.13</td>
<td>0.22</td>
<td>0.12</td>
<td>0.07</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Phenol identified by pK measurements as a trifluorophenol

Biaryl identified as \( \text{C}_6\text{F}_5\text{C}_6\text{F}_3\text{H}_2 \).
2.6.3 Thermal decomposition of perfluorobenzoyl peroxide in 1,4-difluorobenzene

**Experiment 11** Perfluorobenzoyl peroxide (1.02 g, 0.24x10⁻² mole) were allowed to decompose in 1,4-difluorobenzene (10 ml) as described (2,6). In this experiment, the organic fraction from stage 1 of the work up was not subjected to alkaline hydrolysis. Ether was removed from this fraction which was then quantitatively analysed by g.l.c. in an effort to collect any esters which may be present.

For the g.l.c. analysis an Apiezon L column was used with injection block and manifold oven temperature at 250°. (i) Under the conditions for collecting biaryls, (column temperature 130° and gas pressure 1.6 kp/cm²), a single component was isolated with extrapolated yield of 0.13 g (2.2.1 iv) and the following properties:

(a) Mass spectrum

Mass Peak Calculated for C₁₂H₃F₇  280.0123
   Measured  280.013

This indicates that this component is a biaryl resulting from pentafluorophenyl substitution at a hydrogen carrying position.

(b) i.r. spectrum

Strong: triplet (1510, 1500, 1495), 1460, 1060, 995 cm⁻¹
Medium: 1660, 1550, 1360, 1250, 1160, 1105 cm⁻¹
(c) m.p. 39-40°.

(ii) Under the conditions for collecting high boiling components (column temperature 180°, gas pressure 1.6 kp/cm²) one product was isolated with an extrapolated yield (2.2.1 iv) of 0.01 g, and the following properties:

(a) Mass spectrum

<table>
<thead>
<tr>
<th>Mass Peak Calculated for C₁₃H₄₀₂F₆</th>
<th>306.012</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured</td>
<td>306.012</td>
</tr>
</tbody>
</table>

This indicates that the product isolated would be the ester 4-fluorophenyl pentafluorobenzoate, which results from substitution by the pentafluorobenzoyloxy radical at a fluorine carrying position in 1,4-difluorobenzene.

(b) i.r. spectrum (solvent - carbon tetrachloride)

Strong: 1760, triplet (1525, 1510, 1500), 1300, 1200 cm⁻¹
Medium: 1650, 1420, 1180, 1090, 1000 cm⁻¹.

This spectrum is very similar to that of phenyl pentafluorobenzoate (strong: 1750, 1525, 1500, 1495, 1300, 1205; Medium: 1650, 1600, 1160, 1100, 1070, 1000 cm⁻¹).

The chromatogram for the g.l.c. separation described above is shown in Figure 9. The results for experiment 11 are summarised in Table 3.

Experiment 12 Perfluorobenzoyl peroxide (1.186 g, 0.44x10⁻² mole) was allowed to decompose in 1,4-difluorobenzene (10 ml) and the reaction worked up as described (2.6). 100 ml of
0.1001N sodium hydroxide solution were used for the alkaline hydrolysis (stage 2). For g.l.c. analysis (stage 3) and Apiezon L column was used and the manifold oven and injection block temperatures were 250°. For the collection of biaryl components, the column temperature was 130° and the gas pressure 1.6 kp/cm². One product was isolated under these conditions. This was found to have the same properties as the biaryl collected under the same conditions in Experiment 11 (i). The properties are as follows:

(a) Mass spectrum

| Mass Peak Calculated for C_{12}H_{3}F_{7} | 280.0123 |
| Measured                                   | 280.012 |

This indicates, as in Experiment 11, the formation of a biaryl resulting from pentafluorophenyl substitution at a hydrogen carrying position.

(b) i.r. spectrum

Strong: triplet (1510, 1500, 1495), 1460, 1060, 995 cm⁻¹
Medium: 1660, 1550, 1360, 1250, 1160, 1105 cm⁻¹

(c) m.p. 38-40°.

In an effort to collect high boiling components, the column temperature was raised to 180°, but no other components were collected.

Experiment 13 Perfluorobenzoyl peroxide (1.024g, 0.024x10⁻² mole) was allowed to decompose in 1,4-difluorobenzene (12 ml) and the reaction worked up as described (2.6). 100 ml of
0.1001N sodium hydroxide solution were used for the alkaline hydrolysis (stage 2). Attempts to collect the reaction products by g.l.c. separation, (stage 3), under conditions described in experiments 11 and 12, were unsuccessful.

The results for experiments 12 and 13 are summarised in Table 3.
EXPERIMENT 11
Solvent: $C_6F_2H_4$
Separation of Components

Column Temp: 180°
Gas Pressure: 1.6 kN/cm²

Retention Time
TABLE 3

Yields (mole/mole p-oxide) of species identified from reaction of perfluorobenzoyl peroxide
with 1,4-difluorobenzene

<table>
<thead>
<tr>
<th>Ex. No. (mole/litre)</th>
<th>Peroxide</th>
<th>Free $\text{C}_6\text{F}_5\text{CO}_2\text{H}$</th>
<th>Free HF</th>
<th>Phenol (1)</th>
<th>Phenol (2)</th>
<th>Total acid from esters isolated</th>
<th>Acid isolated</th>
<th>Saponifiable</th>
<th>Biaryl isolated</th>
<th>Ester isolated</th>
</tr>
</thead>
<tbody>
<tr>
<td>12. 0.441</td>
<td>0.11</td>
<td>0.084</td>
<td>0.07</td>
<td>0.50</td>
<td>1.5</td>
<td>0.72</td>
<td>0.53</td>
<td>0.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11. 0.242</td>
<td>0.15</td>
<td>0.043</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.19</td>
<td>0.014</td>
</tr>
<tr>
<td>13. 0.20</td>
<td>0.07</td>
<td>0.61</td>
<td>0.03</td>
<td>0.33</td>
<td>1.23</td>
<td>0.52</td>
<td>0.52</td>
<td></td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Phenol (1) identified by pK measurements as a monofluorophenol.
Phenol (2) identified by pK measurements as a difluorophenol.
Biaryl identified as $\text{C}_6\text{F}_5\text{C}_6\text{F}_2\text{H}_3$.
Isolated ester identified as $\text{C}_6\text{F}_5\text{CO.OC}_6\text{FH}_4$.
- Indicates species not measured or isolated.
2.6.4 Thermal decomposition of perfluorobenzoyl peroxide in pentafluorobenzene

In this experiment, perfluorobenzoyl peroxide (2.0436 g, 0.483\times10^{-2} \text{ mole}) was dissolved in pentafluorobenzene (5 ml) and the reaction carried out and worked up in the usual manner (2.6). Efforts to isolate biaryls by g.l.c. were unsuccessful. Results are summarised in Table 4.
TABLE 4

Yields (mole/mole peroxide) of species identified from reaction of perfluorobenzoyl peroxide with pentafluorobenzene

<table>
<thead>
<tr>
<th>Ex. No.</th>
<th>Peroxide (mole/litre)</th>
<th>Free ( C_{6}F_{5}CO_{2}H )</th>
<th>Free HF</th>
<th>Phenol</th>
<th>Acid isolated</th>
<th>Saponifiable fluorine</th>
<th>Total acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>0.967</td>
<td>0.086</td>
<td>0.094</td>
<td>0.209</td>
<td>0.215</td>
<td>0.60</td>
<td>1.10</td>
</tr>
</tbody>
</table>

Phenol identified by pK measurements as either a pentafluoro- or tetrafluorophenol.
2.6.5 Thermal decomposition of perfluorobenzoyl peroxide with sulphuryl chloride

Perfluorobenzoyl peroxide (2.632 g, 0.624x10^-2 mole) was dissolved in sulphuryl chloride (50 ml) and the solution refluxed until sulphur dioxide was no longer evolved. Sulphuryl chloride was distilled off using a Dufton column and the remaining solution washed well with water to remove any remaining sulphuryl chloride.

The aqueous solution was thoroughly extracted with ether. The ethereal solution was thoroughly dried (MgSO₄), ether distilled off under reduced pressure and the remaining organic fraction examined by g.l.c. using an internal standard as described (2.2.1).

Results:
Yield of chloropentafluorobenzene 0.12 g (0.946 mole/mole peroxide).
Reactions of this type were carried out to determine the nature and yields of products resulting from the abstraction reactions of pentafluorophenyl radicals. Since the yields and distribution of the products are dependant upon the order of addition of the reagents, a number of synthetic reaction methods were devised to determine the optimum conditions. The reaction of pentafluoroaniline with amyl nitrite in bromotrichloromethane was chosen for this purpose.

2.7.1 Reaction of pentafluoroaniline with amyl nitrite in bromotrichloromethane

Method 1

Amyl nitrite (2.00 g, 0.17 mole) dissolved in bromotrichloromethane (10 ml) was added slowly to a solution of pentafluoroaniline (3.03 g, 0.017 mole) in an excess of bromotrichloromethane (50 ml) at room temperature. Evolution of bubbles of gas indicated the commencement of the reaction which was allowed to proceed without heating until the evolution of gas ceased. The mixture was then refluxed for two hours.

The excess of solvent was removed by fractional distillation using a Dufton column. The distillate was retained for g.l.c. investigation. The orange red residue was trans-
ferred to a Claisen flask and the contents distilled under reduced pressure (20 mm). The temperature of distillation was then raised until orange-red products began to distill over (130°, 20 mm). The distillate was collected in a receiver surrounded by a freezing mixture. A second trap, in series with this receiver and surrounded by an acetone-DriKold mixture was used to collect any low-boiling products which were not collected in the first receiver.

The contents of both receivers were transferred to a weighed flask which was then reweighed. A portion of the solution was removed for qualitative g.l.c. analysis (2.2.1) the flask being reweighed once more and its contents being retained for quantitative g.l.c. analysis (2.2.1).

Similar g.l.c. analysis was performed on the excess solvent removed from the reaction mixture.

Results:

- Bromopentafluorobenzene 25.2%
- Chloropentafluorobenzene 0.9%
- Products identified qualitatively: decafluorobiphenyl, hexachloroethane.

This reaction work up and g.l.c. analysis were carried out in all reactions of polyfluoroanilines with amyl nitrite in polyhalogenmethanes.

Method 2

In this method, the order of addition of reagents was the reverse of that in method 1. A solution of pentafluoroaniline (3.00 g, 0.17 mole) in the minimum amount of bromo-
trichloromethane was added slowly to a solution of amyl nitrite (2.00 g, 0.17 mole) in bromotrichloromethane (50 ml). When, after addition of about one third of the pentafluoroaniline solution, there was no indication of the reaction having started, the solution was heated gently until evolution of gas was noticed. The source of heat was then removed and the reaction allowed to proceed without heating until evolution of gas ceased, after which time the solution was refluxed for two hours.

The reaction was then worked up in the manner described in method 1.

Results:

Bromopentafluorobenzene 8.23%
Chloropentafluorobenzene 0.5%

Method 3

In this method the order of addition of method 2 was adopted, however, the pentafluoroaniline solution (2.90 g, 0.17 mole in a minimum of bromotrichloromethane) was added slowly to a refluxing solution of amyl nitrite (4.00 g, 0.34 mole) in bromotrichloromethane (50 ml).

The molar ratio of amyl nitrite to pentafluoroaniline was 2:1 to allow for some decomposition of amyl nitrite which takes place at the boiling point of bromotrichloromethane (104°, 760 mm).

After addition of pentafluoroaniline, the solution was refluxed for two hours. The reaction was then worked up in
the manner described in method 1.

Results:

Bromopentafluorobenzene 42.65%
Chloropentafluorobenzene 1.1%
Products identified qualitatively:
decafluorobiphenyl, hexafluoroethane.

Method 4

The procedure for method 3 was followed except for the length of time for which the solution was refluxed, being six hours instead of two.

Results:

Bromopentafluorobenzene 42.0%
Chloropentafluorobenzene 1.0%

2.7.2 Method selected for subsequent experiments

Methods 3 and 4 gave the optimum product yields, but as the increased reaction time did not increase the product yields, method 3 was selected as the method for use with future reactions.

