

FREE RADICAL REACTIONS
OF
POLYHALOGENOAROMATIC COMPOUNDS

A thesis presented for the degree of
Doctor of Philosophy in the Faculty
of Science of the University of London

by

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I would like to dedicate this thesis
to my Father and to my late Mother,
who died during the course of this work.

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Abstract

Pentachlorophenyl radicals, previously unreported in the literature, have been obtained by a variety of routes analogous to those used for the generation of pentafluorophenyl radicals. These include the decomposition of pentachloroaniline by amyl nitrite, the oxidation of pentachlorophenylhydrazine, the photolysis of pentachloriodobenzene and the thermal decomposition of pentachlorophenylazotriphenylmethane. 2,3,4,5,6-Pentachlorobiphenyl is obtained when the radicals are generated in benzene. Mixtures of isomers of the respective biaryls are obtained from reactions in chlorobenzene and in toluene.

The formation of penta- and hexa-chlorobenzene in reactions with pentachloroaniline and amyl nitrite are investigated and discussed.

The reaction with benzene of 2,4- and 2,6-dichloro- and 2,4,6-trichlorophenyl radicals, generated from the corresponding amines with amyl nitrite were studied. Evidence has been found which suggests that crowding of the radical site may be a possible explanation for the relatively low yields of binuclear products formed in the reactions of the pentachlorophenyl radical.

The thermal decomposition of benzoyl peroxide in chloropentafluorobenzene and in 1,3,5-trichlorotrifluorobenzene, and the effect on it of catalytic amounts of trichloroacetic acid, have been investigated. The overall yield of biaryl material is increased by the addition of the acid, but there is no change in the isomer distribution.

A study was also made of the thermal decomposition of benzoyl peroxide in mixed solvents. The solvent pairs studied were hexafluorobenzene/chloropentafluorobenzene and hexafluorobenzene/1,3,5-trichlorotrifluorobenzene. Partial rate factors and relative rates were evaluated and are discussed.

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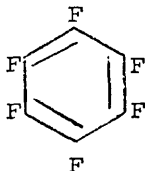
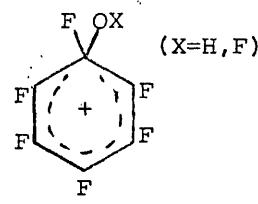
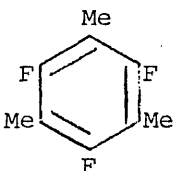
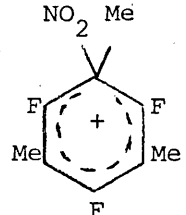
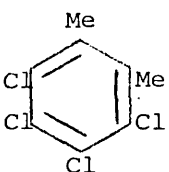
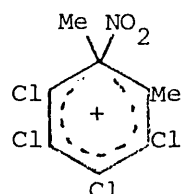
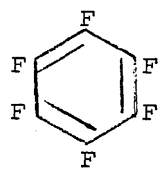
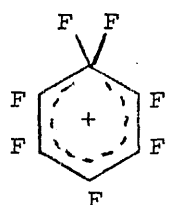
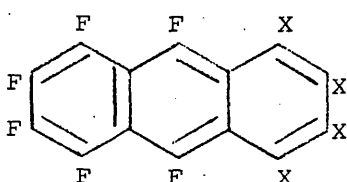
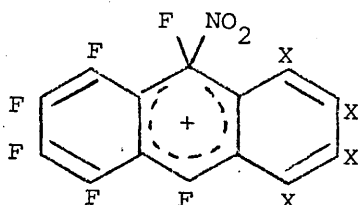
1.1. Heterolytic Mechanisms of Substitution in Polyhalogenoarenes

1.1.1. Electrophilic Aromatic Substitution

Electrophilic substitution in these systems is not a favoured process, since those very factors which lead to the high reactivity of the polyhalogenobenzenes towards nucleophiles inevitably ensure their low reactivity towards electrophilic species. The high electronegativity of the halogens leads to withdrawal of electrons from the ring carbon atoms, resulting in a low electron density at the aromatic nucleus. As well as this deactivation at all sites of the ring, and involving loss of hydrogen or halogen atoms, another contributory factor is that displacement of a positively charged halogen atom is an unlikely process. Molecular orbital calculation has been applied to the hypothetical (benzene - F⁺) system, this describes electrophilic substitution in these compounds as difficult.

There are reports in the literature²⁻⁶ which suggest that intermediates arising from the attack of electrophiles upon polyhalogenobenzenes have their counterparts in electrophilic aromatic substitution. The identification of benzenium ions in these reaction mixtures show characteristics similar to the σ -intermediates formed during electrophilic aromatic substitution in simple benzene systems. Table 1 shows some of the reactions of polyhalogenoarenes with electrophiles and the intermediates which have been detected or postulated.

Table 1

Substrate	Reagent	Intermediate	Ref.
	CrOF or Cr(OH)F (CrF ₃ , HF)		2
	HNO ₃		3
	HNO ₃		4
	Co ³⁺ F ₃		5
	HNO ₃		6

X=F, H

1.1.2. Nucleophilic Aromatic Substitution

1.1.2.1. Introduction

Nucleophilic substitution is to polyhalogenobenzenes as electrophilic substitution is to aromatic hydrocarbons.

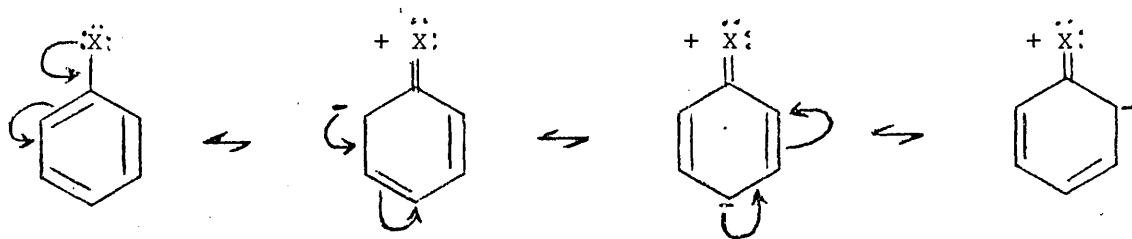
The complementary nature of these two systems is seen in the fact that while the hydrocarbons are the natural choice for the study of mechanisms involving electrophilic attack, It can be argued that the polyhalogenobenzenes are ideal compounds for a study of mechanisms involving nucleophilic aromatic attack. Thus from a study of these reactions information regarding rates of reaction, reactivities and orientations of attack has been collected⁷⁻⁹.

1.1.2.2. The Halogen Atom as a Substituent

A. Electronic Effects

The influence of a substituent on the π -electrons of an aromatic system, such as benzene or naphthalene, may be divided to a first approximation, into an inductive effect (I) and a resonance or conjugative effect (M).

A strongly electronegative substituent, e.g. fluorine, will increase the effective positive nuclear charge on the carbon atom to which it is attached. The resonance effect takes into account the capacity of the substituent itself to contribute electrons to the π -system. Thus the halogens all possess a negative inductive effect (-I, largest for fluorine) and a positive (+M) mesomeric effect. Canonical structures representing the delocalisation of negative charge over the benzene nucleus are used to illustrate these effects. Fig.(i).



X = F, Cl, Br, I

Fig. (i)

The ease of replacement of the halogen in S_NAr reactions depends upon a variety of inter-related factors such as the solvent and the type of nucleophile, and for the first row nucleophiles the order lies in the sequence, $F \gg Cl > Br > I$. This has been ascribed to the predominant influence of the electronegativity of the incipient leaving group on the energetics of bond formation by the nucleophile^{10,11,12}. Hence by the inclusion of a halogen atom into the aromatic nucleus the activation energy is lowered sufficiently to enable the σ -complexes to be formed, resulting in the bimolecular mechanism observed in these reactions, Fig. (ii), where k_1 is rate-determining.

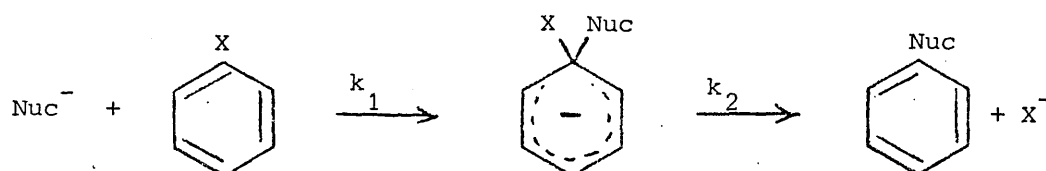


Fig. (ii)

In addition to the inductive and mesomeric effects of the halogens, a further substituent effect has been associated with them, namely the so-called I_π effect. Spectroscopic measurements showed values of mesomeric effects for halogen substituents different from those derived by kinetic and thermodynamic measurements¹³ and these differences were attributed to

Coulombic (inductive) repulsion between the p-electrons on the halogen and the ring π -electrons on the neighbouring carbon atom, or to unfavourable penetration of filled orbitals containing the same electrons^{14,15}. This was called the I_{π} effect.

The (C-F) bond is, compared to the rest of the (C-halogen) bonds, relatively short and because of the similar sizes of the orbitals containing the p- and π -electrons their interaction is at a maximum. This means that for the remainder of the halogens the p- π electron repulsions decrease in the order $F > Cl > Br > I \sim H$, and this is the order of destabilisation of a negative charge on an adjacent atom. Although this is contrary to the normal electron-attracting behaviour of the halogens, it arises because the negative charge in question is in a π -electron system.

The concept of the I_{π} effect has been applied by Burdon¹⁴ to nucleophilic substitution in the polyfluoro- and polychloro-benzenes. His approach to the problem was to assume that the classical concepts of the inductive and mesomeric effects could not forecast the orientation of attack in these substrates. The I_{π} effect was assumed to be the predominant factor controlling the orientation of attack in these reactions.

In making this assumption, Burdon considered that the inductive and mesomeric effects cancelled each other out. The following example illustrates the use of the I_{π} concept when applied to chloropentafluorobenzene and pentachlorofluorobenzene (Fig.iii).

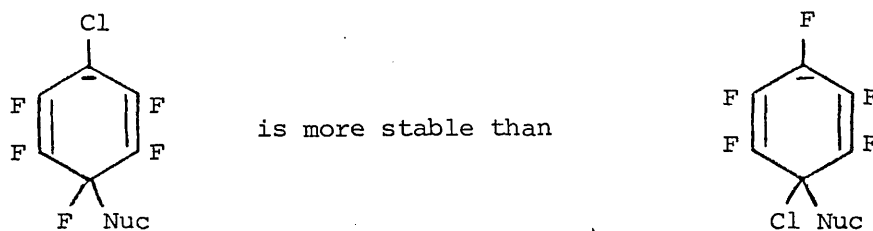
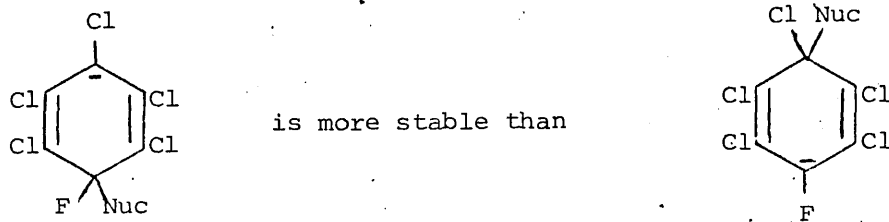


Fig. (iii)

By using the I_{π} effect in the above manner the orientation of nucleophilic attack in the polyhalogenobenzenes can be correctly predicted.

Bolton and Sandall¹⁶ have shown that the orientation of attack of nucleophiles on polyhalogenobenzenes can be predicted by using the mesomeric effect. This means that the above assumption used by Burdon does not apply in this case and the order for the mesomeric effect of the halogens, $(F > Cl > Br > I \sim H)$, can be used to forecast the orientation of attack in the polyhalogenobenzenes as illustrated in Fig. (iv).