The reaction was carried out for a series of p-substituted fluorinated anilines in bromotrichloromethane and chloroform and the results are summarised in Table 5. For two of the reactions, there was a slight departure from the described procedure:

(1) For the quantitative g.l.c. analysis of the reaction
products from 4-bromotetrafluoroaniline and 1,4-dichlorobenzene was used as internal standard (instead of toluene or cyclohexane) as its retention time is closer to that of the products under investigation.

(ii) In the reaction of 4-methoxy-2,3,5,6-tetrafluoroaniline with amyl nitrite in chloroform, the retention time of unreacted amyl nitrite is the same as that of one of the products. The solution was therefore washed with sodium hydroxide solution to remove unreacted amyl nitrite, followed by thorough washing with water and drying (CaCl$_2$). Chlorobenzene was added to the solution and chloroform was distilled off.
<table>
<thead>
<tr>
<th>D-XC$_6$F$_4$NH$_2$</th>
<th>Solvent</th>
<th>Wt. Amine-% (mole)</th>
<th>Wt. AmONO-% (mole)</th>
<th>XC$_6$F$_4$H(%)*</th>
<th>XC$_6$F$_4$Cl(%)*</th>
<th>XC$_6$F$_4$Br(%)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>X=F</td>
<td>CCl$_4$</td>
<td>4.51 (0.025)</td>
<td>5.79 (0.046)</td>
<td>-</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>CHCl$_3$</td>
<td>6.36 (0.035)</td>
<td>7.90 (0.068)</td>
<td>18.3</td>
<td>0.58</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>CBrCl$_3$</td>
<td>2.90 (0.017)</td>
<td>4.00 (0.034)</td>
<td>1.10</td>
<td>42.65</td>
<td></td>
</tr>
<tr>
<td>X=H</td>
<td>CHCl$_3$</td>
<td>2.90 (0.018)</td>
<td>4.1 (0.035)</td>
<td>20.5</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CBrCl$_3$</td>
<td>3.60 (0.022)</td>
<td>4.90 (0.034)</td>
<td>-</td>
<td>10.8</td>
<td>22.00</td>
</tr>
<tr>
<td>X=MeO</td>
<td>CHCl$_3$</td>
<td>1.05 (0.0067)</td>
<td>1.59 (0.013)</td>
<td>46.50</td>
<td>3.00</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>CBrCl$_3$</td>
<td>1.57 (0.0099)</td>
<td>2.10 (0.018)</td>
<td>-</td>
<td>7.60</td>
<td>71.48</td>
</tr>
<tr>
<td>X=Br</td>
<td>CHCl$_3$</td>
<td>0.96 (0.0042)</td>
<td>1.0 (0.0087)</td>
<td>18.2</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CBrCl$_3$</td>
<td>1.11 (0.0045)</td>
<td>1.1 (0.009)</td>
<td>2.80</td>
<td>31.50</td>
<td></td>
</tr>
</tbody>
</table>

* Yields expressed in terms of actual yield/theoretical yield x 100%, assuming one mole of aniline gives one mole product.
Investigation of high boiling residues from the reactions of polyfluoroaniline with amyl nitrite in polyhalogenomethanes

In all the reactions considered (2.7), a large quantity of tarry byproduct is formed. In view of the generally low yields of simple arenes obtained, efforts were made to investigate these residues. In particular, the residues from the reaction of pentafluoroaniline with amyl nitrite in bromotrichloromethane were considered.

(i) Chromatographic separation. Attempts to separate the residue into its components by g.l.c. analysis were unsuccessful, so separation was carried out by chromatography on activated alumina, eluting first with petroleum ether (b.p. 40-60), then with benzene and finally with chloroform. The solvent was distilled from the extract in each case and the fractions rechromatographed, the purity being checked by eluting each component with a variety of solvents using thin layer chromatography.

Each fraction was dried under vacuum, to ensure removal of solvents, and in each case a reddish oil was obtained, attempts to recrystallise these being unsuccessful.

(ii) The infra-red spectrum of each oil was recorded. $^1$H N.M.R. failed to determine conclusively the nature and position of substituents. The infra-red spectra of the oils separated were found to be similar and exhibited the following peaks:
Strong: 3,4000 (broad), 2900, 2850, 1530, 1500, 1490 peaks between 1400 and 1000 cm\(^{-1}\).

Weak: 3050, 1590 cm\(^{-1}\).

The doublet in the region of 2900 cm\(^{-1}\) could indicate C-H alkyl frequencies, 1590 and the triplet at 1500 cm\(^{-1}\) aromatic frequencies for fluorinated aromatic compounds and the peaks between 1000 and 1400 cm\(^{-1}\) C-F frequencies.

Bearing in mind the nature of the reaction, the spectra indicated that these oils were of a polyaryl nature, containing possibly amyloxy-substituents.

(iii) Acid-Alkali separation A residue was separated first with acid and then with alkali and the isolated bases and acids subjected to chromatographic separation as described (2.7.3 i). The separated products were again red oils and their infra-red spectra were recorded.

Spectra similar to those described above were obtained. For the alkali soluble components, broad peaks in the region of 3,300 cm\(^{-1}\) were obtained, which might indicate the presence of phenolic hydroxyl groups.

For the acid-soluble components, broad peaks centred on 3,500 cm\(^{-1}\) occurred, which might indicate the presence of amine groups.

(iv) U.v. spectra U.V. analysis of the oils obtained were inconclusive.
2.8  THE REACTION OF PENTAFLUOROANILINE WITH AMYL NITRITE

2.8.1  In cumene

Pentafluoroaniline (1.022 g, 0.558 x 10^{-2} mole) was added to a solution of amyl nitrite (1.32 g, 0.0112 mole) in purified cumene, the solution being maintained at a temperature of 80°. After evolution of nitrogen ceased, the solution was refluxed for two hours. All products present in solution with boiling points lower than that of cumene (150°) were removed from the solution by distillation. The distillate was then analysed by g.l.c. in the usual manner (2.2.1).

Results:

- Pentafluorobenzene 16.44%
- 2,3,4,5,6-pentafluorotoluene 1.92%

Further analysis of the residue

As 2,3,4,5,6-pentafluorotoluene was found in a small amount in the reaction mixture, the residue from the distillate was analysed by g.l.c. to determine if products resulting from the combination of radicals of the type

\[ C_6H_5C(II)CH_3 \]

with other radicals could be found.

However, a sample of one of the possible products, racemic 2,3-diphenyl butane, gave a very broad spread-out peak when injected into the g.l.c. As this product is only likely to be formed in very small amounts during the reaction its
presence could not be detected by g.l.c.

2.8.2 In carbon tetrachloride in the presence of methylmercuric iodide

As the purpose of this experiment was to study the reaction of the pentafluorophenyl radical with methylmercuric iodide, it was necessary to choose a solvent towards which the pentafluorophenyl radical is not reactive. Carbon tetrachloride was chosen, although methylmercuric iodide is only sparingly soluble in it.

A suspension of methylmercuric iodide (15 g, 0.081 mole) in refluxing carbon tetrachloride (100 ml) was used. To this suspension was added amyl nitrite (1.69 g, 0.0144 mole), followed by slow addition of pentafluoroaniline (1.3 g, 0.0073 mole) in the minimum amount of carbon tetrachloride. The reaction was then worked up as described in method 1 (2.7.1).

G.l.c. analysis indicated the presence of a trace of 2,3,4,5,6-pentafluorotoluene.

2.8.3 In iodobenzene

A solution of pentafluoroaniline (0.95 g, 0.038 mole) in the minimum amount of iodobenzene was added to amyl nitrite (8.69 g, 0.074 mole) in iodobenzene (100 ml) maintained at 80°. The solution was maintained at 80° for two hours after evolution of gas had ceased.
Reaction work up

The reaction mixture was distilled under reduced pressure (20 cm) and components with boiling points up to 100\degree at this pressure were collected. This fraction was retained for g.l.c. analysis in the usual manner and contained pentafluoriodobenzene in 44.8% yield.

Above 100\degree (20 cm) a yellowish oil was distilled over and the fraction with boiling range 100-120\degree (20 cm) was collected. G.l.c. analysis indicated the absence of pentafluoriodobenzene from this fraction.

Efforts to separate biaryls components from either of these fractions were unsuccessful.
DISCUSSION
3.1 SUMMARY OF PREVIOUS ARYLATION MECHANISMS

Before discussing the products of thermolysis of perfluorobenzoyl peroxide in polyfluorobenzene, it is relevant to review: (i) the proposed mechanism of reaction of perfluorobenzoyl peroxide with benzene and its simple derivatives, and (ii) the proposed mechanism of arylation of hexafluorobenzenes by benzoyl peroxide, since in the present work, we shall be considering the displacement by the pentafluorophenyl radical of both hydrogen and fluorine from the aromatic substrate presumably by mechanisms similar to those described.

3.1.1 The decomposition of perfluorobenzoyl peroxide in derivatives of benzene

From the kinetics of the reaction and the nature of the products previous workers have postulated a reaction scheme (shown below with benzene as substrate) which is summarised below for convenient reference.

\[
(C_6F_5CO.O)_2 \longrightarrow 2C_6F_5CO.O \quad (36a)
\]

\[
C_6F_5CO.O \longrightarrow C_6F_5^+ + CO_2 \quad (36b)
\]

\[
C_6F_5^+ + C_6H_6 \longrightarrow C_6F_5\text{ }}^{\text{V (\sigma-complex)}} \quad (36c)
\]
Perfluorobenzoyl peroxide decomposes to give two pentafluorobenzoyloxy-radicals (Equation 36a), which undergo decarboxylation (Equation 36b) to give pentafluorophenyl radicals and carbon dioxide. Attack of a pentafluorophenyl radical on a molecule of solvent then occurs (Equation 36c) to give a complex (XV), which is dehydrogenated by reaction with a further molecule of peroxide (Equation 36d). Chain termination takes place either by disproportionation (Equation 36e) or by dimerisation (Equation 36f).

With halogenobenzenes as solvents (section 1.7.3 ii), however, the formation of large yields of esters led to the postulate that the pentafluorobenzoyloxy-radical was stabilised by formation of a charge transfer complex with a molecule of solvent, in the following manner:

$$\sigma^* + \left(\text{C}_6\text{F}_5\text{CO.}0\right)_2 \rightarrow \text{C}_6\text{F}_5\text{H}_5 + \text{C}_6\text{F}_5\text{CO.}0\text{H} + \text{C}_6\text{F}_5\text{CO.}0^*$$

(36d)

$$2\sigma^* \rightarrow \text{C}_6\text{F}_5\text{H}_5 + \text{C}_6\text{H}_5\text{H}$$

(36e)

$$2\sigma^* \rightarrow \text{C}_6\text{F}_5\text{C}_6\text{H}_5\text{H}$$

(36f)

XVII

Equation 36

With halogenobenzenes as solvents (section 1.7.3 ii), however, the formation of large yields of esters led to the postulate that the pentafluorobenzoyloxy-radical was stabilised by formation of a charge transfer complex with a molecule of solvent, in the following manner:
The $\sigma$-complex (XIX) formed from the charge transfer complex (Equation 35) was thought to be dehalogenated by reaction with a pentafluorobenzoyloxy-radical (Equation 37) giving a pentafluorobenzoyl hypohalite which would be hydrolysed during work-up of the reaction mixture.

$$\begin{array}{c}
\text{O.CO.C}_{6}F_{5}^{0} \quad + \quad C_{6}F_{5}CO.0^{*} \quad \rightarrow \quad C_{6}F_{5}CO.OC_{6}H_{5}^{+} \\
\quad + \quad C_{6}F_{5}CO.OX
\end{array}$$

XIX

3.1.2 The decomposition of aroyl peroxides in aromatic fluorocarbon solvents

A mechanism for the decomposition of benzoyl peroxide and its reaction with an aromatic fluorocarbon solvent, similar to that for its decomposition and reaction with aromatic hydrocarbon solvents, was proposed on the basis of the nature of the products (section 1.6.2 ii) and the kinetics of the reaction (section 1.6.2 iii).

$$\begin{array}{c}
(C_{6}H_{5}CO.O)_{2} \quad \rightarrow \quad 2C_{6}H_{5}CO.0^{*} \quad (38a) \\
C_{6}H_{5}CO.0^{*} \quad \rightarrow \quad C_{6}H_{5}^{*} \quad + \quad CO_{2} \quad (38b) \\
C_{6}H_{5}^{*} \quad + \quad C_{6}F_{6} \quad \rightarrow \quad C_{6}H_{5}^{X} (38c)
\end{array}$$

XI (6-complex)
Benzoyl peroxide was thought to decompose to give two benzoyloxy-radicals (Equation 38a) which undergo decarboxylation to give phenyl radicals (Equation 38b). A $\sigma$-complex (IX) is then formed between a phenyl radical and a molecule of solvent (Equation 38c). Four methods of defluorination of the $\sigma$-complex have been suggested (section 1.6.2 ii):

1. The removal of a fluorine atom by a benzoyloxy-radical
to give benzoyl hypofluorite, which is subsequently hydrolysed during work-up of the reaction mixture, and a molecule of biaryl (Equation 38d).