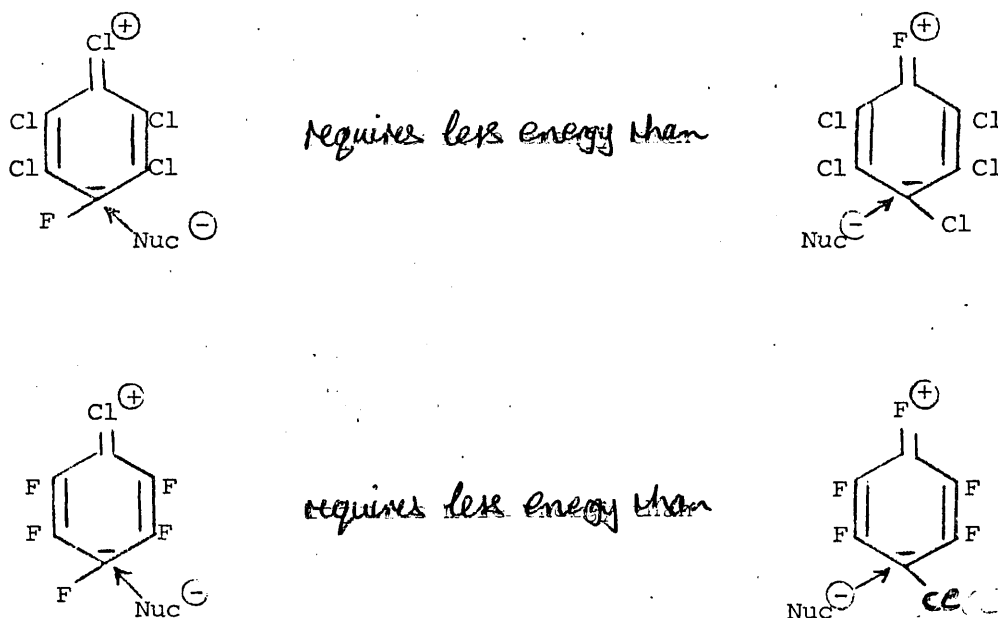


Fig. (iv)

This approach has been used to predict correctly the orientation and rates of displacement arising from nucleophilic attack on the polyhalogenobenzenes, without the need to invoke a third electronic effect. Bolton and Sandall have produced a simple algebraic method for determining orientations and rates of attack in these systems.

B. Orientation effects

The problem of orientation of attack by a nucleophile in polyhalogenobenzenes occurs when there is more than one possible site for substitution and in such a case the relative stabilities of the σ -intermediates need to be determined.

This can be illustrated by consideration of a specific example, e.g. nucleophilic reactions involving halogen derivatives of 1,2,3,4-tetrafluorobenzene^{17,18}. The following Wheland intermediates can be drawn, using the para-quinonoid form as the model to represent the transition state; (Fig.(v)).

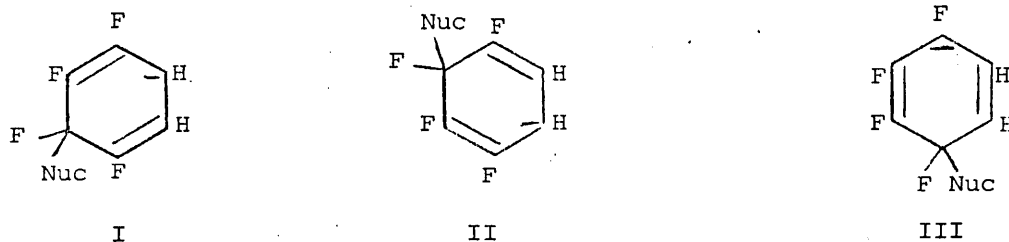


Fig.(v)

By using the I_{π} effect, assuming that the inductive and mesomeric effects cancel each other out, the order of stability of the above intermediates is $I=II>III$.

Hence for the three isomeric tetrafluorobenzenes substitution occurs mainly at the starred positions, Fig.(vi), i.e. when the negative charge in the transition state is located on a carbon bearing hydrogen rather than a carbon-bearing fluorine atom.

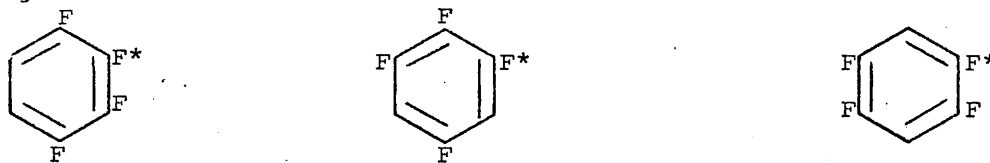


Fig.(vi)

In most cases nucleophilic displacement in C_6F_5X compounds occurs para to the substituent X. Using Wheland intermediates to represent the transition state, the resonance hybrids I and II, III and IV, V and VI, approximate to the transition states for attack by a nucleophile on C_6F_5X derivatives (Fig.(vii)).

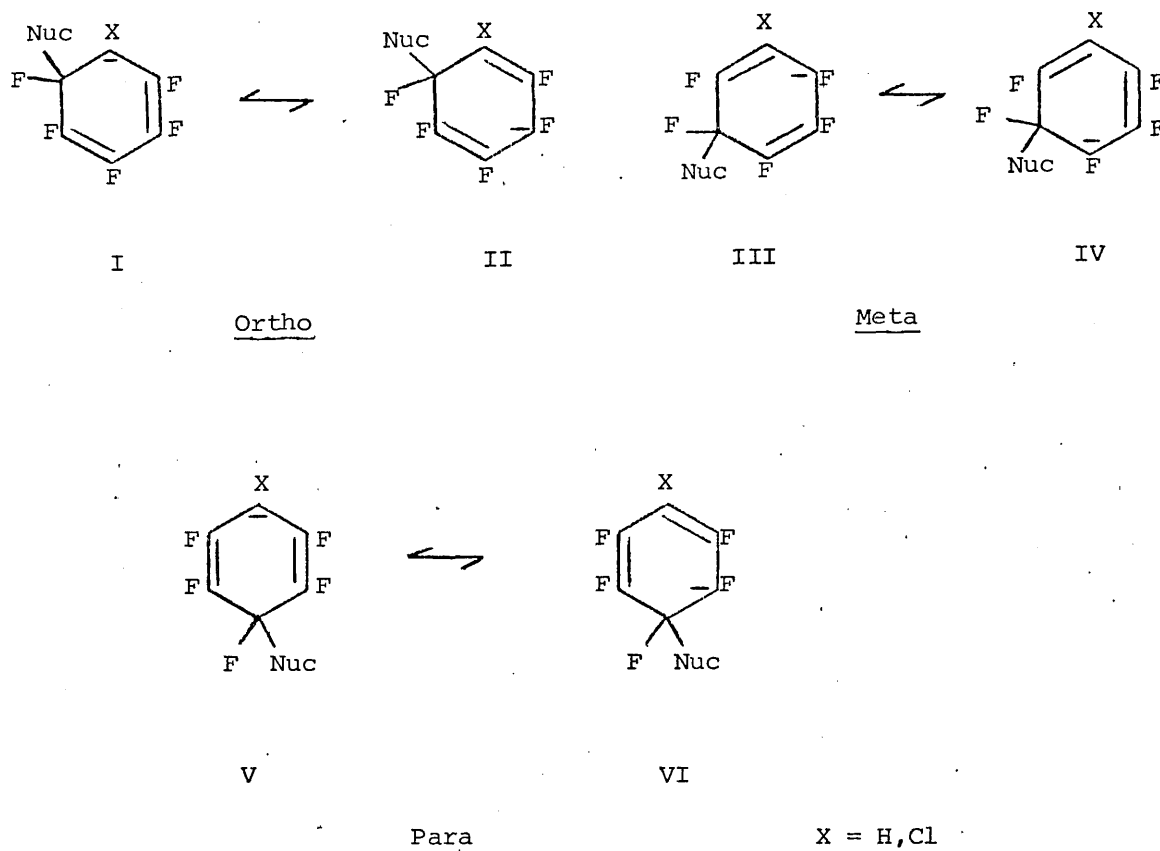


Fig.(vii)

In terms of the I_{π} effect, the resonance structures in which the negative charge is situated upon the carbon atom bearing the substituent X make the largest contribution to the transition state, i.e. structures I and V. This is borne out experimentally, chloropentafluorobenzene giving ca. 25% of ortho replacement with sodium methoxide and hydrazine hydrate¹⁹, the majority being para replacement. Similarly pentafluorobenzene and pentachlorobenzene react predominantly at sites para to the hydrogen atom.

To summarise, there are two theories available for the prediction and interpretation of nucleophilic attack in the polyhalogenobenzenes. One theory (the I_{π} effect) uses the interaction between the electrons in the p-orbital on the substituent and the π -electron system, while the second makes use of the classical concept of the mesomeric effect to interpret the experimental observations. The majority of the experimental data concerns the polyfluorobenzenes and only recently have studies concerning the polychloro-, polybromo- and polyiodobenzene systems been conducted^{16a,16b}.

1.2 Homolytic Aromatic Substitution

1.2.1. Introduction

The aim of this section is to show the reactions of radicals with aromatic substrates, and specifically the effect that substituents, such as the halogens (both in the radical and the substrate), have upon the orientation in homolytic aromatic substitution.

Unless otherwise stated the reactions covered here involve the displacement of a hydrogen atom from an aromatic nucleus by a phenyl or a substituted phenyl radical. It must be pointed out, however, that this is not the only homolytic aromatic substitution process possible. There have been several reports^{20,21} of alkyl radical substitution process occurring ~~with~~ aromatic substrates, and the displacement of nuclei other than hydrogen is also well documented. (Part 1.2.7, p.38).

Homolytic aromatic arylation has received exhaustive coverage in the numerous review articles that have been published²²⁻²⁵, and only a few salient features need be covered here.

1.2.2. The Phenyl Radical and its Precursors

One of the most useful sources of aryl radicals has been the diaryl peroxides, whose ease of handling and "clean" decomposition makes them useful precursors for the generation of aryl radicals²⁶⁻²⁹. The kinetics of their decomposition in a range of aromatic substrates has been carried out as well as using them for studying the aryl radicals themselves.

It has been found that^{28,29} the kinetic law representing decomposition of the peroxide P, in an aromatic solvent involves two terms, the first representing a primary, unimolecular mode of decomposition and the second an induced (chain) decomposition which proceeds concurrently

with the primary decomposition. Thus the observed rate-constant k_1 is a composite term containing both the spontaneous and induced decompositions, e.g.;

$$-\frac{d[P]}{dt} = k_1[P] + k_{3/2}[P]^{3/2} \quad \dots\dots (1)$$

For the decomposition of benzoyl peroxide in benzene at 80°C the proportion of peroxide decomposed by the induced mechanism reaches 20% for an initial concentration of 0.01 M of benzoyl peroxide^{30,31}. This figure can reach 80% of the total peroxide decomposition when the solvent is bromobenzene³⁰.

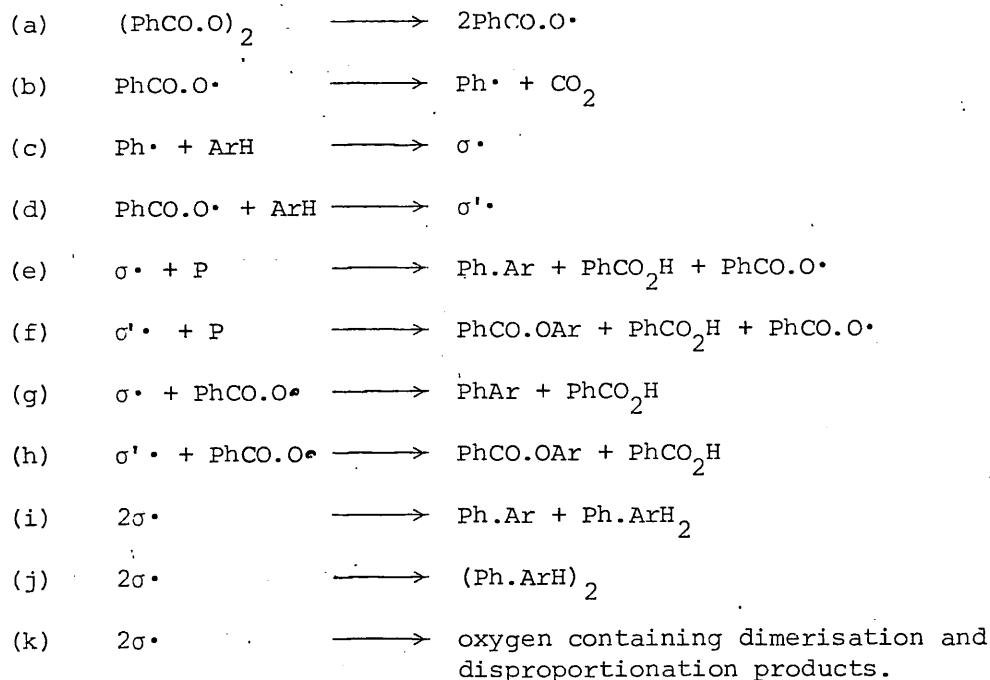
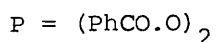
Gill and Williams³⁰ have reported a detailed investigation into the kinetics and products of the decomposition of benzoyl peroxide in benzene over a wide range of initial peroxide concentrations. The rate expression (2), where k_1 and k_1' are the first-order rate constants, while $k_{3/2}$ is a 1.5-order rate constant, derived by these workers indicates that two types of termination reaction are possible, Scheme 1 (p. 21).

$$-\frac{d[P]}{dt} = k_1[P] + k_1'[P] + k_{3/2}[P]^{3/2} \quad \dots\dots (2)$$

The kinetics of the decomposition have been found to depend upon initial concentrations of peroxide, and at high peroxide concentrations the kinetics of the peroxide decomposition follow the kinetic expression³⁰ (3);

$$-\frac{d[P]}{dt} = k_1[P] + k_1'[P] \quad \dots\dots (3)$$

The sequence for the decomposition of benzoyl peroxide in an aromatic solvent is represented in Scheme 1 (p. 21);



Scheme 1

Confirmation of the formation of σ -complexes (c), (d) as intermediates in the arylation process has been obtained by isolation of the products of their disproportionation and dimerisation^{32,33}. The relative contributions made by disproportionation and dimerisation should increase if the decomposition is conducted using low peroxide concentrations, as the oxidising agents required for the conversion of the σ -complexes to biaryls would be scarce. Evidence has been found to support this³³. A dihydro-biphenyl ((i) Scheme 1) has been shown³² to be present among the products of the decomposition of benzoyl peroxide in very dilute benzene solutions.

Dimerisation of the σ -complexes which may occur with union of the nuclei at either the 2- or 4-positions, can lead to a number of isomeric

and stereoisomeric derivatives of tetrahydroquaterphenyls and these compounds have been identified as the main constituents of the high boiling residues formed in the decomposition of benzoyl peroxide in aromatic substrates³³. Dehydrogenation of the tetrahydroquaterphenyls to the corresponding quaterphenyl derivatives has made possible the identification of the three predicted isomers of quaterphenyls in the reaction of benzoyl peroxide and benzene³² Fig. (viii);

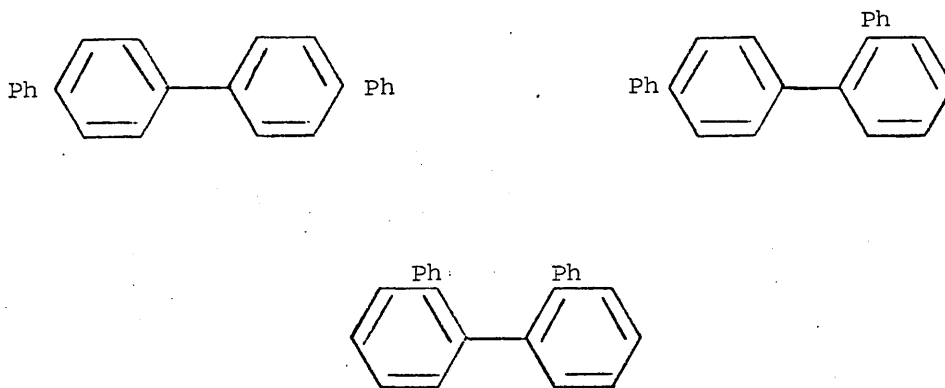


Fig (viii)

1.2.3. Partial Rate Factors for Arylation

Most of the work concerned with the arylation of aromatic substrates has been directed towards the measurement of the relative rates of attack at various positions in the substrate and comparing these rates with those obtained from the arylation of benzene, i.e. the determination of partial rate factors. A partial rate factor f_r expresses the change in the specific rate of substitution at position r in the nucleus of a benzene derivative, PhX , compared to the rate of reaction at any one position in benzene. Partial rate factors (p.r.fs) are usually expressed as a ratio and are deduced from the relative yields of the biaryl products arising from the arylation reaction.

Table 2 shows isomer ratios and p.r.f.'s for the phenylation of a variety of benzene derivatives.

Table 2

Partial rate factors and isomer distribution for phenylation with benzoyl peroxide (80 °C) ^{34,35}

Substrate PhX	Relative Rate $C_6H_6 = 1$	Isomer Distribution			Partial Rate Factors		
		<u>o</u> -	<u>m</u> -	<u>p</u> -	f_o	f_m	f_p
PhNO ₂	2.94	62.5	9.8	27.7	5.5	0.86	4.9
PhF	1.03	55.2	29.8	15.0	1.7	0.92	0.93
PhCl	1.06	56.9	25.6	17.5	1.8	0.81	1.1
PhBr	1.29	55.7	28.8	15.5	2.2	1.1	1.2
PhI	1.32	51.7	31.6	16.7	2.0	1.3	1.3
PhMe	1.23	65.4	20.0	14.6	2.4	0.74	1.1
PhEt	0.90	51.0	28.0	21.0	1.4	0.76	1.1
PhPr ⁱ	0.64	30.0	42.0	28.0	0.58	0.81	1.1
PhBu ^t	0.64	24.0	49.0	27.0	0.46	0.94	1.0
PhCN	3.7	60.0	10.0	30.0	6.5	1.1	6.5

The data presented in Table 2, provides the following information:

- (a) All the substituents (X) (except where X = Et, Prⁱ, Bu^t) activate the nucleus towards attack by phenyl radicals, quite independently of their polar characteristics. Groups which can undergo conjugation with the aromatic nucleus to produce resonance structures, e.g. cyano- and nitro- groups are capable of stabilising the σ -complexes resulting from ortho- and para- attack on these substrates by phenyl radicals. The ability of

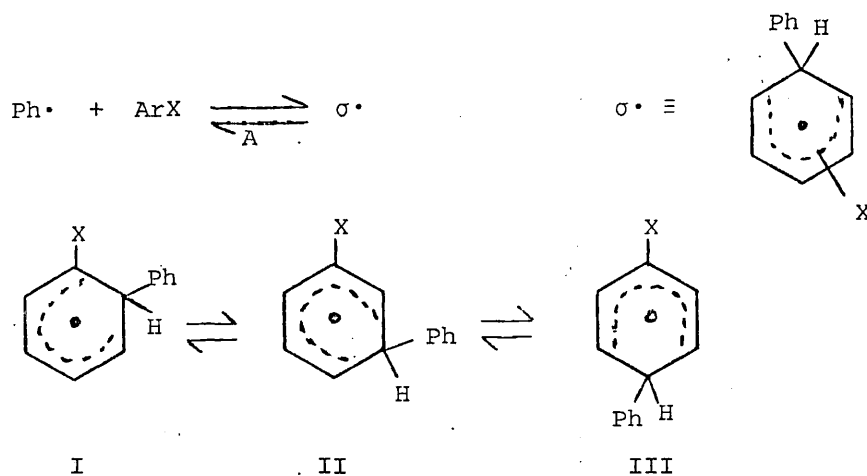
these groups to undergo conjugation gives rise to higher p.r.f's at the ortho- and para- positions. However, the interpretation of the p.r.f's for these compounds (PhX, where X = CN, NO₂) has been questioned and in the light of recent studies upon the validity of the p.r.f's themselves and their interpretation, the deductions arising from this data need careful consideration.

(b) The presence of a steric effect can be seen in the lower yields of the ortho- isomers for phenyl radical attack on iso-propyl benzene and t-butyl benzene.

(c) The absence of any apparent correlation between the partial rate factors for phenylation and the polar properties of the directing groups suggest that the phenyl radical is an almost neutral reagent.

As was mentioned earlier, dimerisation and disproportionation of the σ -complexes arising from phenyl radical attack upon aromatic substrates has been found to be significant in the absence of an oxidising agent^{32,33}. Such a result raises doubts^{33,36} concerning the assumption necessary for the validity of p.r.f's, that the rate of formation of biaryls is directly related to the rate of formation of the σ -complexes. Thus if the σ -complexes formed in the arylation reaction find alternative fates, other than the formation of biaryls, then the above statement is invalid.

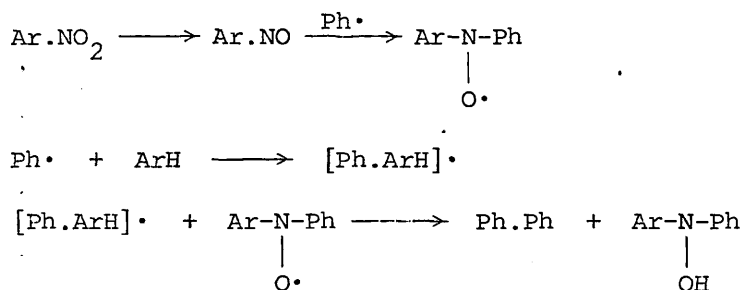
The experimental work so far discussed is based upon the assumption that the first step in homolytic aromatic substitution, i.e. the formation of the σ -complex, is irreversible and so kinetically product determining. This assumption has been questioned by a number of workers^{37,38,38a} and an alternative picture has emerged from their studies. These workers envisage a reversible arylation step leading to thermodynamically controlled products. Scheme 2 shows the addition of a phenyl radical to an aromatic nucleus; step A is thought to be reversible leading to the isomeric σ -complexes, I, II and III, as a result of aryl migration.



Scheme 2

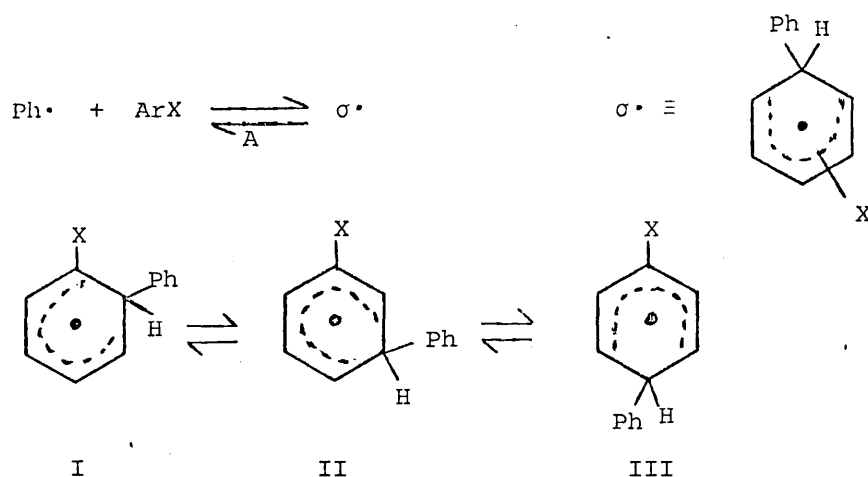
The presence of an electron transfer agent may increase the yield of biaryls and it has been suggested³⁹ that reliable values for the relative rates of phenylation of aromatic substrates could be obtained if the measurements were carried out in reactions containing a catalytic quantity of the electron transfer agent.

The presence of an aromatic nitro-compound in homolytic arylation reactions using diaryl peroxides has been shown to increase the yield of biaryls^{22,40,41}. The mechanism for the reaction of benzoyl peroxide with benzene in the presence of nitrobenzene is shown in Scheme 3.



Scheme 3

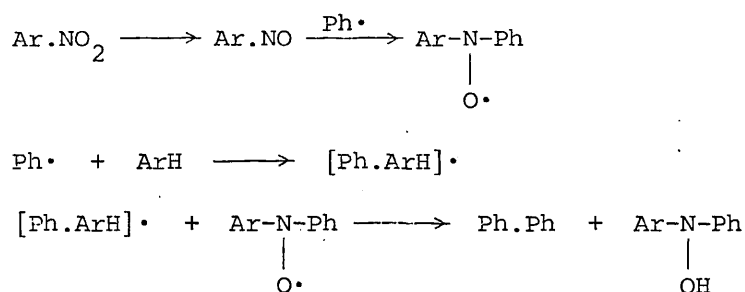
The nitro-group is converted into a nitroxide and then to a diaryl nitroxide by reaction with a phenyl radical. It is the diaryl nitroxide which is involved in dehydrogenation of the σ -complex, thereby preventing dimerisation and disproportionation reactions^{42,43}. The



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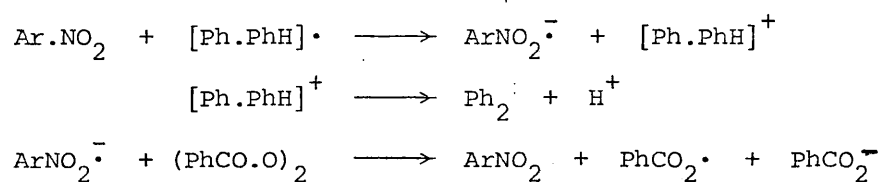


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evidence for this mechanism was largely based on the detection of diphenyl nitroxide by e.s.r. spectroscopy.

Recently there has been a report showing that aromatic nitro-compounds containing electron-withdrawing groups are much more effective than those containing electron-donating groups in increasing the yield of biaryls⁴⁴. The mechanism was explained in terms of an electron-transfer process and is outlined in Scheme 4;



Scheme 4

The ability of aromatic nitro-compounds to effect oxidation of radicals is well documented⁴⁵⁻⁴⁸, the ease of oxidation being increased by electron-withdrawing substituents in the aromatic nucleus. The effectiveness of nitro-compounds as radical scavengers is in the order; $\underline{p}\text{-NO}_2 \cdot \text{C}_6\text{H}_4\text{NO}_2 > \underline{m}\text{-NO}_2 \cdot \text{C}_6\text{H}_4\text{NO}_2 > \text{Ph.NO}_2$ ⁴⁸. E.s.r. studies on nitroaromatic radical anions also indicate that the unpaired electron is more extensively delocalised by electron-withdrawing groups in the aromatic nucleus and that a group in the para-position is more effective in delocalising the unpaired electron, than one in the meta-position⁴⁶. This evidence supports the claim that nitro-compounds are more effective as oxidising agents when they contain electron-withdrawing groups, and this is reflected in the yields of biaryls when using those compounds as additives (Table 3).