(2) Elimination of a molecule of fluorine between two $\sigma$-complexes to give two molecules of biaryl (Equation 38e).

(3) The disproportionation of $\sigma$-complexes to give a molecule of biaryl and a molecule of heptafluorodihydrobiphenyl (XII), (Equation 38f).

(4) The dimerisation of the $\sigma$-complex to give (XII) (tetrahydrododecafluoro-$p$-quaterphenyl) (Equation 38g). This could decompose on distillation to give two molecules of biaryl (Equation 38h).
3.2 PROPOSED MECHANISM FOR REMOVAL OF FLUORINE FROM A \( \sigma \)-COMPLEX

The analogy between fluorine and hydrogen is not as complete as the proposals in section 3.1 suggest and, as will be shown below, unique mechanism whereby fluorine is lost during arylation of polyfluorobenzenes must be sought.

1) Removal of fluorine from a \( \sigma \)-complex by a benzoyloxy-radical (Section 3.1.2, Equation 38d).

This mechanism involves the formation of an aroyl hypofluorite and is unlikely for two reasons. Firstly such a process would be energetically unfavourable by 55 k.cal.mole\(^{-1}\). Secondly, the formation of pentafluorobenzoyl hypofluorite would affect the observed kinetics of a reaction followed by a potassium iodide titration method, since being an oxidising agent, it would liberate iodine. However, the same kinetic results are obtained for the unimolecular dissociation whether the titration method or a radical scavenging method is used to follow the reaction.

2) Elimination of fluorine between two \( \sigma \)-complexes giving two molecules of biaryl (Section 3.1.2, Equation 38e).

In this case, the breakdown of two carbon-fluorine bonds\(^{127}\) would require 204 k.cal.mole\(^{-1}\), whereas only 37 k.cal.mole\(^{-1}\) from the formation of a fluorine molecule and 66 k.cal.mole\(^{-1}\) from the aromatisation of two \( \sigma \)-complexes would be gained. The process is then endothermic to the extent of approximately 100 k.cal.mole\(^{-1}\).

The thermal decomposition of perfluorobenzoyl peroxide
has been studied in hexafluorobenzene as solvent and very little biaryl is formed during the reaction. As this method of defluorination would also allow the defluorination of $\sigma$-complexes formed from hexafluorobenzene in this reaction, the low yields of biaryl shows that such a process is unlikely.

We now suggest that when the solvent is a partially fluorinated one, a molecule of hydrogen fluoride is eliminated between two $\sigma$-complexes, one of which ($\sigma_A$) has resulted from attack at a fluorine bearing carbon atom (XX) and the other ($\sigma_B$) from a hydrogen bearing carbon atom (XXI), (Equation 39).

$$\begin{align*}
\text{Ar}_F \\
\text{or} \\
\text{Ar}_H
\end{align*}$$

$$\text{H, F}$$

$$\text{H, F}$$

$$\begin{align*}
\text{Ar}_F \\
\text{or} \\
\text{Ar}_H
\end{align*}$$

XXI ($\sigma_B$)

$$\begin{align*}
\text{Ar}_F \\
\text{or} \\
\text{Ar}_H
\end{align*}$$

XX ($\sigma_A$)

$$\text{H, F}$$

In this process, 201 k.cal.mole$^{-1}$ are needed to break one carbon-hydrogen bond and one carbon-fluorine bond, whilst 135 k.cal.mole$^{-1}$ from the formation of hydrogen fluoride and 66 k.cal.mole$^{-1}$ from the aromatisation of two $\sigma$-complexes are gained. The mechanism is thus just energetically feasible.

The mutual aromatisation reaction need not be single-staged. Benzoic acid may act as a catalyst in the following series
σ\textsuperscript{H} \cdot + BzO\cdot(BzO)\textsubscript{2} \longrightarrow Biaryl\textsubscript{I} + BzOH(+Bz\cdot) \quad (40a)

BzOH + σ\textsuperscript{F} \longrightarrow Biaryl\textsubscript{II} + HF + Bz\cdot \quad (40b)

Here the benzoyloxy-radical is regenerated in a process similar to that to be described in a proposed mechanism of arylation of hexafluorobenzene\textsuperscript{128} (Section 3.5 1A).
3.3 ANALYSIS OF THE REACTION PRODUCTS OF THE THERMAL DECOMPOSITION OF PERFLUOROBENZOYL PEROXIDE IN POLYFLUOROAROMATIC SOLVENTS

3.3.1 Method used to analyse reaction and results obtained

A summary of the analyses for the products of the above reactions is given in Table 6. The products obtained from the thermal decomposition of perfluorobenzoyl peroxide in hexafluorobenzene and the yields of biaryl for pentafluorobenzene are also indicated for comparison. These products were detected by the procedures summarised in outline below (Fig. 10).

![Diagram]

**Figure 10**
**TABLE 6**

Products identified from the thermolysis of perfluorobenzoyl peroxide in fluorinated aromatic solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Free C$_6$F$_7$CO$_2$H</th>
<th>Free C$_6$F$_5$CO$_2$HF</th>
<th>Phenol (1)</th>
<th>Phenol (2)</th>
<th>Phenol Acid from Saponifiable fluorine</th>
<th>Biaryl (1)</th>
<th>Biaryl (2)</th>
<th>Isolated ester*</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_6$F$_6$ 109</td>
<td>-</td>
<td>-</td>
<td>0.07</td>
<td>-</td>
<td>0.04</td>
<td>0.07$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_6$F$_5$H</td>
<td>0.08</td>
<td>0.09</td>
<td>-</td>
<td>0.21</td>
<td>0.60</td>
<td>0.06$^{109}$</td>
<td>0.14$^{109}$</td>
<td>0.12$^{a,109}$</td>
</tr>
<tr>
<td>1,4-C$_6$F$_4$H$_2$</td>
<td>0.08$^{\pm 2}$</td>
<td>0.16$^{\pm 4}$</td>
<td>0.05$^{\pm 2}$</td>
<td>0.21$^{\pm 3}$</td>
<td>0.40$^{\pm 10}$</td>
<td>0.11</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>1,3,5-C$_6$F$_3$H$_3$</td>
<td>0.86$^{\pm 2}$</td>
<td>0.07</td>
<td>-</td>
<td>0.19$^{\pm 5}$</td>
<td>0.19$^{\pm 3}$</td>
<td>0.08$^{\pm 2}$</td>
<td>0.58</td>
<td>-</td>
</tr>
<tr>
<td>1,4-C$_6$H$_4$F$_2$</td>
<td>0.10$^{\pm 2}$</td>
<td>0.07$^{\pm 2}$</td>
<td>0.05$^{\pm 2}$</td>
<td>0.42$^{\pm 8}$</td>
<td>0.62$^{\pm 10}$</td>
<td>0.53$^{\pm 10}$</td>
<td>0.34</td>
<td>0.01$^4$</td>
</tr>
</tbody>
</table>

Yields in moles/mole peroxide

* signifies ester isolated by g.l.c.

Phenol (1) pK > 8. Phenol (2) pK < 8.

Biaryl (1) resulting from substitution at a hydrogen carrying position

Biaryl (2) resulting from substitution at a fluorine carrying position

(a) C$_6$F$_5$CO.OC$_5$F$_5$  (b) C$_6$F$_5$CO.OC$_6$FH$_4$. 
Table 6 shows that with the more highly fluorinated solvents (hexafluorobenzene, pentafluorobenzene and 1,2,4,5-tetrafluorobenzene), pentafluorobenzoic acid (identified in stage 1) is formed either in very low yields, or not at all in the case of hexafluorobenzene. For these solvents the products identified represent only a small proportion of the total reaction, the yields of biaryls (stage 3) also being low. The residue, which forms the greater part of the products, is thought to consist of quaterphenyls and higher polymers. The decomposition of perfluorobenzoyl peroxide in hexafluorobenzene has been shown to give 50% yields of \( \text{P,F-bis-} \left( \text{pentafluorobenzoyloxy} \right) -1,1',4,4'-\text{tetrahydroperfluorobi-phenyl} \), (XXII).

![](image)

When the solvent is 1,3,5-trifluorobenzene, it can be seen that there is a very large increase in the yields of pentafluorobenzoic acid and biaryl, and it can also be seen that with the decreasing fluorine substitution in the solvent, biaryls resulting from attack by a radical on a hydrogen bearing carbon atom becomes increasingly predominant.

For all solvents, there is good agreement between the yields of phenols and pentafluorobenzoic acid identified in stage 2 of the work-up, and it can also be seen that
hydrolysis leads to the liberation of large quantities of fluoride ion.

Hydrogen fluoride was identified as a reaction product (stage 1) for all the solvents investigated in the present work.

3.3.2 Nature of phenols separated at stage 2

It was hoped that esters formed in the reaction could be identified through the phenols formed as a result of hydrolysis.

Many fluorinated phenols\textsuperscript{129} are much stronger acids than non-fluorinated phenols because of the strong inductive effects of the fluorine atoms. However, resonance structures of the following type can be drawn:

\[
\begin{array}{c}
\begin{array}{c}
\text{F} \quad \text{F} \\
\text{F} \quad \text{F} \\
\text{F} \quad \text{F}
\end{array}
\quad \rightarrow \\
\begin{array}{c}
\begin{array}{c}
\text{F} \quad \text{F} \\
\text{F} \quad \text{F} \\
\text{F} \quad \text{F}
\end{array}
\end{array}
\end{array}
\]

and these resonance effects offset the inductive effects, as has been shown\textsuperscript{130} by the pK values of the three mono-substituted phenols below (Table 7)

<table>
<thead>
<tr>
<th>Phenol</th>
<th>pK (10% methanolic solution)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\diamondsuit$-$\text{FC}_6\text{H}_4\text{OH}$</td>
<td>9.37</td>
</tr>
<tr>
<td>$\downarrow$-$\text{FC}_6\text{H}_4\text{OH}$</td>
<td>10.59</td>
</tr>
<tr>
<td>$\uparrow$-$\text{FC}_6\text{H}_4\text{OH}$</td>
<td>9.82</td>
</tr>
<tr>
<td>$\text{C}_6\text{H}_5\text{OH}$</td>
<td>10.49</td>
</tr>
</tbody>
</table>
It can be seen that the pK value of p-fluorophenol is slightly higher than that of phenol.

Esters can be formed during the reaction in a number of ways and these are exemplified below with 1,2,4,5-tetrafluorobenzene as solvent:

(1) By recombination of pentafluorophenyl and pentafluorobenzoyloxy-radicals to give pentafluorophenyl pentafluorobenzoate.

\[ C_6F_5^* + C_6F_5CO.O^* \rightarrow C_6F_5CO.OC_6F_5 \]  
(42)

This ester would yield pentafluorophenol and pentafluorobenzoic acid upon hydrolysis.