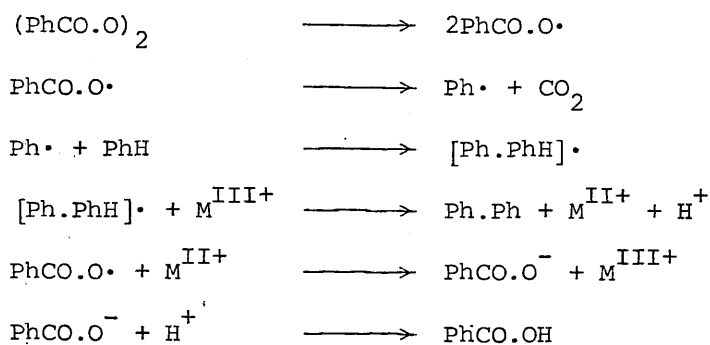
Table 3

Yields of 2,5-dichlorobiphenyl from the phenylation of *p*-dichlorobenzene (0.25 mol) with benzoyl peroxide (2.5 m mol) at 80°C⁴⁴.

Additive	2,5-Dichlorobiphenyl [†]	Relative Yield of biaryl (%)
PhNO ₂	1.96	78
<i>m</i> -NO ₂ ·C ₆ H ₄ ·NO ₂	2.01	80
<i>p</i> -NO ₂ ·C ₆ H ₄ ·NO ₂	2.43	97
PhNO	2.00	80
(CH ₃ CO ₂) ₂	1.84	74
Cu(O.COPh) ₂	2.36	94

[†] Yields are expressed as mole per mole % of benzoyl peroxide

Transition-metal compounds such as copper(II)⁴⁹ and iron(III)⁵⁰ salts have also been found to increase the yield of biaryl material at the expense of the high boiling polynuclear residues. One of several reaction schemes which can be used to depict the role of these metal salts is given in Scheme 5;



Scheme 5

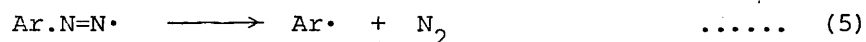
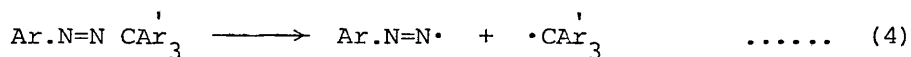
1.2.4 Alternative Sources of Phenyl Radicals

The phenylation of aromatic substrates using alternative sources of phenyl radicals has been extensively studied and partial rate factors, isomer ratios and rates of reaction have all been measured.

The sources of radical that have been studied include the decomposition of acylarylnitrosoamines^{51,52}, of the 1-aryl-3,3-dimethyltriazenes in the presence of dry hydrogen chloride⁵³ and the decomposition of aromatic amines at elevated temperatures in aromatic solvents by amyl nitrite⁵⁴⁻⁵⁶.

The mechanism for the decomposition of acylarylnitrosoamines has been clarified only recently⁵⁷⁻⁵⁹ and it appears that the decomposition proceeds via two competing routes, an ionic pathway and a radical pathway.

The decomposition of phenylazotriphenylmethane (PAT)¹¹⁰ has also been used as a source of phenyl radicals to obtain quantitative results on the phenylation of a number of aromatic substrates⁶⁰⁻⁶². Equations (4), (5) show the stages involved in the decomposition of PAT;



PAT has also been used to illustrate the reactions of arylcyclohexadienyl radicals^{29,37}. Decomposition of phenylazotriphenylmethane in chlorobenzene³⁷ results in the formation of 2-chloro-1,4-dihydrotritylbiphenyl Fig.(ix), which is formed at the expense of the six isomeric biphenyls.

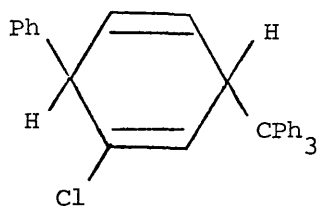
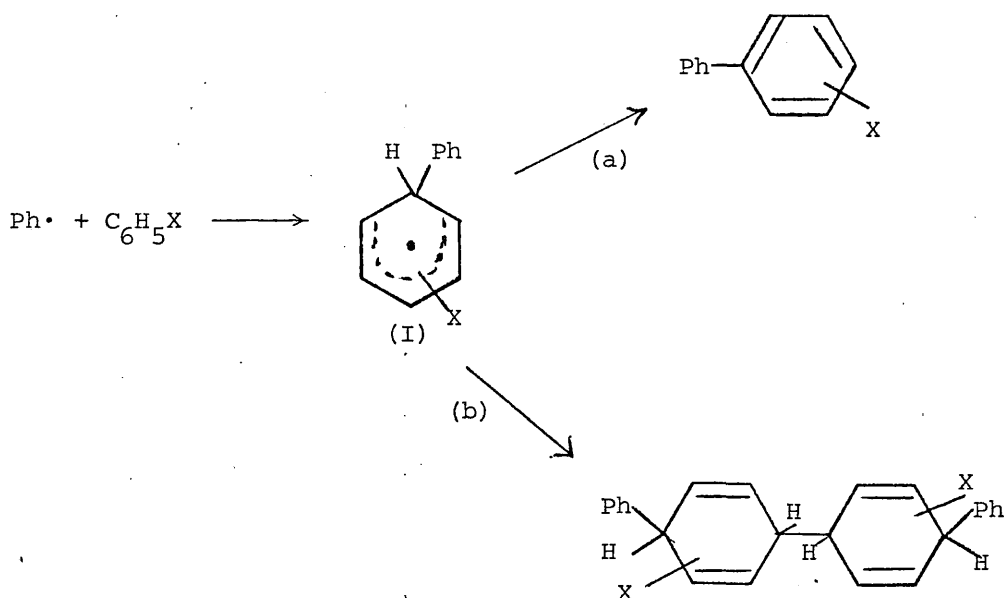


Fig (ix)

This indicates that anomalous isomer distribution in phenylation reactions found using phenylazotriphenylmethane³⁷ may be general.

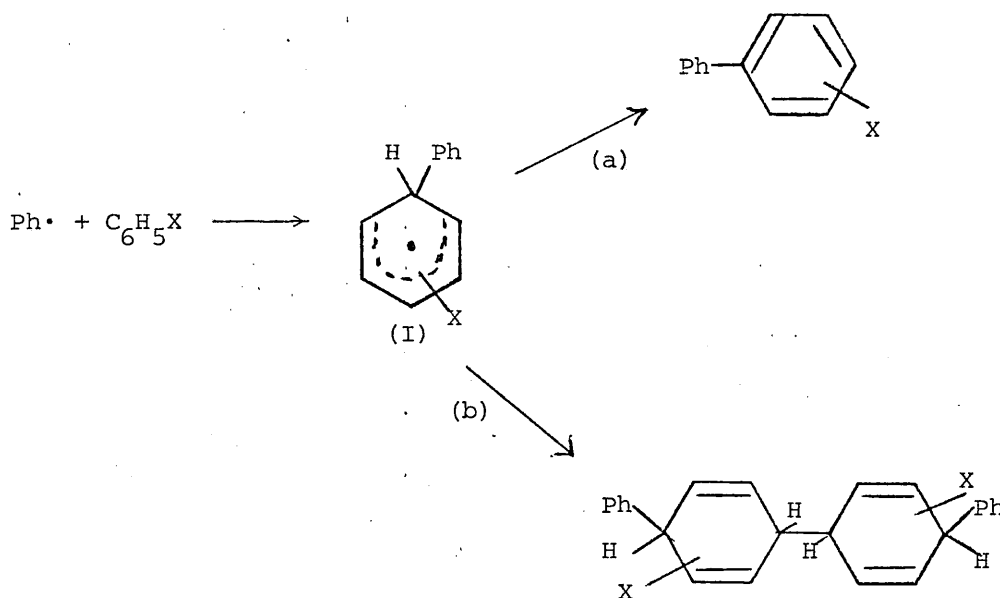
An outstanding feature of homolytic aromatic phenylation reactions is that in the phenylation of a given substrate PhH, the proportions of the resulting isomeric biphenyls, Ph.C₆H₄X, are almost independent of the phenyl radical source and the experimental conditions. This is surprising because the isomeric intermediates in biaryl formation, i.e. the phenylcyclohexadienyl radicals (I, Scheme 6), are intermediates in dimerisation and disproportionation reactions, and because of the electronic and steric effects of the substituent X it is not easy to envisage circumstances in which the position and nature of the substituent does not influence the relative extents of reactions (a) and (b), Scheme 6. Therefore when investigating the effect that a substituent has upon a reaction, the experiment is conducted under "high yield" conditions, i.e. a catalytic quantity of a "hydrogen-atom acceptor" is added to reduce the amount of products resulting from route (b).



Scheme 6

This indicates that anomalous isomer distribution in phenylation reactions found using phenylazotriphenylmethane³⁷ may be general.

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Scheme 6

1.2.5. Substituted Phenyl Radicals

The effect of placing a substituent in a radical centre may manifest itself in two ways:

- (a) the radical will show electrophilic or nucleophilic behaviour, according to the electron-withdrawing or electron-donating properties of the substituent;
- (b) steric influences affecting the yields of isomeric biaryls, particularly o-substituted radicals, will become more pronounced.

The phenyl radical precursors previously mentioned have all been adapted to produce substituted phenyl radicals and Table 4 shows partial rate factors and isomer distributions for the arylation of nitrobenzene with diaryl peroxides.

Table 4

Partial rate factors for arylation of nitrobenzene with aryl peroxides (80°C)⁶³

Radical	Relative Rate PhNO ₂ ArH ² K	Isomer Distribution %			P. R. F.		
		<u>o</u> -	<u>m</u> -	<u>p</u> -	f _o	f _m	f _p
<u>o</u> -NO ₂ .C ₆ H ₄ •	0.26	55	18	27	0.43	0.14	0.42
<u>m</u> -NO ₂ .C ₆ H ₄ •	0.43	52.9	18.0	29.1	0.68	0.23	0.75
<u>p</u> -NO ₂ .C ₆ H ₄ •	0.94	58.0	15.0	27.0	1.64	0.42	1.52
<u>o</u> -Cl.C ₆ H ₄ •	0.82	35.8	24.2	40.0	0.88	0.60	1.97
<u>m</u> -Cl.C ₆ H ₄ •	1.3	56.7	15.1	28.2	2.2	0.58	2.2
<u>p</u> -Cl.C ₆ H ₄ •	1.5	59.0	13.8	27.2	2.7	0.63	2.5
<u>o</u> -Br.C ₆ H ₄ •	0.79	35.0	25.0	40.0	0.83	0.59	1.90
<u>p</u> -Br.C ₆ H ₄ •	1.76	57.7	13.2	29.1	3.1	0.7	2.9
<u>o</u> -Me.C ₆ H ₄ •	2.2	41.2	18.7	40.1	2.7	1.2	5.2
<u>m</u> -Me.C ₆ H ₄ •	3.0	60.7	13.2	26.1	5.5	1.2	4.7
<u>p</u> -Me.C ₆ H ₄ •	3.4	59.5	11.9	28.6	6.1	1.2	5.8

If a nitro-group is introduced into a radical in the para-position then the region about the position which bears the unshared electron would be expected to suffer a deficiency in electron-density due to the polarisation of the radical brought about by the nitro-group. Therefore the p-nitrophenyl radical may be expected to show a certain degree of electrophilic character, and this is confirmed by the data presented in Table 4. Nitrobenzene is deactivated towards attack by electrophilic reagents (predominantly meta attacking) and activated towards nucleophilic attack (predominantly ortho and para attacking). Thus the relative rate $\frac{\text{PhNO}_2}{\text{ArH}} k$, should diminish if the attacking radical is electrophilic and increase if it is nucleophilic. An examination of the data presented in Table 4 shows this to be true, e.g. nitrophenyl radicals are electrophilic and have a small relative rate, whereas methylphenyl radicals are nucleophilic and consequently have a much higher value for the relative rate.

Substitution ortho to X in PhX by a radical which itself contains a bulky ortho-substituent (particularly chloro-; bromo; or methyl) is sterically inhibited⁶⁴. This can be illustrated from the data in Table 4. Attack by the o-, m- and p- methylphenyl radicals on nitrobenzene produced a decrease in the yield of the ortho-isomer, which is greatest for the ortho-methylphenyl radical. This can be associated with steric interaction between the radical and the substituent in the substrate.