(2) By attack of a pentafluorobenzoyloxy-radical at a hydrogen bearing carbon atom in a solvent molecule.

\[ C_6F_5CO.O^* + H\begin{array}{c}
\end{array}F \begin{array}{c}
\end{array}F \begin{array}{c}
\end{array}F \begin{array}{c}
\end{array}F \begin{array}{c}
\end{array}F \begin{array}{c}
\end{array}F \begin{array}{c}
\end{array}F \begin{array}{c}
\end{array}F \begin{array}{c}
\end{array} \rightarrow \begin{array}{c}
\end{array}F \begin{array}{c}
\end{array}F \begin{array}{c}
\end{array}F \begin{array}{c}
\end{array}F \begin{array}{c}
\end{array}F \begin{array}{c}
\end{array}F \begin{array}{c}
\end{array}F \begin{array}{c}
\end{array}F \begin{array}{c}
\end{array}F \begin{array}{c}
\end{array}O\begin{array}{c}
\end{array}H \begin{array}{c}
\end{array}.C.ArF \]  
(43)

Upon hydrolysis, this would yield 2,3,5,6-tetrafluorophenol and pentafluorobenzoic acid.

(3) By attack of a pentafluorobenzoyloxy-radical at a
fluorine-bearing carbon atom in a solvent molecule (Equation 45a), yielding an ester which upon hydrolysis would give 2,4,5-trifluorophenol (Equation 45b)

\[
\begin{align*}
\text{C}_6\text{F}_5\text{CO.O}^+ + & \quad \begin{array}{c}
\text{F} \\
\text{F} & \text{H} & \text{H} \\
\text{F} & \text{F} & \text{F}
\end{array} & \xrightarrow{(a)} & \begin{array}{c}
\text{F} \\
\text{H} & \text{F} & \text{F} \\
\text{H} & \text{F} \\
\end{array} \\
\text{C}_6\text{F}_5\text{OH} & \xrightarrow{(b)} & \begin{array}{c}
\text{F} \\
\text{F} & \text{H} \\
\text{H} & \text{F} & \text{OH} \\
\end{array}
\end{align*}
\]

It was thought that by analogy with phenol and \( p \)-fluorophenol, 2,3,5,6-tetrafluorophenol might have a lower \( pK \) value than pentafluorophenol. However, measurement of the \( pK \) value (Section 2.4) of the three phenols mentioned above, showed that their \( pK \)'s were as follows

**TABLE 8**

*Acidities of polyfluorophenols*

<table>
<thead>
<tr>
<th>Phenol</th>
<th>( pK(10% \text{ methanolic solution}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4,5-trifluorophenol</td>
<td>7.7</td>
</tr>
<tr>
<td>( p^-\text{HC}_6\text{F}_4\text{OH} )</td>
<td>5.7</td>
</tr>
<tr>
<td>( \text{C}_6\text{F}_5\text{OH} )</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Hence, no distinction between pentafluorophenol and
2,3,5,6-tetrafluorophenol can be made by pH titration methods. The phenol possessing the pK value ca. 7 could thus be identified as originating from the hydrolysis of an ester resulting from attack by a pentafluorobenzoyloxy-radical on a solvent molecule at a fluorine bearing carbon atom. Whether or not the phenol of lower pK value results from route 1 (Equation 41) or route 2 (Equation 42) could not be determined.

Infra-red spectral studies of acid fractions separated from stage (2) also proved insufficient to identify any components.
3.4 PROPOSED MECHANISM FOR THE THERMAL DISSOCIATION OF PERFLUOROBENZOYL PEROXIDE IN POLYFLUOROAROMATIC SOLVENTS

The nature of the products formed in such reactions (biaryl, ester and acids) suggest that perfluorobenzoyl peroxide decomposes in a manner similar to its decomposition in benzene and the halogenobenzenes: that is, the peroxide undergoes unimolecular decomposition to give two pentafluorobenzoyloxy-radicals which can either attack the solvent or undergo decarboxylation to give pentafluorobenzenyl radicals.

\[ \text{C}_6\text{F}_5\text{CO.O.O.CO.C}_6\text{F}_5 \rightarrow 2\text{C}_6\text{F}_5\text{CO.O}^\cdot \] (46a)

\[ \text{C}_6\text{F}_5\text{CO.O}^\cdot \rightarrow \text{C}_6\text{F}_5^\cdot + \text{CO}_2 \] (46b)

These conclusions are true whether the peroxide decomposes by a spontaneous or an induced mechanism.

The induced mechanism,

\[ \text{C}_6\text{H}_5^\cdot + (\text{C}_6\text{H}_5\text{CO.O})_2 \rightarrow \text{Biaryl} + \text{C}_6\text{H}_5\text{CO.OH} + \text{C}_6\text{H}_5\text{CO.O}^\cdot \]

offers a unique route of aromatisation by loss of hydrogen. Although it is observed in the decomposition of benzoyl peroxide in hexafluorobenzene, it cannot represent (Section 3.2.1) a direct means of aromatisation by loss of fluorine.

3.4.1 Formation of \( \pi \)-complexes

The observed formation of \( \pi \)-complexes between hexa-
fluorobenzene and benzene has been mentioned (Section 1.5.2). The term 'molecular complex' has been given to a variety of types of association product of one or two molecules. The complex is formed between a substance functioning as an electron donor and one functioning as an electron acceptor. Of particular interest is the class of complex known as a \( \pi \)-complex. These are formed between a species in which the electrons available for sharing are contained in a \( \pi \)-molecular orbital (\( \pi \)-donor), and a species known as a \( \pi \)-acceptor, which is often to be found in an olefinic or aromatic system containing highly electronegative substituents. The term 'outer complex' has been used to describe such adducts to indicate that the acceptor does not make deep penetration into the \( \pi \)-orbital.

The second major class of donors are known as '\( n \)-donors' and the electrons available for sharing are lone-pair or non-bonding electrons.

The role of \( \pi \)- and \( \sigma \)-complexes in electrophilic heterolytic substitution reactions has been the subject of much investigation. Wheland discussed a model for the transition state of an electrophilic substitution reaction in which the attacking species \( E^+ \) and the departing proton are simultaneously bonded to a tetrahedrally hybridised ring carbon atom. Diagrammatic formulae such as that shown in XXIII are used to describe \( \sigma \)-complexes.

\[
\text{XXIII}
\]
The presence of π-complexes as intermediates in electrophilic substitution reactions was first suggested by Dewar, although the rate determining formation of a π-complex has not been widely accepted, since the energy barrier for π-complex formation is generally much lower than that for activation in electrophilic substitution processes.

3.4.2 The role of π-complexes in the reaction of the perfluorophenyl radical with polyfluoroaromatic solvents

It has previously been noted that large yields of biaryls are obtained in the reactions of perfluorophenyl radicals with aromatic solvents, and in the reactions of phenyl radicals with polyfluoroaromatic solvents.

It has also been reported, and we have confirmed, that the reaction of perfluorobenzoyl peroxide with highly fluorinated solvents gives only low yields of esters and biaryls: the products consist mainly of tarry residues.

To account for the large yields of phenyl pentafluorobenzoate formed in the reaction of perfluorobenzoyl peroxide with benzene, it has been suggested that the pentafluorobenzoyloxy-radical is stabilised by formation of a π-complex with the solvent. Both pentafluorophenyl radicals and pentafluorobenzoyloxy-radicals would be expected to form a π-complex with aromatic solvents with high hydrogen content. Such a π-complex would be in equilibrium with its components and would also collapse in a σ-complex as follows:
Similarly, a phenyl or a benzoyloxy-radical can form a π-complex with a highly fluorinated aromatic solvent, before formation of the σ-complex. A stable (energetically significant) π-complex will only form between a radical and a solvent of very different electronegativities. When a highly fluorinated phenyl radical is attacking a highly fluorinated solvent, the radical cannot be stabilised by formation of such a π-complex, and the radical is very reactive and therefore relatively unselective with regard to its attack on fluorine- or hydrogen-bearing carbon atoms of the solvent. In contrast to this, when such a π-complex can be formed, the radical can be stabilised and the π-complex would be an oriented one. The radical would therefore be more selective in its position of attack on the substrate.

There is an opposing effect governing the reactivity of a fully fluorinated radical towards an aromatic substrate, namely, that when an aromatic solvent contains few or no substituents, the solvent itself becomes more susceptible to attack by the radical. This increased susceptibility arises because of the greater ease of stretching and/or breaking of the C-H bond in comparison with the C-F bond.

The two effects can be represented as follows (Figure 11)
3.4.3 Chain termination reactions

Kinetic studies\textsuperscript{100} of the thermal decomposition of perfluorobenzoyl peroxide in benzene (at high peroxide concentrations) and in halogenobenzenes (at all concentrations studied) suggested that chain termination occurred by reaction of dissimilar radical species, i.e. by chain termination steps of the following type,

$$\ce{C_6F_5CO.0'} + \ce{C_6F_5CO.0'} \rightarrow \text{Biaryl} + \ce{C_6F_5CO.OH} \quad (48)$$

It is possible that similar chain terminations are prevalent in the thermal decomposition of perfluorobenzoyl peroxide in polyfluorobenzenes at high concentrations. For example
Chain termination between two different $\sigma$-complexes can also occur, for example,

$$
\begin{align*}
\text{Ar}^\text{CO.O} & \quad \text{F} \\
\text{H} & \quad \text{Ar}^\text{F} \\
\text{F} & \quad \text{H,F} \\
\end{align*}
\quad + \quad 
\begin{align*}
\text{C}_6\text{F}_5\text{CO.O}' & \\
\text{H,F} & \\
\end{align*}
\rightarrow
\begin{align*}
\text{Ar}^\text{F} & \\
\text{H,F} & \\
\end{align*}
\quad + \quad 
\begin{align*}
\text{C}_6\text{F}_5\text{CO.OH} & \\
\end{align*}
\quad \text{(49)}

Dimerisation and disproportionation reactions between radicals may also contribute to a lesser extent.

**Dimerisation**

$$
\begin{align*}
\text{Ar}^\text{F}^\text{CO.O} & \quad \text{F} \\
\text{H} & \quad \text{Ar}^\text{F} \\
\text{F} & \quad \text{H,F} \\
\end{align*}
\quad + \quad 
\begin{align*}
\text{Ar}^\text{F}^\text{CO.O} & \quad \text{F} \\
\text{H} & \quad \text{Ar}^\text{F} \\
\text{F} & \quad \text{H,F} \\
\end{align*}
\rightarrow
\begin{align*}
\text{HF} & \\
\text{Ar}^\text{F}^\text{CO.OAr}^\text{F}' & \\
\text{Ar}^\text{F} & \\
\end{align*}
\quad \text{(50)}

**Disproportionation**

$$
\begin{align*}
2 \quad \text{Ar}^\text{F} & \quad \text{H} \\
\text{F} & \quad \text{F} \\
\end{align*}
\rightarrow
\begin{align*}
\text{Ar}^\text{F} & \quad \text{Ar}^\text{F}' & \\
\text{F} & \quad \text{H} \\
\end{align*}
\quad + \quad 
\begin{align*}
\text{Ar}^\text{F} & \quad \text{H} \\
\text{F} & \quad \text{F} \\
\end{align*}
\quad \text{(52)}$$
However, the kinetics of decomposition of benzoyl peroxide in hexafluorobenzene shows 1.5 order kinetics, suggesting termination between like radicals. Since no detailed kinetic studies have been made of the thermolysis of perfluorobenzoyl peroxide in highly fluorinated aromatic solvents, there is no compelling evidence in favour of either mode of termination and hence for any particular termination product.
Equation 53 - continued over
Equation 53 continued

\[ \text{ArF} + \text{CO}_2 \rightarrow \text{ArF} - \text{Solvent} \rightarrow \text{ArF} - \text{π-complex} \]

\[ \text{Dimer} \rightarrow \text{Dimer and Disproportionation} \]

\[ \text{ArF} \text{COO} \cdot \]

\[ \text{G}_H, \text{XXI} \]

\[ \text{ΔG}^\circ, \text{XX} \]
3.4.4 Proposed reaction scheme for the thermal decomposition of perfluorobenzoyl peroxide in polyfluoroaromatic solvents

The proposed reaction scheme is illustrated in Equation 53. This mechanism is similar to that suggested for the thermal decomposition of benzoyl peroxide in benzene\textsuperscript{45} and is a modification of other proposed mechanisms for the decomposition of a fluorinated peroxide or peroxides in aromatic solvents (3.1).

Perfluorobenzoyl peroxide undergoes a decomposition to give two perfluorobenzoyloxy-radicals. If these radicals are unstabilised, then decarboxylation to give perfluorophenyl radicals will take place (Equation 53e). Dimerisation of perfluorophenyl radicals to give decafluorobiphenyl, or combination of a pentafluorophenyl radical with a pentafluorobenzoyloxy-radical to give pentafluorophenyl pentafluorobenzoate, may also take place (Equation 53a). That the latter combination does in fact take place seems possible as pentafluorophenyl pentafluorobenzoate has been isolated\textsuperscript{111} from the decomposition of perfluorobenzoyl peroxide in benzene.

Perfluorobenzoyloxy-radicals may then be stabilised by formation of a π-complex with a solvent molecule (Equation 53b). Such a π-complex would be in equilibrium with its components and could collapse into a σ-complex (Equation 53c).

Attack on the aromatic ring can take place either at a hydrogen bearing carbon atom to give $\sigma^*_{H}(XXV)$ or at a fluorine bearing carbon atom to give $\sigma^*_{F}(XXIV)$. If attack on the ring
takes place to give $\sigma_{H}^*$ (Equation 53c), then the $\sigma_{H}$ complex can be dehydrogenated by reaction with another benzoyloxy-radical (Equation 53c) to give an aromatic ester and pentafluorobenzoic acid. The $\sigma_{H}^*$ complex can also undergo dimerisation and disproportionation reactions (Equation 53 cii).

If attack on the aromatic ring takes place at a fluorine bearing carbon atom (Equation 53d) then defluorination (Equation 53dii) of the $\sigma_{F}^-\text{complex}$ can take place by elimination of hydrogen fluoride between this $\sigma_{F}^-\text{complex}$ and another hydrogen substituted $\sigma_{H}^-$ complex, to give an ester and either a hydrogen substituted ester or a biaryl (see below).

This complex can also undergo dimerisation and disproportionation reactions (Equation 53e).

As mentioned above, the pentafluorobenzoyloxy-radical can undergo decarboxylation to give a pentafluorophenyl radical (Equation 53e) which can itself react in a manner analogous to the pentafluorobenzoyloxy-radical. It can be stabilised by the formation of a $\pi$-complex with solvent molecule, and this $\pi$-complex which is in equilibrium with its components, can collapse into a $\sigma$-complex. As with a pentafluorobenzoyloxy-radical, attack on the ring can take place either at a hydrogen bearing carbon atom to give a $\sigma_{H}^*$-complex (XXI), or at a fluorine carrying position, to give a $\sigma_{F}^-$-complex (XX). If a $\sigma^-$-complex is formed (Equation 53g) then oxidation of the $\sigma_{H}^*$-complex can take place either by reaction with a pentafluorobenzoyloxy-radical to give a molecule of biaryl and a molecule of pentafluorobenzoic acid (Equation 53gi).
or by reaction with a $\sigma^-_F$ or $\sigma^-_P$-complex with elimination of hydrogen fluoride between the two complexes (Equation 53hi), or the $\sigma^-_H$-complex can undergo dimerisation and disproportionation reactions, (Equation 53gii).

If attack on a fluorine bearing carbon atom takes place to give a $\sigma^-_F$-complex, then the complex can react further either by elimination of hydrogen fluoride with another $\sigma^-_H$ or $\sigma^-_H$-complex (Equation 53hi) or dimerisation and disproportionation reactions can take place (Equation 53hii).

Whether any of these processes are predominant in a particular reaction is dependent on several factors. The extent to which the pentafluorobenzoyloxy-radical takes part in the reaction depends upon its stabilisation by the solvent, decarboxylation (to give perfluorophenyl radical) taking place when the degree of stabilisation is small. The nature of the chain termination process depends upon the original peroxide concentration and the stabilities of the different $\sigma$-complexes.
3.5 AGREEMENT OF PREVIOUS RESULTS WITH THE PROPOSED MECHANISM

In the following sections, the results of previous workers will be discussed in relation to the mechanism proposed in Section 3.4.

3.5.1 Reaction of benzoyl peroxide with fluorinated solvents

In the thermal decomposition of benzoyl peroxide in fluorinated aromatic solvents, previous workers have not proved the presence of phenol esters in the reaction products. Detection by g.l.c. of biaryl products had been carried out using a column temperature of $150^\circ$, when no evidence for the presence of esters was found. The same workers showed that esters (in the products resulting from the thermal decomposition of perfluorobenzoyl peroxide in chlorobenzene) could be resolved, using the same instrument, with column temperatures of $180^\circ$. We have also found that higher column temperatures, $30^\circ$ above that for sharp resolution of biaryls, are necessary for the resolution of ester peaks. Hence non resolution of esters at lower column temperatures does not prove that they are not present.

As the phenyl (and benzoyloxy-) radicals and the fluorinated solvent have widely differing electronegativities, the radicals should be stabilised by the formation of a $\pi$-complex with the solvent, before attack on the ring occurs to give a $\sigma$-complex. If esters are not formed in these reactions, then either the formation of a $\pi$-complex between a benzoyloxy-
radical and the solvent is not energetically significant, or the $\sigma$-complexes formed by the attack of a benzoyloxy-radical on the solvent are removed by dimerisation reactions. In these reactions about 1-2% of biphenyl resulting from recombination of radicals (Equation 55(i)) was found for each solvent investigated.

(i) Hexafluorobenzene$^{98,99,199,128}$

The yields of biaryl found in this reaction varied from (a) 0.92 mole/mole peroxide$^{100}$ to 1.43 mole/mole peroxide$^{98}$ when the products were obtained by distillation to (b) 0.68 mole/mole peroxide$^{100}$ when the products were analysed by g.l.c.

A little benzoic acid was found but the yields were not quoted.

Preliminary kinetic investigations$^{100}$ gave an equation of the form of (11), indicating chain termination between similar radicals (Section 1.2.5).

$$-d[p]/dt = k_1[p] + k_{1.5}[p]^{1.5}$$

(11)

This gives evidence for the formation of pentafluorobiphenyl by disproportionation of the $\sigma$-complexes.

The following scheme (Equation 54) agrees with the proposed mechanism (Section 3.4, Equation 53). (Routes are numbered as in the proposed scheme.)
Other fates of the $\sigma$-complex, such as rearrangement, may occur

Aromatisation of the $\sigma$-complex may also involve benzoic acid as a catalyst, without any disparity with the proposed mechanism:
Rearrangement product + BzO₂ → 2-FC₆H₄C₆F₅ + BzOH + BzO⁻

σ_F' + BzOH → Ph.C₆F₅ + HF + ¹⁰O.C₆F₅

Equation 56

(ii) Pentafluorobenzene

The products reported were biphenyl (0.02 mole/mole peroxide), 2,3,4,5,6-pentafluorobiphenyl (0.04 mole/mole peroxide), 2,3,4,5-tetrafluorobiphenyl (0.22 mole/mole peroxide), 2,3,4,6-tetrafluorobiphenyl (0.06 mole/mole peroxide).

The following scheme (Equation 57) is in agreement with the proposed mechanism (Section 3.3, Equation 53).

Equation 57
Defluorination of the $\delta^-_{F}$-complex can take place either by elimination of hydrogen fluoride with a $\delta^-_{H}$- or $\delta^-_{F}$-complex (hi) or by dimerisation and disproportionation reactions (gii).

There is also the possibility that rearrangement of the $\delta^-_{F}$-complex can occur, as with hexafluorobenzene. The rearrangement product has not however, been identified for this solvent.

$$\delta^-_{F} \rightarrow \begin{array}{c}
\text{XXI} \\
 \begin{array}{c}
\text{H} \\
 \text{F} \\
 \text{C}_6\text{F}_{4}\text{H}
\end{array}
\end{array}$$

$$\text{XXI} + (\text{C}_6\text{H}_5\text{CO.O})_2 \rightarrow (56b)$$

$$\begin{array}{c}
\text{2-F.C}_6\text{H}_4\cdot\text{C}_6\text{F}_{4}\text{H} + \text{C}_6\text{H}_5\text{CO.OH} + \text{C}_6\text{H}_5\text{CO.O}^* \\
\end{array}$$

A $\delta^-_{H}$-complex can be oxidised by removal of a hydrogen atom either by a benzoyloxy-radical to give benzoic acid (gi) or by elimination of hydrogen fluoride with a $\delta^-_{F}$-complex (hi).

Hydrogen fluoride formed in the reaction was not measured and it is therefore uncertain which of these reactions predominates. Dimerisation reactions account for the large proportion of high boiling products.

(iii) $1,2,4,5$-Tetrafluorobenzene

The products reported for this reaction were biphenyl (0.02 mole/mole peroxide), $2,3,5,6$-tetrafluorobiphenyl (0.46 mole/mole peroxide) and $2,4,5$-trifluorobiphenyl (0.06 mole/mole peroxide). The reaction scheme for pentafluorobenzene as solvent is also applicable here. However, attack
by the phenyl radical at a hydrogen bearing carbon atom of the substrate molecule now predominates. No yields of benzoic acid were quoted and the formation of hydrogen fluoride during the reaction was not investigated. It is therefore uncertain if the removal of hydrogen atom from the $\gamma^+_H$ complex (viia) by a benzoyloxy-radical accounts for most of the hydrogen substituted biaryl formed, or if some is removed by elimination of hydrogen fluoride by reaction with a $\gamma^+_F$-complex (viiia) or if some hydrogen-substituted biaryl is formed by disproportionation reactions. Again dimerisation reactions can account for the high boiling products.

(iv) Chloro- and bromo- pentafluorobenzene

For both of these solvents, yields of benzoic acid (ca. 20%) and of the isomeric chloro- or bromo-tetrafluorobiphenyls were reported. As with hexafluorobenzene, the disproportionation of two $\gamma^+_F$-complexes is one possible route for the formation of biaryls. However, approximately 20 mole % of benzoic acid is formed and the abstraction of fluorine atoms from a $\gamma^+_F$-complex by benzoyloxy-radicals to give benzoyl hypofluorite and subsequently benzoic acid during working-up seems unlikely. (Section 3.2).

We now suggest that intramolecular rearrangement of the $\gamma^+_F$-complex can occur as follows (Equation 58)
A similar rearrangement has been described previously for the reaction of benzoyl peroxide with hexafluorobenzene (Section 3.5.1) and with pentafluorobenzene.

3.5.2 The thermal decomposition of perfluorobenzoyl peroxide in benzene and monosubstituted benzenes

Pentafluorophenyl and pentafluorobenzoyloxy-radicals have sufficiently different electronegativities to that of the solvent, for benzene and monosubstituted benzenes, to allow stabilisation of the radicals by formation of π-complexes with the solvent. The formation of esters resulting from attack by a pentafluorobenzoyloxy-radical on the solvent indicates that the formation of π-complexes between radical and solvent is energetically significant for pentafluorobenzoyloxy-radicals and aromatic solvents.

The formation of pentafluorophenyl pentafluorobenzoate (0.04 mole/mole peroxide) indicates the occurrence of recombination of radicals as in route (a), (Equation 53)
Yields of biaryl (0.61 mole/mole peroxide), phenyl pentafluorobenzoate (0.13 mole/mole peroxide), pentafluorobenzoic acid (0.75 mole/mole peroxide) and pentafluorophenyl pentafluorobenzoate (0.04 mole/mole peroxide) have been reported. Investigation of the kinetics showed that the kinetic equation was of the form of equation (11) for peroxide concentrations up to 0.028 M, indicating that chain termination was probably by dimerisation and or disproportionation (Equation 53, gi or cii) of G-complexes at low concentrations.

\[-d[P]/dt = k_1[P] + k_{1.5}[P]^{1.5}\]  \hspace{1cm} (11)

The yield of pentafluorobenzoic acid, formed by the oxidation of G-complexes [routes (ci) and (gi), Equation 53] is equal to the sum of the ester and biaryl yields, indicating that the biaryl and ester are formed only by this route and not by the disproportionation reactions at low concentrations. Hence chain termination is probably by combination of G-complexes.