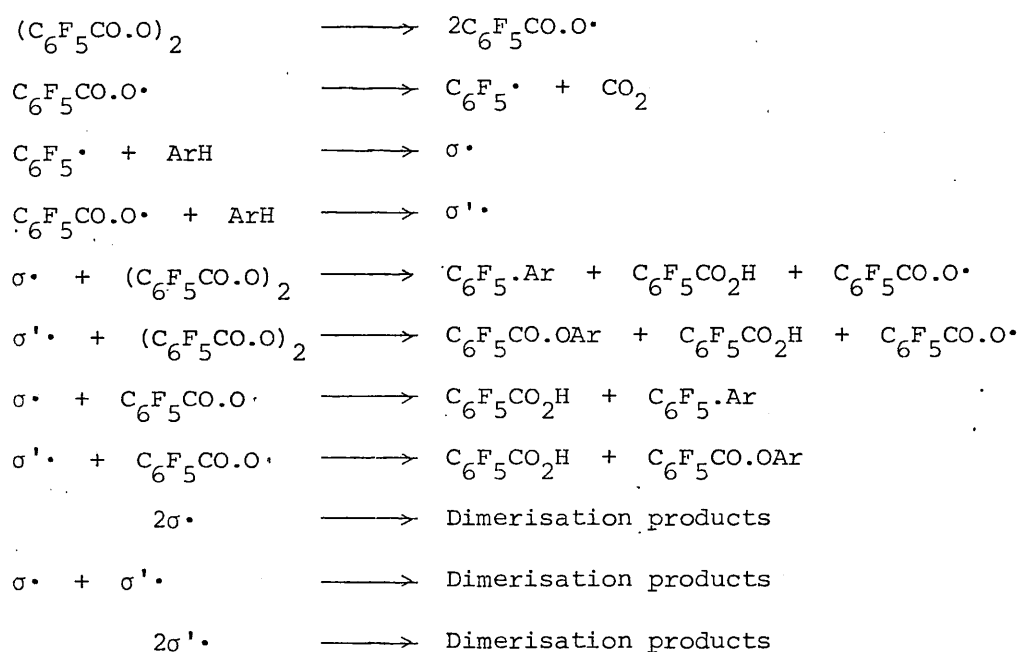
1.2.6. Homolytic Reactions of Polyfluoroaromatic Compounds

The replacement of five hydrogen atoms by fluorine atoms in a phenyl radical to give the pentafluorophenyl radical, has been shown to alter drastically the behaviour of this intermediate in homolytic arylation reactions²⁵.

The aim of this section is to illustrate the behaviour of this radical and outline some of its properties.

The thermal decomposition of pentafluorobenzoyl peroxide⁶⁵⁻⁶⁸ in benzene has been shown to produce 2,3,4,5,6-pentafluorobiphenyl, phenyl pentafluorobenzoate, pentafluorobenzoic acid and a high boiling residue.

The proposed⁶⁸ mechanism for the decomposition of the peroxide in benzene is given in Scheme 7.



Scheme 7

The kinetics of the decomposition⁶⁸ are consistent with those already obtained for the decomposition of benzoyl peroxide in aromatic substrates, and can be expressed by the kinetic expression (6);

$$-\frac{d[\text{P}]}{dt} = k_1[\text{P}] + k_1'[\text{P}] \quad \dots\dots (6)$$

where [P] represents the initial peroxide concentration.

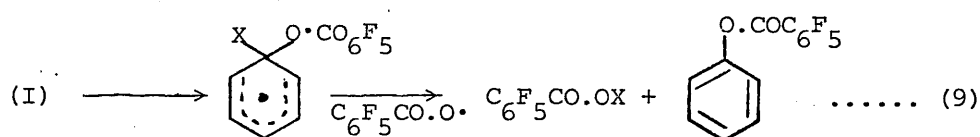
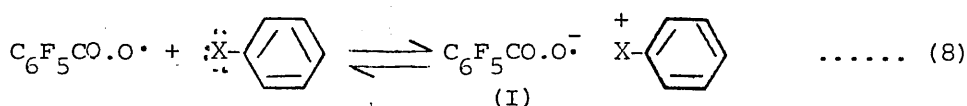
When initial concentrations of peroxide are very small a kinetic law of the type expressed in eqn. (7) has been found to apply. This type of expression is similar to that obtained for the decomposition of benzoyl peroxide in aromatic substrates under similar conditions^{27,28}.

$$\frac{-d[P]}{dt} = k_1[P] + k_1'[P] + k_{3/2}[P]^{3/2} \quad \dots\dots (7)$$

Decomposition of pentafluorobenzoyl peroxide has been carried out in chlorobenzene and bromobenzene^{65,68}. The main product being phenyl pentafluorobenzoate and not the products arising from direct pentafluorophenylation. Thus it appears from the above result that carbon-halogen bond breaking occurs in preference to carbon-hydrogen bond fission and that the reaction is so rapid, or assisted so successfully that the aryloxy radicals react before decarboxylation.

The above observations have been explained by assuming the formation of charge-transfer complexes between the aryloxy radical and the halogen substituents³⁰. This would make the process of decarboxylation less likely to occur and so reduce the concentration of pentafluorophenyl radicals available for arylation.

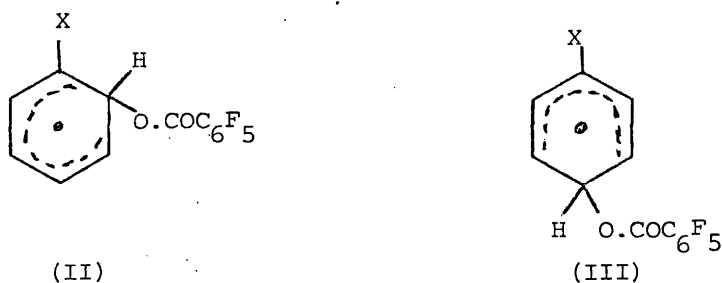
The formation of charge-transfer complexes has been used to explain the results obtained in phenylation reactions using chloro- and bromobenzene³⁰. The mechanism which has been proposed is shown in equations (8) and (9); Scheme 8.



Scheme 8

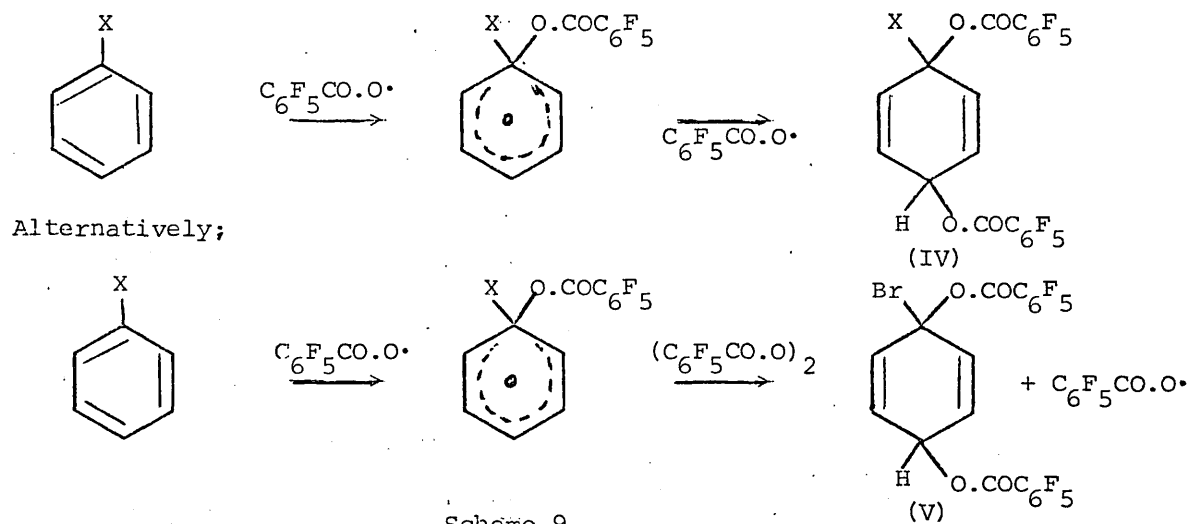
Certain points regarding this mechanism need to be pointed out;

(a) If an electron-transfer process of the type shown above takes place the donation of electrons from a halogen to an oxygen atom would be unlikely, and so collapse of (I) will not be restricted to attack at carbon atom one. As the pentafluorobenzoyloxy radical is nucleophilic and the charge-transfer complex (I) (Scheme 8) is stabilised by delocalisation of the positive charge in the aromatic nucleus, then (I) could also collapse to form intermediates (II) and (III);



(b) The formation of chlorine pentafluorobenzoate or bromine pentafluorobenzoate has not been detected in these reactions.

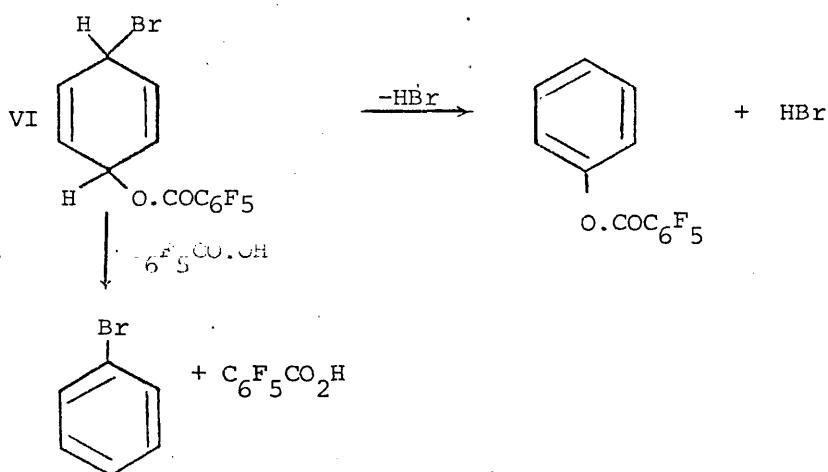
(c) The formation of the reaction products can be explained using alternative reactions to those described on p. 33 e.g., pentafluorobenzoyloxylation can occur at the carbon bearing halogen atom, subsequent attack by a pentafluorobenzoyloxy radical will produce (IV) which can then lose the elements of hydrogen and halogen to give the ester;



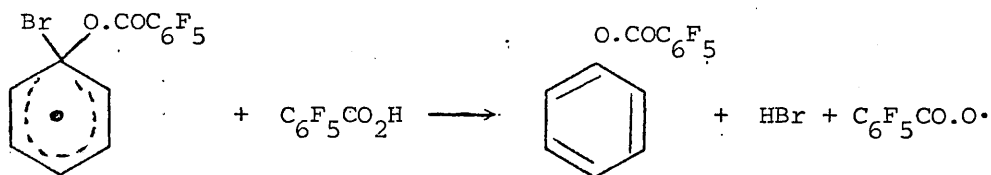
Scheme 9

Removal of the elements of hydrogen and halogen from VI, Scheme 10, will result in the formation of phenyl pentafluorobenzoate, a 1,4-elimination, while removal of pentafluorobenzoic acid, will revert back to the starting material.

Scheme 11:



Similarly,



Both of the schemes outlined above can be used to explain the experimental observations and more work needs to be carried out before the mechanism is clarified.

Generation of the pentafluorophenyl radical by the oxidation of the corresponding hydrazine⁷⁰ and the decomposition of pentafluoroaniline by amyl nitrite in aromatic substrates give rise to normal aromatic

substitution products in the halogenobenzenes⁷¹. Some results for the pentafluorophenylation of a range of non-substituted aromatic substrates are given in Table 5, together with the equivalent data for the phenylation reaction.

Table 5

Phenylation and pentafluorophenylation of some aromatic substrates (80°C)^{65,69}

Radical	Substrate	Isomer Distribution			(o + p)/m Ratio
		<u>o</u> -	<u>m</u> -	<u>p</u> -	
$C_6H_5\cdot$	C_6H_5F	46.7	35.4	17.9	1.8
$C_6H_5\cdot$	C_6H_5Cl	56.9	25.6	17.5	2.9
$C_6H_5\cdot$	C_6H_5Br	55.7	28.8	15.5	2.5
$C_6H_5\cdot$	$C_6H_5NO_2$	62.5	9.8	27.7	9.2
$C_6F_5\cdot$	C_6H_5F	42.5	30.7	26.9	2.3
		42.0	26.0	32.0	2.8
$C_6F_5\cdot$	C_6H_5Cl	64.7	20.6	14.7	3.9
$C_6F_5\cdot$	C_6H_5Br	61.6	26.3	12.1	2.8
$C_6F_5\cdot$	$C_6H_5NO_2$	20.8	53.4	25.8	0.87

Source of $C_6H_5\cdot$ = benzoyl peroxide

Source of $C_6F_5\cdot$ = pentafluoroaniline-amyl nitrite.