At higher concentrations (0.028 M), the kinetic equation is of the form of Equation 12, indicating that chain termination takes place by routes (bi) and (gi) [Equation 53].

\[-d[P]/dt = k_1[P] + k_1'[P]\]  \hspace{1cm} (12)

The reaction can be represented as in Equation (59). (Routes are numbered as in Equation 53).
\[ \text{Equation 59} \]

\[ \text{(gii)} \quad (\text{ArF} \text{COO})_2 \]

\[ \text{C}_6\text{F}_5\text{C}_6\text{H}_5 + \text{ArFCOOH} + \text{ArFCOO}^* \]
(11) Chlorobenzene, fluorobenzene and bromobenzene

For chlorobenzene as solvent, yields of pentafluorobenzoic acid (1.10 moles per mole peroxide) and phenyl pentafluorobenzoate (1.6 moles per mole peroxide) were claimed. For all solvents, some traces of isomeric halogenophenyl pentafluorobenzoates and isomeric halogenopentafluorobiphenyls were also reported. The main products were formed by attack of a pentafluorobenzoyloxy-radical upon a halogen bearing position in the substrate. The kinetic equations were found to be of the form of Equation (11), indicating chain termination between similar radicals (Section 1.2.5).

\[-d[P]/dt = k_1[P] + k_{1.5}[P]^{1.5} \]  (11)

To account for the formation of similar esters in the reaction of benzoyl peroxide with bromobenzene, it was postulated (Section 1.2.7) that the benzoyloxy-radical could be stabilised by the formation of an n-type charge transfer complex (X) as in Equation (60).

\[
C_6H_5CO.O^* : X \rightleftharpoons C_6H_5CO.0^* : X
\]

\[
C_6H_5CO.0^* : X = C_6H_5CO.0^* : X^+ + X
\]

\[
C_6H_5CO.O^* : X
\]

Equation 60
and it has been postulated that the formation of such a complex is responsible for the predominating attack at a halogen bearing position in the substrate. \(^{101,103}\)

However, for the formation of a \(\sigma\)-complex, we suggest that it is also possible for an oriented \(\pi\)-complex to be formed, leading to collapse into a \(\sigma\)-complex as in Equation (61) (Section 3.4.2).

\[
\begin{align*}
\text{C}_6\text{F}_5\text{CO}.O^+ & \quad \xrightarrow{\text{C}_6\text{H}_5X} \quad \text{C}_6\text{H}_5X & \quad \xrightarrow{\text{O}^+} \quad \text{C}_6\text{F}_5\text{CO}.O^+ \\
\pi\text{-complex XIX} & \quad \xrightarrow{\sigma\text{-complex XVIII}} & \quad \sigma\text{-complex XVIII}
\end{align*}
\]

**Equation 61**

Similar interactions may occur in the decomposition of pentafluorobenzoyl peroxide in polyfluorinated benzenes \((X=\text{F})\), giving pentafluorobenzoic acid esters of polyfluorophenols. The extent of formation of such species will depend upon the relative stabilities of the complexes involved; it may well be that the pentafluorobenzoyloxy-radical is not nearly as well stabilised in polyfluorinated benzenes as in fluorobenzene, and so the yields of the products derived from \(\sigma\)-complexes analogous to \((\text{XVIII})\) may be low.
3.6 AGREEMENT BETWEEN PROPOSED MECHANISM AND EXPERIMENTAL RESULTS

3.6.1 Hexafluorobenzene\textsuperscript{104,109,110}

Table 9 shows the yields of identified products from the thermolysis of pentafluorobenzoyl peroxide in hexafluorobenzene.

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decafluorobiphenyl\textsuperscript{109}</td>
<td>0.04 mole/mole peroxide</td>
</tr>
<tr>
<td>Pentafluorophenyl pentafluorobenzoate\textsuperscript{109}</td>
<td>0.07 mole/mole peroxide</td>
</tr>
<tr>
<td>4,4'-Bis(pentafluorobenzoyloxy)-1,1',4,4'-tetrahydrododecafluorobiphenyl\textsuperscript{110}</td>
<td>1.0 mole/mole peroxide</td>
</tr>
</tbody>
</table>

The radicals first formed by the thermolysis of pentafluorobenzoyl peroxide in this solvent are not appreciably stabilised by complex formation, and are therefore very reactive. Also, the $\sigma$-complexes which result from pentafluorophenylation of hexafluorobenzene do not have the ready route to defluorination that is available in the phenylation of hexafluorobenzene, where benzoic acid is formed during side-reactions and permits the removal of fluorine as hydrogen fluoride. Hence it seems that the identified products result from collapse of radical pairs within a solvent cage, and that $\sigma$-complexes which are formed from solvent attack account for the very large amounts of high boiling
products.

3.6.2 Pentafluorobenzene

The yields of identified products (mole/mole peroxide decomposed) from the thermolysis of pentafluorobenzoyl peroxide in pentafluorobenzene are shown in Table 10.

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield (mole/mole peroxide)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentafluorobenzoic acid</td>
<td>0.08</td>
</tr>
<tr>
<td>Hydrogen fluoride</td>
<td>0.09</td>
</tr>
<tr>
<td>Pentafluorobenzoate esters (as acid)</td>
<td>0.21</td>
</tr>
<tr>
<td>Pentafluorophenyl pentafluorobenzoate</td>
<td>0.12(*)</td>
</tr>
<tr>
<td>Saponifiable fluorine (as fluoride)</td>
<td>0.60</td>
</tr>
<tr>
<td>Decafluorobiphenyl</td>
<td>0.14(*)</td>
</tr>
<tr>
<td>Nonafluorobiphenyl (isomeric mixture)</td>
<td>0.06(*)</td>
</tr>
</tbody>
</table>

(*) Identified by gas chromatography

The radicals first formed in the thermolysis of pentafluorobenzoyl peroxide, as in hexafluorobenzene, are not appreciably stabilised through $\pi$-complex formation. Here, however, attack can take place at hydrogen-bearing positions, giving $\sigma_H^\cdot$ or $\sigma_H^\prime\cdot$ and allowing a route for the defluorination of some $\sigma_F^\cdot$ or $\sigma_F^\prime\cdot$ complexes. The precursors to the isomeric nonafluorobiphenyls ($\sigma_F^\prime\cdot$, 0.06 mole/mole peroxide, route $\text{hi}$) and to decafluorobiphenyl ($\sigma_H^\cdot$, 0.14 mole/mole peroxide, route $\text{g}$) result from the collapse of a $\pi$-complex; decafluorobiphenyl may also arise from the collapse of an initially
formed pair of radicals within a solvent cage, in the same way as is envisaged in hexafluorobenzene.

Oxidation of $\sigma_H^\cdot$ by $\sigma_F^\cdot$ allows the concomitant formation of nonafluorobiphenyl (0.06 mole/mole peroxide).

$$\sigma_H^\cdot + \sigma_F^\cdot \rightarrow C_{12}F_{10} + C_{12}F_9H + HF$$

(53, route hi)

Oxidation of $\sigma_H^\cdot$ by a pentafluorobenzoyloxy-radical (route gi) allows the formation of free pentafluorobenzoic acid (0.08 mole/mole peroxide) and of decafluorobiphenyl and so accounts for some $\sigma_H^\cdot$ (0.08 mole/mole peroxide).

$$\sigma_H^\cdot + C_6F_5CO.O' \rightarrow C_{12}F_{10} + C_6F_5CO.OH$$

(53, route gi)

Free hydrogen fluoride can arise partly through route (hi) described above, which accounts for most (0.06 mole/mole peroxide) of this product. It can also arise by aromatization of $\sigma_F^\cdot$ and $\sigma_H^\cdot$ to give tetrafluorophenyl esters (0.03 mole/mole peroxide) and pentafluorophenyl pentafluorobenzoate (0.03 mole/mole peroxide), (route di).

$$\sigma_F^\cdot + \sigma_H^\cdot \rightarrow C_6F_5CO.OCC_6F_5 + C_6F_5CO.OCC_6F_4H + HF$$

(53, route di)

Pentafluorophenyl pentafluorobenzoate can also arise by collapse of the radicals formed initially (route a).

$$C_6F_5CO.O' + C_6F_5^\cdot \rightarrow C_6F_5CO.OCC_6F_5$$

(53 route a).
The analytical technique used in this work identified pentafluorobenzoic acid (0.21 mole/mole peroxide) from the hydrolysis of esters. Pentafluorophenyl pentafluorobenzoate identified by g.l.c. techniques accounts for 0.12 mole/mole peroxide. It is suggested above that tetrafluorophenyl esters are also formed (0.03 mole/mole peroxide) although the technique used could not distinguish between these and pentafluorophenyl esters. The remaining acid (0.06 mole/mole peroxide) could result from the hydrolysis of dimerisation species such as

\[
\text{Ar}_F^+\text{CO}_2\text{OH}
\]

\[
\begin{array}{c}
\text{F} \\
\text{H} \\
\text{F} \\
\text{H} \\
\text{F} \\
\text{F} \\
\text{F} \\
\end{array}
\]

\[
\text{O} \cdot \text{CO} \cdot \text{Ar}_F^+
\]

XVIII

This would also yield fluoride ion upon hydrolysis (0.06 mole/mole peroxide). Hydrolysis of the following dimerisation species will also yield fluoride ion.

\[
\text{Ar}_F^+\text{CO}_2\text{OH}
\]

\[
\begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{H} \\
\end{array}
\]

\[
\text{Ar}_F^+
\]

3.6.3 1,2,4,5-tetrafluorobenzene

Table 11 shows the yields of products identified from the thermolysis of perfluorobenzoyl peroxide in
1,2,4,5-tetrafluorobenzene.

TABLE 11

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mole/mole Peroxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free pentafluorobenzoic acid</td>
<td>0.08</td>
</tr>
<tr>
<td>Free hydrogen fluoride</td>
<td>0.16</td>
</tr>
<tr>
<td>Pentafluorobenzoate esters (as acid)</td>
<td>0.21</td>
</tr>
<tr>
<td>Phenol with pK &gt; 8</td>
<td>0.05</td>
</tr>
<tr>
<td>2,3,5,6-tetrafluorophenol</td>
<td>0.21</td>
</tr>
<tr>
<td>2,3,4,5,6-pentafluorophenol</td>
<td></td>
</tr>
<tr>
<td>Saponifiable fluorine</td>
<td>0.41</td>
</tr>
<tr>
<td>4-H-nonafluorobiphenyl</td>
<td>0.11</td>
</tr>
<tr>
<td>2,2',3,4',5',5',6-octafluorobiphenyl</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Again the radicals first formed in the thermolysis of perfluorobenzoyl peroxide are not appreciably stabilised through π-complex formation with 1,2,4,5-tetrafluorobenzene. As with pentafluorobenzene, \(\sigma_F\)- or \(\sigma_F'\)- complexes may be formed, providing a route for the defluorination of \(\sigma_F'\) complexes. The precursors to 2,2',3,4',5,5',6-octafluorobiphenyl (\(\sigma_F'\), 0.01 mole/mole peroxide, route h) and 4-H-nonafluorobiphenyl (\(\sigma_H'\), 0.11 mole/mole peroxide, route c) arise from collapse of a π-complex.
4-H-Nonafluorobiphenyl can be obtained by oxidation of \( \mathrm{SF}_2 \) by either (i) \( \mathrm{SF}_2 \) (Equation 53 route hi): (ii) pentafluorobenzoyloxy-radicals (Equation 53, route gi): or (iii) \( \mathrm{SF}_2 \) (Equation 53, route di).