The polar properties of the radical can be inferred from an examination of the (ortho- + para-/meta-) ratios given in Table 5. The incidence of ortho-:para- substitution in the halogenobenzenes is greater for the pentafluorophenyl radical than the phenyl radical. As the halogenobenzenes undergo ortho- and para- substitution with electrophilic species it can be inferred that the pentafluorophenyl radical shows electrophilic behaviour. Using nitrobenzene as the substrate the meta- isomer is formed in the higher yield when the pentafluorophenyl radical is

used as the attacking species. As the nitro-group in nitrobenzene is meta-directing towards electrophiles the results from the pentafluorophenylation of nitrobenzene give further evidence to support the claim that this radical is electrophilic.

Alternative sources of the pentafluorophenyl radical that have been reported are irradiation of hexafluorobenzene with 1.5 MeV electrons⁷², photolytic decomposition of bis(pentafluorophenyl) mercury⁷³ and the oxidation of pentafluorophenylhydrazine using silver-oxide or bleaching powder.

Pentafluorophenylazotriphenylmethane has been prepared⁷⁴ and its thermal decomposition in benzene gives 2,3,4,5,6-pentafluorobiphenyl together with triphenylmethane and nitrogen.

Bolton, Sandall and Williams⁷⁵ have shown that competition reactions involving phenylation of polyfluoroaromatic substrates do not give consistent partial rate factors. This has been attributed to complexing between the reagents and the substrate which leads to a failure of the radical to select freely among sites in a substrate molecule, thus denying one of the basic pre-requisites needed for the successful interpretation of competition reactions.

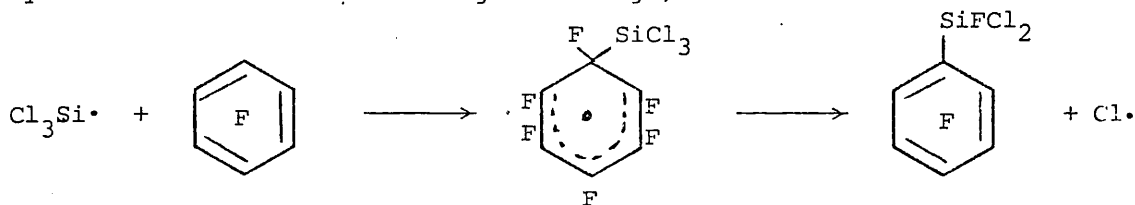
It has already been shown that mixtures of benzene and polyfluorobenzenes show non-ideal behaviour⁷⁵⁻⁷⁸. A phenyl radical in a polyfluoroaromatic solvent would therefore experience considerable van der Waals forces bonding it to specific molecules, as quite strong complexes are known to exist between simple benzene derivatives and hexafluorobenzene^{79,80}. This would suggest that the phenyl radical may spend all of its life in the vicinity of one polyfluoroaromatic molecule. Although the life-time of the radical is apparently sufficient to select among the more reactive sites of attack,^{within the one molecule} it is insufficient to enable distinction between sites in different molecules, i.e. the competition for the radical does not reflect the relative molecular

reactivation towards phenyl radicals alone, although true competition conditions may exist for phenyl radicals between sites within a molecule.

Such behaviour, leading to complications in the measurement of p.r.f.'s, and an obscuring of the selectivity of the aryl radical itself, are found to be general.

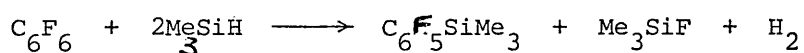
1.2.7. Homolytic Displacement of Atoms other than Hydrogen

Homolytic attack on the nucleus of hexafluorobenzene by trichlorosilyl radicals has been shown to proceed with the displacement of chlorine atoms⁸¹, although the products of substitution are complicated by side reactions such as halogen exchange, Scheme 12.

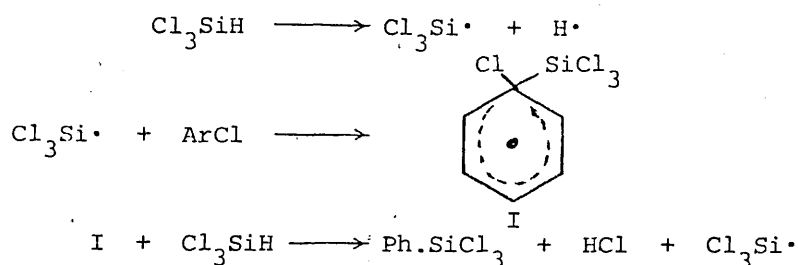


Scheme 12

Trimethylsilylation does occur when a mixture of trimethylsilane and hexafluorobenzene is irradiated with ultra-violet light, the reaction being given as;



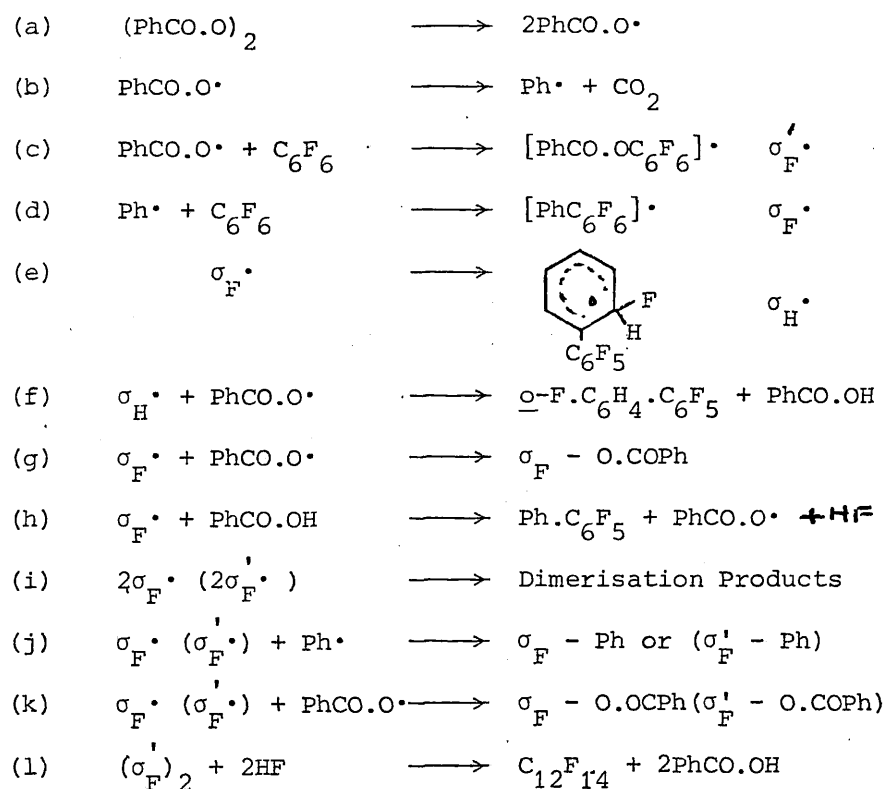
Homolytic displacement of aromatic chlorine by silyl radicals has been reported⁸²⁻⁸⁴ the reaction taking place in the gas phase. The reaction sequence involves an internal homolytic dissociation of silicon hydride and this is then followed by two simultaneous chain processes. The first, leading to condensation, involves attack of the $\text{Cl}_3\text{Si}\cdot$ radical on the aromatic ring and the second, leading to reduction, involves abstraction of a chlorine atom from the ring, Scheme 13.



Scheme 13

The arylation of hexafluorobenzene, using benzoyl peroxide as the radical source^{85,86}, gives a good yield (76%) of the corresponding biaryl. The products obtained from the reaction being; 2,3,4,5,6-pentafluorobiphenyl, benzoic acid, 2,2',3,4,5,6-hexafluorobiphenyl and a high boiling residue.

The proposed^{86,87} reaction scheme which explains the experimental observations is given below;



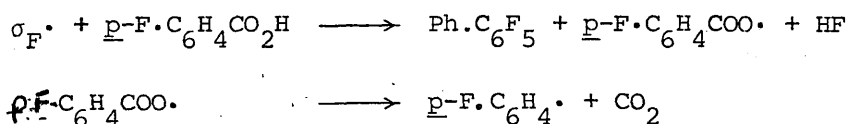
Scheme 14

The defluorination of the σ -complex formed by attack of a phenyl radical on hexafluorobenzene has been shown to occur by benzoic acid. The benzoic acid is initially formed either from attack on the reagent itself or by aryl or aryloxy-radicals or from the rearrangement of σ_F which leads to 2,2',3,4,5,6-hexafluorobiphenyl⁸⁸. The benzoic acid may then cause the defluorination of another σ_F radical (h) Scheme 14, to give benzoyloxy radicals 2,3,4,5,6-pentafluorobiphenyl and hydrogen fluoride. The mechanism shown in Scheme 14 successfully explains the following;

- (i) the formation of relatively small amounts of hydrogen fluoride;
- (ii) the formation of benzoic acid and (iii) the observed kinetics of the reaction.

The formation of tertiary esters, allows the regeneration of benzoic acid by transesterification using hydrogen fluoride. This allows benzoic acid to be returned to the system for the defluorination, the reaction being limited by the availability of tertiary esters to supply benzoic acid or of σ_F radicals to be defluorinated.

In the presence of added carboxylic acid it has been found^{89,90} that the yield of 2,3,4,5,6-pentafluorobiphenyl was increased at the expense of (a) the yield of radical-radical addition products and (b) the formation of 2,2',3,4,5,6-hexafluorobiphenyl. As well as the expected products of the reactions (Scheme 14) some 2,3,4,4',5,6-hexafluorobiphenyl was formed when p-fluorobenzoic acid was added. This product arises from the arylation of hexafluorobenzene by p-fluorophenyl radicals arising from the p-fluoro-benzoic acid.



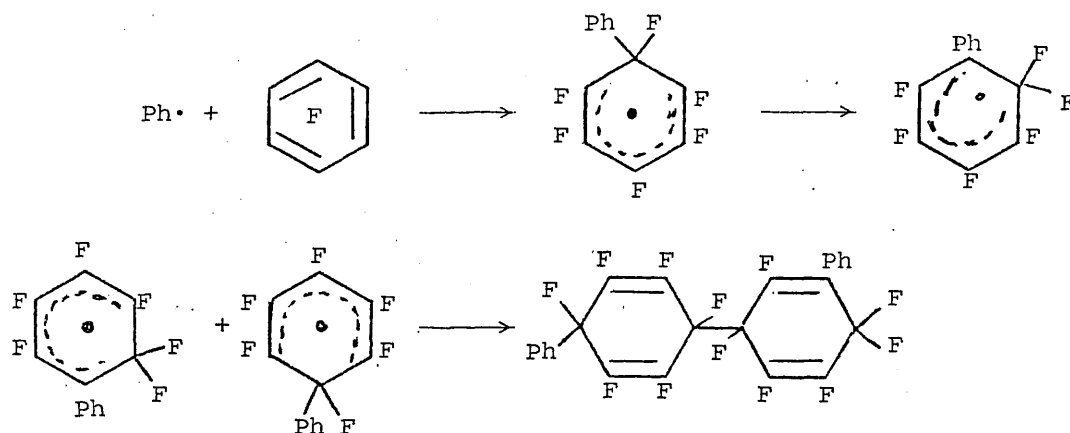
Scheme 15

The above reaction scheme shows how the σ_F^\bullet complex undergoes defluorination to give the observed reaction products.

Fields and Meyerson⁸⁸ have also observed the rearrangement of σ_F^\bullet and they found that at high temperatures rearrangement was preferred over defluorination suggesting that the former process has a higher energy of activation than the defluorination reaction.

Investigation into the nature of the high boiling residue from the reaction of benzoyl peroxide and hexafluorobenzene has produced evidence for the reversibility of the dimerisation reactions of σ_F^\bullet and the occurrence of a 1,2 fluorine migration⁹¹.

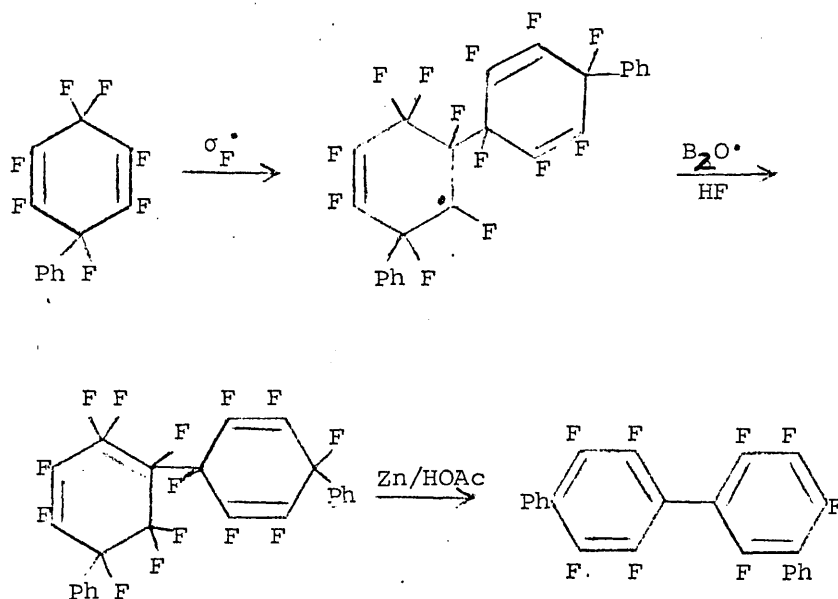
Dehalogenation of the high boiling residues gives derivatives of 3,4'- and 4,4'-bis(phenyl)biphenyl. The former structure (the 3,4'-isomer) is not expected from combination reactions of the σ_F^\bullet intermediate, and 1,2-migration of a fluorine atom in this intermediate was suggested to explain the orientation of the derived polyfluoroquaterphenyls, Scheme 16.



Scheme 16

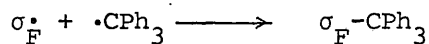
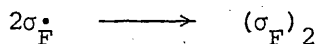
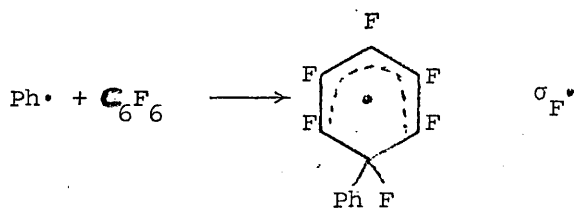
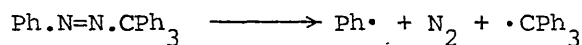
Addition reactions between the σ_F^\bullet intermediate and the heptafluoro-dihydrobiphenyls could produce fluorine analogues to the dihydrophenyls which were found among the products arising from the decomposition of benzoyl peroxide

in benzene⁹². These polyfluoropolyhydroquaterphenyls have been identified among the products arising from the phenylation of hexafluorobenzene⁹³ (Scheme 17).



Phenylation of hexafluorobenzene using phenylazotriphenylmethane (PAT) gives no pentafluorobiphenyl⁹⁴. The products from the reaction are addition products arising from radical-radical combination between σ_F^\bullet and triphenylmethyl radicals, Scheme 18.

However addition of small amounts of benzoic acid to the reaction mixture does result in the formation of some pentafluorobiphenyl⁹⁰.



Scheme 18

1.2.8. Summary.

The following points emerge from the data;

- (1) From the reactions involving the phenyl radical in a variety of aromatic substrates the mechanisms for the phenylation reaction have been determined for a number of phenyl radical precursors. Partial rate factors have been determined for the phenylation of a number of aromatic substrates using a variety of phenyl radical precursors. The data reveal that the common reactive intermediate is the phenyl radical although some differences in isomer distribution exist which arise from causes other than temperature difference alone. This has led to a re-examination of the evidence which suggests that the reactive intermediate may not always be as "free" to select among sites in a substrate molecule as originally thought.
- (2) Substituted phenyl radicals have been shown by Hammett equations, and isomer ratios, to exhibit electrophilic or nucleophilic properties depending upon the polar nature of the substituent.
- (3) The reactions and properties of the pentafluorophenyl radical have been investigated using radical sources analogous to those used for the generation of the phenyl radical. Partial rate factors have been determined for pentafluorophenylation of a range of aromatic substrates and from this data the electrophilic properties of the pentafluorophenyl radical have been deduced.
- (4) Arylation processes involving the displacement of atoms other than hydrogen have been discussed. However only aryldefluorination has been reported.
- (5) The effect of catalysts upon the arylation mechanism has been discussed. The role of aromatic nitro-groups in the mechanism for homolytic arylation has been examined, as has the effect of catalysis by transition-metal compounds. Both of these types of catalysts have been found to increase the yield of biaryls.

Chapter 2 - EXPERIMENTAL

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2.1 Instrumentation

- (a) All melting points quoted are uncorrected and were carried out using an electrothermal melting point apparatus.
- (b) Infra-red spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer, using Nujol or hexachlorobutadiene as mulling agents.
- (c) Ultra-violet spectra were recorded on a Hitachi 127 instrument.
- (d) Nuclear magnetic resonance spectra, ^1H and ^{19}F were taken on a Perkin-Elmer R12 instrument, at 60 MHz.
- (e) Gas-liquid chromatography was carried out on a Pye 104 instrument using a flame-ionisation detector and nitrogen as carrier gas. Peak heights were taken as the mean of at least four samples and quantitative results obtained by the method of internal standardisation using triangulation to calculate peak areas. Peak areas were calculated as the average of at least four runs.
- (f) Mass spectra were taken on a VG-Micromass instrument; probe potential = 4kV., chart speed = 4 inches sec^{-1} , 10 sec scan time.

2.2. Purification of Solvents and Compounds

- (a) Benzene: Sodium-dried benzene (M & B) was distilled through a short fractionating column, b.p. 80° - 81° /758 mmHg.. This material was shown to be pure by g.l.c.
- (b) Alkyl benzenes: Redistilled toluene (b.p. 109° - 111° /761 mm Hg) and cumene (b.p. 151.5° - 153° /754 mmHg) showed no detectable impurities by g.l.c.
- (c) Halogenobenzenes: Redistillation through a short fractionating column gave pure (g.l.c.) samples of fluorobenzene (b.p. 84.5° - 85.5° /755 mmHg), chlorobenzene (b.p. 131° - 132.8° /758 mmHg), and bromobenzene (b.p. 155° - 157° /763 mmHg).
- (d) Polyfluorobenzenes: m-Difluorobenzene and chloropentafluorobenzene (Bristol Organics), and hexafluorobenzene (Imperial Smelting Corp.) were

used without further purification, and showed no substantial impurities by g.l.c.

(e) Amyl Nitrite: The redistilled reagent (b.p. $102^{\circ}-4^{\circ}/762$ mmHg) was free from amyl alcohol (g.l.c.) and was stored in the dark at 5°C .

(f) Iodomethane: The commercial reagent was redistilled (b.p. $41.5^{\circ}-42.4^{\circ}/768$ mmHg). (Lit. b.p. $41^{\circ}-42^{\circ}\text{C}$)⁹⁵

(g) Bromotrichloromethane and Amyl Alcohol: Commercial samples were used without further purification.

Table 6

Compound	Recryst. Solvent	m.p. $^{\circ}\text{C}$	Lit. m.p. $^{\circ}\text{C}$
Biphenyl (B.D.H.)	Ethanol	70-71	$70-70.5$ ⁹⁵
Dibenzyl (B.D.H.)	Ethanol	51.5-53	$52-53$ ⁹⁵
Hexachlorobenzene (Aldrich)	Benzene	227-228	$228-229$ ⁹²
Nitropentachlorobenzene (Aldrich)	Toluene/Methanol	144.5-145	$144-145$ ⁹⁸
Pentachlorobenzene (Aldrich)	Ethanol	84-85	$85-86$ ⁹⁶
1,3,5-Trichlorotrifluorobenzene (Bristol Organics)	Ethanol	72-73	$71-72$ ⁹⁶
<u>p</u> -Terphenyl (Koch-Light)	Ethanol	211-212	213 ⁹⁶

(a) Benzoyl Peroxide:⁹⁹ The commercial reagent (B.D.H.) was dissolved in the minimum quantity of chloroform and the aqueous layer rejected. The solution was filtered under suction and two volumes of ice-cold methanol was added with stirring, bringing about precipitation of benzoyl peroxide as fine white needles. The solution was filtered and the peroxide recrystallised further by the above procedure. The purified peroxide

was dried in vacuo m.p. 106° - 197° C (Lit. m.p. 106° - 108° C)⁹⁶.

(b) 2,4,6-Trichloroaniline (Aldrich; 97%); 2,4,-dichloroaniline (Aldrich; 98%); 2,6-dichloroaniline (Aldrich; 97%) and 1,3,5,-trichloro-benzene (Aldrich; 98%), were used without further purification.

2.3. Synthesis of Organic Compounds

2.3.1 Pentachloroaromatic Compounds

Pentachloroaniline

Pentachloronitrobenzene (30 g; 0.10 mole) was suspended in glacial acetic acid (100 ml) in the presence of tin (20 g; 0.16 mole). The solution was heated under reflux while concentrated hydrochloric acid (12 M; 60 ml) was added slowly down the condenser. A thick white precipitate formed and the flask was shaken periodically during a two and a half hour reflux period.

The hot solution was then poured into water (1 litre) containing concentrated hydrochloric acid (12 M; 10 ml). Any residual organic material was removed from the flask by gently warming it with a small quantity of glacial acetic acid in a heating mantle, and adding this solution to water.

The precipitated solids were then filtered off and washed with water. The crude amine was recrystallised from toluene, to give fine, long white needles. M.p. 231° - 233° C. (Lit. m.p. 232° C)¹⁰⁰, yield 74.8%.

The product was separated from hexachlorobenzene, a contaminant of the recrystallised nitro-compound, by the following procedure.

The solid was dissolved in chloroform (150 ml) and this solution was carefully extracted by sulphuric acid (3 x 30 ml; 18 M). Separation of the acid extracts followed by dilution of this layer resulted in precipitation of the amine. Calc. for $C_6Cl_5NH_2$: C, 27.11; H, 0.75; N, 5.27; Cl, 64.39%; found: C, 27.33; H, 0.71; N, 5.37; Cl, 64.20%.

(b) PentachlorophenylhydrazineMethod (i)

Pentachloroaniline (10 g; 0.036 mole) was stirred in acetic acid (50 ml) at 55°-60°C, and a solution of sodium nitrite (2.9 g; 0.04 mole) in sulphuric acid (d = 1.84, 24 ml) was slowly added while the solution was being stirred. The solution turned a deep red colour as the diazonium ion was being formed. The mixture was held at this temperature for 20 mins and then cooled in an ice-salt mixture to 5°C with continual stirring. An ice-cold solution of stannous chloride dihydrate (35 g) in concentrated sulphuric acid (d = 1.8; 30 ml) was slowly added at such a rate that the temperature of the solution did not rise above 15°C. Addition of the stannous chloride dihydrate solution produced a thick white cream-like solid. When the addition was complete the mixture was stirred at room temperature for 30 min.

The residue was filtered off, using a sintered glass funnel, washed with a small amount of water, basified with ammonia solution (d = 0.88), filtered and dried at 80°C.

This white solid was placed in a Soxhlet thimble and extracted with chloroform. After five hours extraction the chloroform was removed in vacuo and the residue recrystallised from ethanol to give 2,3,4,5,6-pentachlorophenylhydrazine (89%). M.p. 178°-179°C. (Lit. m.p. 179°-180°C).¹⁰¹

The presence of the -NHNH₂ group was confirmed by infra-red spectroscopy.

Method (ii)

This second method of Suschitzky¹⁰¹, did not give the yield reported by these workers, even after many repetitions.

Pentachloronitrobenzene (5 g; 0.017 mole) was heated under reflux with hydrazine hydrate (B.D.H. 99%, 4.2 g) in a 1:1 ethanol-dioxan (75 ml)

mixture for six hours. The cool solution was filtered and the filtrate poured into 100 ml of water. This white precipitate was filtered off and recrystallised from ethanol to give a low yield of pentachlorophenylhydrazine (8%) m.p. 177° - 180° C.

Method (iii)

This method is based upon the synthesis of p-bromotetrafluorophenylhydrazine¹⁰² and provided one of the best techniques for the preparation of the hydrazine.

Fluoropentachlorobenzene (2.0 g; 7 m mole) was dissolved in an ethanol:dioxan mixture (1:1; 75 ml). To this solution was added hydrazine hydrate (5 g; 0.1 mole) and the solution was heated under reflux for six hours. Upon cooling the pale, yellow solution was poured into water (250 ml), the resulting solid was filtered off at the pump, dried and recrystallised from ethanol to give pentachlorophenylhydrazine (87.7%) m.p. 178° - 179° C. (Lit. m.p. 178° - 180° C)¹⁰¹.

(c) Pentachloriodobenzene

The method used for the preparation of this compound is based upon that of Willgerodt and Wilke¹⁰³.