(i) Octafluorobiphenyl (0.01 mole/mole peroxide) and free hydrogen fluoride are also formed by this route.

\[
\mathrm{SF}_2 + \mathrm{SF}_2 \rightarrow \text{C}_6\text{F}_5\text{C}_6\text{F}_4\text{H} + \text{C}_6\text{F}_5\text{C}_6\text{F}_3\text{H}_2 \quad (53, \text{route hi})
\]

(ii) Pentafluorobenzoic acid (0.08 mole/mole peroxide) and nonafluorobiphenyl are formed by this route.

\[
\mathrm{SF}_2 + \text{C}_6\text{F}_5\text{CO.O} \rightarrow \text{C}_6\text{F}_5\text{C}_6\text{F}_4\text{H} + \text{C}_6\text{F}_5\text{CO.OH} \quad (53, \text{route gi})
\]

(iii) Methods (i) and (ii) above account for the formation of most (0.09 mole/mole peroxide) of the nonafluorobiphenyl identified. The remainder (0.02 mole/mole peroxide) can be accounted for by oxidation of \( \mathrm{SF}_2 \) by a \( \mathrm{SF}_2 \)-complex, giving also an ester and free hydrogen fluoride. The identification of a phenol with \( \text{pK}_a > 8 \) gave evidence for the formation of such an ester.

\[
\mathrm{SF}_2 + \mathrm{SF}_2 \rightarrow \text{C}_6\text{F}_5\text{C}_6\text{F}_4\text{H} + \text{C}_6\text{F}_5\text{CO.OC}_6\text{F}_3\text{H}_2 + \text{HF} \quad (53, \text{route di})
\]

Pentafluorobenzoic acid (0.21 mole/mole peroxide) and phenols (\( \text{pK}_a 6, 0.23 \) mole/mole peroxide) were identified as products of hydrolysis of esters. As with hexafluorobenzene
and pentafluorobenzene, a possible means of formation of some such esters is by collapse of the radicals formed initially (route a) to give pentafluorophenyl pentafluorobenzoate.

\[ C_{6}F_{5}CO.O^{*} + C_{6}F_{5}^{*} \rightarrow C_{6}F_{5}CO.OC_{6}F_{5} \]  (53 route a)

As the analytical technique used did not identify between pentafluorophenyl esters and the tetrafluorophenyl esters resulting from \( 6_{H} \)-complexes, it is suggested by analogy with pentafluorobenzene, that pentafluorophenol (0.09 mole/mole peroxide) is formed by collapse of radicals in route (a).

Dimerisation reactions may give rise to hydrolysable species such as (XXIX)

\[
\begin{align*}
\text{ArF}CO.O^* & \quad \text{F} \quad \text{F} \\
\text{H} & \quad \text{H} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{H} \\
\text{F} & \quad \text{O.CO.Arf} \\
\end{align*}
\]

XXIX

Hydrolysis of such a species (0.05 mole/mole peroxide) would provide the pentafluorobenzoic acid from esters (0.10 mole/mole peroxide) so far unaccounted for. The hydrogen fluoride concomitantly formed (0.10 mole/mole peroxide) is also found. This acid is also formed in the hydrolysis of quaterphenyls of the type XXX arising from dimerisation reactions.
### 3.6.4 1,2,5-trifluorobenzene

The yields of products identified from the thermolysis of perfluorobenzoyl peroxide in 1,3,5-trifluorobenzene are shown in Table 12 (moles/mole peroxide).

<table>
<thead>
<tr>
<th>Product</th>
<th>Moles/mole peroxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free pentafluorobenzoic acid</td>
<td>0.86</td>
</tr>
<tr>
<td>Free hydrogen fluoride</td>
<td>0.07</td>
</tr>
<tr>
<td>Pentafluorobenzoate esters (as acid)</td>
<td>0.19</td>
</tr>
<tr>
<td>Phenol as esters</td>
<td>0.19</td>
</tr>
<tr>
<td>Saponifiable fluorine</td>
<td>0.08</td>
</tr>
<tr>
<td>2,2',3,4,4',5,6,6'-octafluorobiphenyl</td>
<td>0.58</td>
</tr>
</tbody>
</table>

The possibility of some stabilisation of the radicals resulting from the thermolysis of perfluorobenzoyl peroxide is offset by the increasing susceptibility of the solvent to attack. The predominance of the former effect is shown by the identification only of products resulting from attack at a hydrogen bearing carbon atom.

The precursor to octafluorobiphenyl ($\sigma_{H}^{i}$) may result from the collapse of an oriented π-complex (53 route g). As substitution takes place predominantly at hydrogen carrying carbon atoms, the oxidation of $\sigma_{H}^{i}$ complexes will be by pentafluorobenzoyloxy-radicals, rather than by elimination of hydrogen fluoride with a $\sigma_{P}^{*}$ or $\sigma_{P}^{i}$ species. Oxidation by pentafluorobenzoyloxy-radicals (53 route gi) yields 2,2',3,4,4',5,6,6'-octafluorobiphenyl (0.58 mole/mole peroxide)
and pentafluorobenzoic acid (0.58 mole/mole peroxide)

\[
\mathbf{6}_{\text{H}}^* + \text{C}_6\text{F}_5\text{CO.}^* \rightarrow \text{C}_6\text{F}_5\text{C}_6\text{F}_3\text{H}_2 + \text{C}_6\text{F}_5\text{CO.}^\text{OH}
\]  
(53 route gi)

Similarly, oxidation of a \( \mathbf{6}_{\text{H}}^* \) complex to give an ester (0.19 mole/mole peroxide) and pentafluorobenzoic acid (0.19 mole/mole peroxide) would account for most of the remainder of the free acid identified.

\[
\mathbf{6}_{\text{H}}^* + \text{C}_6\text{F}_5\text{CO.}^* \rightarrow \text{C}_6\text{F}_5\text{CO.}^\text{OH} + \text{C}_6\text{F}_5\text{CO.}^\text{OC}_6\text{F}_3\text{H}_2
\]  
(53 route ci)

3.6.5 1,4-Difluorobenzene

Table 13 shows the yields (moles/mole peroxide) of products identified from the thermolysis of perfluorobenzoyl peroxide in 1,4-difluorobenzene.

<table>
<thead>
<tr>
<th>TABLE 13</th>
<th>Moles/mole peroxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free pentafluorobenzoic acid</td>
<td>0.10</td>
</tr>
<tr>
<td>Free hydrogen fluoride</td>
<td>0.07</td>
</tr>
<tr>
<td>Pentafluorobenzoate esters</td>
<td>0.62</td>
</tr>
<tr>
<td>Phenol (1)</td>
<td>0.05</td>
</tr>
<tr>
<td>Phenol (2)</td>
<td>0.42</td>
</tr>
<tr>
<td>Saponifiable fluorine</td>
<td>0.53</td>
</tr>
<tr>
<td>2,2',3,4,5,5',6-Heptafluorobiphenyl</td>
<td>0.34</td>
</tr>
</tbody>
</table>
With this solvent, although the attacking radicals are very much more stabilised than in the earlier cases considered so far, the solvent itself is very much more susceptible to attack.

The yield of free pentafluorobenzoic acid (0.10 mole/mole peroxide) suggests that this amount of $\mathcal{G}_H^i$ reacts with pentafluorobenzoyloxy-radicals to give heptafluorobiphenyl (0.10 mole/mole peroxide)

$$
\text{C}_6\text{F}_5\text{CO.}O^* + \mathcal{G}_H^i \rightarrow \text{C}_6\text{F}_5\text{CO.OH} + \text{C}_6\text{F}_5\text{C}_6\text{F}_2\text{H}_3
$$

(53, Route gi)

The remainder of the biaryl (0.24 mole/mole peroxide) is apparently formed by other routes.

Elimination of hydrogen fluoride (0.05 mole/mole peroxide) between a $\mathcal{G}_F^i$ and a $\mathcal{G}_H^i$ complex accounts for the yield of the ester $\text{C}_6\text{F}_5\text{CO.OC}_6\text{H}_4\text{F}$ and of some biaryl.

$$
\mathcal{G}_H^i + \mathcal{G}_F^i \rightarrow \text{C}_6\text{F}_5\text{C}_6\text{F}_2\text{H}_3 + \text{C}_6\text{F}_5\text{CO.CC}_6\text{H}_4\text{F} + \text{HF}
$$

(53, Route di)

The deductions from these analyses are strengthened by the isolation of $\mu$-fluorophenyl pentafluorobenzoate, identified by mass spectrometry.

Disproportionation products (XXXII) may be aromatised during hydrolysis, possibly accounting for the remaining biaryl (0.20 mole/mole peroxide) and hydrogen fluoride (0.20 mole/mole peroxide).
The excess of pentafluorobenzoic acid resulting from the hydrolysis of esters, could result from the hydrolysis of a species which gives a non-aromatisable quaterphenyl-type product.

\[
\begin{align*}
\text{Ar}_F\text{CO}_2\text{O} & \quad \text{H} \quad \text{F} \quad \text{H} \\
\text{H} & \quad \text{F} \quad \text{H} \\
\text{F} & \quad \text{H} \quad \text{F} \\
\text{H} & \quad \text{F} \quad \text{H}
\end{align*}
\]

If \( \sigma \)-complexes formed in this reaction are stabilised by \( \pi \)-complex formation, then these complexes would not be so readily oxidised as other \( \sigma_H \)-complexes. This would lead to an increase in the amounts of dimerisation and disproportionation products.

Two types of disproportionation product resulting from hydrogen transfer between \( \sigma_H' \)-complexes are possible.

\[
\begin{align*}
2 & \quad \text{Ar}_F \quad \text{H} \\
\text{H} & \quad \text{F} \quad \text{H} \\
\text{F} & \quad \text{H} \quad \text{F}
\end{align*}
\rightarrow
\begin{align*}
\text{Ar}_F \quad \text{H} \quad \text{F} \\
\text{H} & \quad \text{F} \quad \text{H} \\
\text{F} & \quad \text{H} \quad \text{F} \\
\text{H} & \quad \text{F} \quad \text{H}
\end{align*}
\]

or

\[
\begin{align*}
\text{Ar}_F \quad \text{H} \quad \text{F} \\
\text{H} & \quad \text{F} \quad \text{H} \\
\text{F} & \quad \text{H} \quad \text{F} \\
\text{H} & \quad \text{F} \quad \text{H}
\end{align*}
\]

Equation 63
3.6.6 Relative rates of displacement of hydrogen and fluorine

The highly fluorinated aromatic compounds are unable to stabilise pentafluorophenyl or pentafluorobenzyloxy-radicals. These radicals are more reactive in solvents in which they are uncomplexed and the results are explained on this basis. Since high reactivity is thought to cause low selectivity between sites of attack in substitution, the discrimination between displacement of hydrogen and displacement of fluorine should be least in pentafluorobenzene and greatest in fluoro­benzene, after allowing for the statistical factor. Table 14 shows this ratio, taken from the yields of biaryl found.

**TABLE 14**

$k_{\text{H}}/k_{\text{F}}$ (relative average rates of attack at hydrogen- and fluorine-bearing aromatic carbon atoms.)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$k_{\text{H}}/k_{\text{F}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentafluorobenzene</td>
<td>11</td>
</tr>
<tr>
<td>1,2,4,5-tetrafluorobenzene</td>
<td>22</td>
</tr>
<tr>
<td>1,3,5-trifluorobenzene</td>
<td>58</td>
</tr>
<tr>
<td>1,4-difluorobenzene</td>
<td>34</td>
</tr>
</tbody>
</table>

Although the last two figures are minimum values, the trend agreed well with our expectation, based upon consider-ation of the relative stabilities of the $\pi$-complex.
3.7 THE REACTION OF FLUORINATED AROMATIC AMINES WITH AMYL NITRITE IN POLYHALOGENOMETHANE SOLVENTS

3.7.1 Products

The yields of the abstraction products resulting from the reaction of various fluorinated aromatic amines with amyl nitrite in polyhalogenomethane solvents are given in Table 15.

**TABLE 15**

Abstraction products resulting from the reaction of $p$-$\text{XC}_6\text{F}_4\text{NH}_2$ with amyl nitrite in polyhalogenomethane solvents

<table>
<thead>
<tr>
<th>X</th>
<th>Solvent</th>
<th>$\text{XC}_6\text{F}_4\text{H}$</th>
<th>$\text{XC}_6\text{F}_4\text{Cl}$</th>
<th>$\text{XC}_6\text{F}_4\text{Br}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>CHCl$_3$</td>
<td>18.3%</td>
<td>0.50%</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>CBrCl$_3$</td>
<td>1.1%</td>
<td></td>
<td>42.6%</td>
</tr>
<tr>
<td>H</td>
<td>CHCl$_3$</td>
<td>20.5%</td>
<td>9.2%</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>CBrCl$_3$</td>
<td></td>
<td>10.8%</td>
<td>22.0%</td>
</tr>
<tr>
<td>Br</td>
<td>CHCl$_3$</td>
<td>18.2%</td>
<td>1.2%</td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>CBrCl$_3$</td>
<td>2.8%</td>
<td></td>
<td>31.5%</td>
</tr>
<tr>
<td>OMe</td>
<td>CHCl$_3$</td>
<td>46.5%</td>
<td>3.0%</td>
<td></td>
</tr>
<tr>
<td>OMe</td>
<td>CBrCl$_3$</td>
<td>7.6%</td>
<td></td>
<td>71.4%</td>
</tr>
</tbody>
</table>

(Yields expressed as yield/theoretical yield x 100%)

3.7.2 Mechanism of the reaction

A mechanism has been proposed for the thermal decomposition of pentafluoroaniline with amyl nitrite in aromatic solvents, similar to that proposed for the reaction of
aniline with amyl nitrite in polyhalogenomethane solvents and in aromatic solvents.

The reaction of fluorinated aromatic amines with amyl nitrite in polyhalogenomethane solvents may well proceed by a similar mechanism, as follows:

\[
\begin{align*}
\text{(a)} & : \quad \text{p-}X\text{C}_6\text{F}_4\text{Ni}_2 + \text{AmONO} \rightarrow \text{p-}X\text{C}_6\text{F}_4\text{N:NOAm} + \text{H}_2\text{O} \\
\text{(b)} & : \quad \text{p-}X\text{C}_6\text{F}_4\text{N:NOAm} \rightarrow \text{p-}X\text{C}_6\text{F}_5^* + \text{N}_2 + \text{AmO}^* \\
\text{(c)} & : \quad \text{p-}X\text{C}_6\text{F}_4^* + \text{XCCl}_3 \rightarrow \text{p-}X\text{C}_6\text{F}_5\text{X}^* + \text{CCl}_3 \\
\text{(d)} & : \quad 2\text{CCl}_3^* \rightarrow \text{C}_2\text{Cl}_6
\end{align*}
\]

\text{Equation 64}

If the reaction proceeds in this way, the fluorinated amine reacts with amyl nitrite to form water and an amyl aryl diazo-ether (64a), which undergoes decomposition to give a fluorinated aryl radical, nitrogen and an amyloxy-radical (64b). The aryl radical can then abstract atoms from the solvent (64c). When the amine is pentafluoroaniline (X=F), hexachloroethane was identified by g.l.c., indicating the dimerisation of trichloromethyl radicals (64d). Dimerisation of aryl radicals also occurs, for with this same amine, traces of decafluorobiphenyl are found.

It had been thought that when the solvent is an aromatic one containing hydrogen, amyl alcohol is formed by aromatisation of a 6-complex(65).

\[
\text{AmO}^* + \text{C}_6\text{F}_5^* \rightarrow \text{AmOH} + \text{C}_6\text{F}_5\text{C}_6\text{H}_5
\]

\text{XV}
However, with polyhalogenomethane solvents this cannot occur. The amyl alcohol shown in the reaction products by g.l.c. investigation, may be formed by reaction of an amyloxy-radical with water (formed during the reaction (64a)) or by attack of amyloxy-radicals upon amino groups.

3.7.3 Variation in product yields with variation of the nature of the para-substituent (X) of the amine

The total product yields resulting from abstraction of atoms from bromotrichloromethane and chloroform as solvents are given in Table 16.

**TABLE 16**

Total yields of products of abstraction reactions by $p$-$XC_6F_4$: radicals from bromotrichloromethane and chloroform

<table>
<thead>
<tr>
<th>X</th>
<th>F</th>
<th>H</th>
<th>Br</th>
<th>OMe</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl$_3$</td>
<td>18.8%</td>
<td>29.1%</td>
<td>19.2%</td>
<td>49.5%</td>
</tr>
<tr>
<td>CBrCl$_3$</td>
<td>43.8%</td>
<td>32.8%</td>
<td>34.3%</td>
<td>79.1%</td>
</tr>
</tbody>
</table>

It can be seen from Table 16 that the total product yields from $p$-methoxymethylfluoromethane are greatly in excess of those resulting from the reactions of the other amines (where X=F, H or Br). An explanation can be found in the manner of formation of the aryl radical from the aryldiazo-ether.

It is likely that the amyl aryldiazo-ether decomposes into radicals in two stages (66). In the first stage, a
nitrogen oxygen bond breaks to give an amyloxy-radical and a diazo-radical. However, the amy1 aryl diazo-ether is probably also in equilibrium with the diazonium ion.

\[
\text{XXXIV} \quad \rightarrow \quad \text{XXXV}
\]

Such a species would be susceptible to nucleophilic attack, and there are two possible nucleophiles present in solution, hydroxide and amyloxide ions. Possible reaction paths for the diazo species are as follows:

Equation 67

The extent of the nucleophilic attack will be dependent
on the nature of \( X \) and an investigation\textsuperscript{134} into the reaction of methoxide ion with fluorinated aromatic species of the type \( XC_6^\mathrm{F}_5 \), has shown that the rates of attack of the methoxide ion on \( XC_6^\mathrm{F}_5 \) are in the order \( X=\text{OMe} < X=\text{H} < X=\text{Br}, \text{Cl} \).

The proportion of the diazonium ion XXXVIII diverted in this way to the phenols XXXIV and (or the corresponding amyl ethers) and consequently not available for the formation of the aryl radical \( \text{p-}XC_6^\mathrm{F}_4 \) is therefore greatest when \( X \) is halogen or hydrogen.

During investigation of the by-products, the presence of phenolic compounds was shown by infra-red spectra and the solubility of part of the residue in alkali.

3.7.4 Abstraction of atoms from the solvent

The bonds which are broken in the various solvent molecules during the abstraction process are: carbon-chlorine, carbon-hydrogen and carbon bromine, whose bond dissociation energies are 77, 99 and 64 k cal.mole\(^{-1}\) respectively.\textsuperscript{127}

It can therefore be seen that in a bromotrichloromethane molecule, bromine can be abstracted more easily from the solvent because of the lower bond dissociation energy. However, the energy necessary to break a carbon-chlorine bond is very much less than that necessary to break a carbon-hydrogen bond, whereas it has been found that hydrogen is abstracted from a solvent molecule in preference to a chlorine atom. As the trichloromethyl radical results from both the abstraction of bromine from bromotrichloromethane and hydrogen
from chloroform, it is possible that the greater stability of this radical is responsible for the preferential removal of hydrogen. However, this radical would also result from the removal of a chlorine atom from carbon tetrachloride and with this solvent, it has been found that very little chlorine abstraction takes place. The other factors which influence a reaction are the non-bonded interactions and the bond making process. The part played by the former cannot be estimated as there are no quantitative measurements of their effects. Although Burdon has proposed that the ground state energy of products of the type \( \text{XC}_6\text{F}_4\text{H} \), which would result from the abstraction reaction (1), is lower than that of products of the type \( \text{XC}_6\text{F}_4\text{Cl} \) which would result from abstraction reactions of the type (2), the effect of this on the overall energy changes of the abstraction reactions is not known. Therefore, no conclusions can be drawn as to whether abstraction of hydrogen or fluorine is the more favourable process energetically.

\[
\begin{align*}
\text{XC}_6\text{F}_4 & \quad \text{----- H ----- CCl}_3 \\
(1) \\
\text{XC}_6\text{F}_4 & \quad \text{----- Cl ----- CHCl}_2 \\
(2)
\end{align*}
\]

3.7.5 **Selectivity of radicals**

The selectivity of the different radicals towards atoms in the solvent can be studied in Table 17.
TABLE 17

Ratio of H/Cl and Br/Cl abstraction for radicals \( \text{XC}_6^\text{F}_4 \)

<table>
<thead>
<tr>
<th>( \text{XC}_6^\text{F}_4 \text{NH}_2 )</th>
<th>H</th>
<th>Cl</th>
<th>Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-</td>
<td>31.5</td>
<td>1</td>
<td>38.8</td>
</tr>
<tr>
<td>H-</td>
<td>2.2</td>
<td>1</td>
<td>2.04</td>
</tr>
<tr>
<td>Br-</td>
<td>15.2</td>
<td>1</td>
<td>11.3</td>
</tr>
<tr>
<td>OMe-</td>
<td>15.5</td>
<td>1</td>
<td>9.41</td>
</tr>
</tbody>
</table>

This information is presented in the form of a graph in Figure 12. The linearity of the graph shows that the trend in selectivity of the radical \( \text{XC}_6^\text{F}_4 \) for the series \( \text{X}=\text{F}, \text{H}, \text{Br}, \text{OMe} \) is the same for H/Cl abstraction as it is for Br/Cl abstraction. That is, the \( \text{C}_6^\text{F}_5^- \) radical is the most selective towards both hydrogen and bromine, \( \text{MeOC}_6^\text{F}_4^- \) and \( \text{BrC}_6^\text{F}_4^- \) have similar selectivities, while \( \text{HC}_6^\text{F}_4^- \) is the least selective radical.

A possible explanation for this order of selectivity can be suggested on the basis of stabilisation of the radicals by resonance interaction of the unpaired electron with the para-substituent. Fluoro-, methoxy- and bromo- substituents would be expected to exert mesomeric effects, thus giving more stable radicals which would be more selective than the \( \text{HC}_6^\text{F}_4^- \) radical, which does not have this stabilisation. This effect is greatest for a para-fluoro-substituent as the overlap of the non-bonding electrons of fluorine with the \( \pi \)-electrons of the aromatic ring is greatest.
Relative rates of displacement of Br/Cl

Relative rates of displacement of H/Cl
The mesomeric effect of substituents however, is considered to have little or no such influence in non-fluorinated aryl radicals, the selectivity differences of $p$-$XC_6H_4^-$ cannot be satisfactorily explained in terms of the stabilising effects of substituent groups in $p$-positions to the unpaired electrons on the radicals.

These differences in selectivity may also be explained in terms of selective removal of products by side reactions. One such reaction is substitution which may take place preferentially with the build-up of aromatic reaction products as the reaction proceeds.
3.8 USEFULNESS OF ABSTRACTION REACTIONS FOR THE PREPARATION OF FLUORINATED AROMATIC SOLVENTS

In general, it was found that the difficulty of separating the products from the by-products detracts from the usefulness of the reaction as compared with the preparation of the same products by methods based on nucleophilic substitution. If, however, these difficulties can be resolved, the reaction of fluorinated aromatic amines with amyl nitrite in the presence of bromotrichloromethane provides a useful method of replacing \(-\text{NH}_2\) by \(-\text{Br}\), particularly for \(\text{D-MeOC}_6\text{F}_4\text{NH}_2\) and \(\text{C}_6\text{F}_5\text{NH}_2\).

If the appropriate amines can be obtained, this method may be useful for the preparation of those di-substituted fluorinated aromatic compounds which cannot be conveniently prepared by methods based on nucleophilic substitution. For example, amines of the type \(\text{m-XC}_6\text{F}_4\text{NH}_2\) would lead to 1,3-disubstituted polyfluoroaromatic compounds.

The decomposition of perfluorobenzoyl peroxide in sulphuryl chloride gave a good yield of chloropentafluorobenzene. Apart from this and those reactions mentioned above, however, the other abstraction reactions carried out gave only very small yields of the desired products.

Since analysis of the reaction mixture for biaryls was unsuccessful in the reaction of pentafluoroaniline with amyl nitrite in iodobenzene, no conclusions can be drawn as to whether or not the pentafluoroiodobenzene formed results directly from the abstraction of iodine from the solvent as suggested by Cadogan (1.4.5).
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