Pentachloroaniline (5 g; 0.018 mole) was dissolved in glacial acetic acid (150 ml) with continuous stirring. To this was added sodium nitrite (5.9 g; 0.085 mole) dissolved in concentrated sulphuric acid (12 M; 25 ml) slowly to the amine solution keeping the temperature below 15° C by means of an ice-salt mixture. When all of this solution had been added, potassium iodide (16.6 g; 0.1 mole) was added to the red solution. A thick brown precipitate appeared together with the evolution of a large volume of gas. The suspension was stirred while coming to room temperature and allowed to stand for thirty minutes, and then filtered. The solid material was dissolved in ether, washed with sodium thiosulphate solution, dried (Na_2SO_4) and concentrated. The solid was then taken up in chloroform

(60 ml) and to this was added sulphuric acid ($d = 1.8$; 30 ml). The layers were separated, the solvent removed under vacuum and the solid recrystallised (twice) from petroleum ether (80° - 100° C).

This gave pentachloriodobenzene (37%) m.p. 213° - 214° C (Lit. m.p. 210° - 211° C)¹⁰³.

Calc. for C_6Cl_5I ; C, 19.12; Cl, 47.14; I, 33.73%; found: C, 19.26; Cl, 47.12; I, 33.52%

(d) Fluoropentachlorobenzene

Anhydrous potassium fluoride (B.D.H., Analar; 50 g) was placed in an oven at 200° C for two hours. 35 g of this solid was ground to a fine powder and placed in a round-bottomed flask (250 ml) together with nitropentachlorobenzene (18.5g; 0.062 mole) and freshly distilled dimethylformamide (55 ml). This mixture was then heated under reflux with stirring for four hours.

After this time the solution was steam distilled. Extraction of the steam distillate with ether and subsequent evaporation of the solvent produced a crop of fine white needles. Recrystallisation from ethanol gave a 23.0% yield of fluoropentachlorobenzene. M.p. 137° - 138° C. (Lit. m.p. 137° - 138° C).¹⁰⁴

Gas-liquid chromatography showed the presence of two impurities in the sample; unchanged nitropentachlorobenzene and a difluorotetrachlorobenzene which arose from further fluorination of the mono-fluorinated compound. These impurities were found in each sample of fluoropentachlorobenzene prepared, even when the sample possessed a sharp melting point.

(e) Pentachlorobromobenzene

This was prepared by the bromination of pentachlorobenzene.

Pentachlorobenzene (30 g) was placed in a round-bottomed flask (500 ml) together with some aluminium powder (1.5 g). The flask was immersed in an ice-salt mixture. To this mixture was slowly added, by means of a dropping

funnel, liquid bromine (15 ml). In some cases the reaction vessel was warmed in a bath of hot water to initiate the reaction. The reaction proceeds with evolution of hydrogen bromide and in some cases the contents of the flask ignited, although this only occurred when the bromine was added too quickly.

When all the bromine had been added, the mixture was heated under reflux on a steam-bath for 4-5 hours until the evolution of hydrogen bromide had ceased.

The white, cake-like mass was then dissolved in ethanol and a preliminary crystallisation carried out using this solvent. This produced a crop of pale yellow needles which were recrystallised from toluene, to give 86% yield of pentachlorobromobenzene, m.p. 235° - 236° C. (Lit. m.p. 237.5° C)¹⁰⁵.

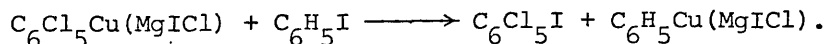
Calc. for C_6Cl_5Br ; C, 21.85; Cl, 53.87; Br, 24.2%; found: C, 22.03; Cl, 53.84; Br, 24.36%.

(f) 2,3,4,5,6-Pentachlorobiphenyl

The method of preparation involves three distinct stages:

- (a) Preparation of a polychloroaromatic Grignard reagent.
- (b) Formation of an organometallic copper intermediate from (a).
- (c) A coupling reaction involving the intermediate formed in (b) and iodobenzene.

Tetrahydrofuran is used as the solvent throughout the preparation to prevent side reactions of the type;



A three-necked 250 ml round-bottomed flask was fitted with a nitrogen flow inlet, a reflux condenser and a mechanical stirrer. A steady flow of nitrogen was passed through the apparatus for a one-and-a-half hour period,

after which time the nitrogen flow was shut off and the reaction flask charged with magnesium turnings (1.2 g), hexachlorobenzene (3.5 g) and sodium dried tetrahydrofuran (30 ml).

In a 50 ml conical flask, magnesium (0.23 g) was dissolved in sodium dried tetrahydrofuran (T.H.F.) (20 ml) and methyl iodide (2 g) was added, a slight reaction ensued and the flask was cooled in ice.

Approximately 5 ml of this Grignard reagent was added to the reaction mixture to initiate the reaction. After 5 - 10 minutes stirring, and warming the reaction vessel on a water-bath, the reaction started. To the refluxing solution was then added, in portions, hexachlorobenzene (10.5 g).

The reaction mixture was then allowed to cool to room temperature, a steady stream of nitrogen being allowed to pass through the apparatus, and cooled further to 0°C by an ice-salt mixture. After cooling the stream of nitrogen was shut off.

To this red-brown liquid was added cupric iodide (9.6 g) and the mixture stirred at 0°C for a further thirty minutes. Iodobenzene (10.2 g) was then added down the reflux condenser to the brown solid, and the mixture heated, under reflux, for three hours on a heating mantle.

The brown solution was then allowed to cool to room temperature with a continuous stream of nitrogen passing through the reaction vessel.

The cooled reaction mixture was then extracted with hot benzene to give a total volume of 150 ml. This was concentrated to 50 ml by distillation.

This brown solution was then eluted through an alumina column. Evaporation of the solvent produced dark brown crystals. These were dissolved in n-hexane and eluted through an alumina column. Evaporation of the solvent produced a crop of white needles.

This material was then recrystallised from ethanol producing 2,3,4,5,6-pentachlorobiphenyl (39%). M.p. 112° - 113° C. (Lit m.p. 123° - 124° C)¹⁰⁶.

Gas-liquid chromatography showed the presence of hexachlorobenzene in the sample.

Calc. for $C_{12}H_5Cl_5$; C, 44.1; H, 1.5; Cl, 54.4%; found: C, 43.9; H, 1.46; Cl, 54.0%.

(g) Bis(Pentachlorophenyl)Mercury

The preparation of this compound is based on a metallation reaction using pentachlorophenyl lithium. The preparation is divided into two parts:

- (a) Preparation of the pentachlorophenyl lithium reagent.
- (b) Metallation involving mercuric chloride.

(a) Pentachlorophenyl lithium

All apparatus was baked in an oven at 150° C prior to use.

The reaction was carried out in a 500 ml, three necked round-bottomed flask equipped with a nitrogen inlet, mechanical stirrer, a pressure-equalising dropping funnel and a double-surface reflux condenser.

The system was flushed through with oxygen free nitrogen. With a stream of nitrogen passing through the system, hexachlorobenzene (5.69 g; 0.02 mole) was added to the flask followed by sodium-dried ether (400 ml). n-Butyl lithium in hexane (0.02 M; 12.5 ml) was displaced from its container by nitrogen into a pre-calibrated pressure equalising dropping funnel.

The reaction vessel was cooled to around -8° to -12° C by means of an ice-salt bath, and with rapid stirring the n-butyl lithium solution was slowly added over a period of 30-45 mins. At the end of this time, the solution acquired a pale yellow colour and a small quantity of unreacted hexachlorobenzene remained in the flask.

(b) A solution of mercuric chloride (2.72 g; 0.01 mole) in sodium-dried ether (120 ml) was added over 1½ hours to the pentachlorophenyllithium solution. The reaction temperature was maintained at -10° to 0°C . A white precipitate formed immediately. The reaction mixture was allowed to warm to room temperature over a 2 hour period. The solvent was evaporated and the residue was washed with hot water and dried.

This material was digested three times with warm ethyl ether and once with hot water. After drying in air there remained 6.83 g (84%) of white crystals. M.p. 381° - 383°C . (Lit. m.p. 383°C)¹⁰⁷.

The infrared (Nujol mull) showed the following characteristic absorptions: 686, 1176, 1202, 1300 cm^{-1} .

Calc. for $(\text{C}_6\text{Cl}_5)_2\text{Hg}$; C, 20.60; Cl, 50.78; Hg, 28.60%; found: C, 20.60; Cl, 50.56; Hg, 28.61%.

(h) Pentachlorophenylazotriphenylmethane

A three-necked 500 ml round-bottomed flask was fitted with a mechanical stirrer and a double-surface reflux condenser.

Pentachlorophenylhydrazine (2.3 g; 0.008 mole) was dissolved in sodium-dried ether (200 ml) with stirring.

In a conical flask triphenylchloromethane (1.35 g; 0.004 mole) was dissolved in sodium-dried ether (100 ml), and this was slowly added to the stirred solution of the hydrazine. When the addition was complete the solution was allowed to stand for 1½ hours, after which time the precipitated hydrochloride was filtered off.

A solution of bromine water (1%; 200 ml) was added to the ethereal solution by means of a dropping funnel with rapid stirring.

The solution was then transferred to a 500 ml separating funnel and the organic layer removed, washed with water (2 x 50 ml) and dried over calcium chloride.

The solution was filtered and the solvent removed under reduced pressure leaving an orange-coloured residue. This solid was dissolved in the smallest quantity of ether, warmed slightly in a hot water-bath and then cooled in an ice bath, the sides of the conical flask being scratched as the solution cooled. This produced fine orange crystals of *pentachloro-phenylazotriphenylmethane* (1.57 g; 45%) m.p. 111°-112°C.

(Found: C, 58.2; H, 3.00; Cl, 34.0; N, 5.13%. $C_{25}H_{15}N_2Cl_5$ requires; C, 57.63; H, 2.88; N, 5.37, Cl, 34.10%).

The infrared spectrum of the sample showed no (N-H) frequency and hence the absence of the hydrazo compound.

2.3.2. Polychloropolyfluoroaromatic Compounds

(a) 4-Chloro-2,3,5,6-Tetrafluorophenylhydrazine

Into a 250 ml round bottomed flask was placed pentafluorochlorobenzene (7.84 g; 0.038 mole) dissolved in dioxan (200 ml). To this solution was added hydrazine hydrate (1.90 g; 0.037 mole) and the solution heated under reflux for six hours.

After this time a portion of the solvent was removed under reduced pressure and to the remaining solution was added 100 g of ice. When all the ice had melted the solution was filtered at the pump, the solid washed with water and dried. The crude product was then recrystallised from petroleum ether (80°-100°), giving light sepia coloured crystals, m.p. 73°-75°C. (Lit. m.p. 75°-76°C)¹⁰⁸ - 56% yield.

Infrared spectroscopy showed the characteristic (N-H) stretching frequency in the 3500 - 3300 cm^{-1} region.

(b) 4-Chloro-2,3,5,6-Tetrafluorobiphenyl

In a 250 ml round-bottomed flask was dissolved 4-chloro-2,3,5,6-tetrafluorophenylhydrazine (3.5 g; 0.016 mole) in sodium-dried benzene (150 ml). To this solution was added, in portions, bleaching powder (35 g). After a brief induction period of 5-10 mins a vigorous, exothermic reaction ensued and the solution changed colour from deep orange to yellow. The

reaction was allowed to proceed at room temperature until all sign of the evolution of gas had ceased.

A further quantity of bleaching powder (15 g) was added and the suspension was refluxed for 2 hours.

The reaction mixture was allowed to cool to room temperature and the deep-red solution filtered at the pump. The reaction vessel and the residue on the funnel were washed through with benzene and the filtrate and washings combined and concentrated, producing a deep red crystalline residue.

These crystals were dissolved in petroleum ether (60° - 80°) and eluted through an alumina column, removal of the solvent after complete elution produced a white crystalline product.

This was then recrystallised from ethanol to give white *crystalline* plates. M.p. 105° - 106° C. (Lit. m.p. 106° - 107° C)⁷¹ - 38% yield. Gas-liquid chromatography showed the absence of any impurities.

Calc. for $C_{12}H_5F_4Cl$; C, 55.2; H, 1.91; Cl, 13.62; F, 29.27%; found: C, 55.0; H, 1.92; Cl, 13.71; F, 29.30%.

(c) 3,5-Difluoro-2,4,6-Trichlorophenylhydrazine

Into a 250 ml two-necked round-bottomed flask was placed 2,4,6-trifluoro-1,3,5-trichlorobenzene (5.60 g; 0.023 mole) together with dioxan (150 ml). To this was slowly added, with shaking hydrazine hydrate (2 ml) and the solution was heated under reflux for 6 hours.

Upon cooling to room temperature the contents of the flask were poured into an ice/water mixture (500 ml) which was rapidly stirred. When all the ice had melted the white product was filtered using a sintered glass funnel. The product was sucked dry at the pump and recrystallised from petroleum ether (60° - 80°), giving the hydrazine (48%) m.p. 119° - 120° (Lit. m.p. 121° - 122° C)¹⁰⁹.

Infrared spectroscopy showed the characteristic NH absorptions $\approx 3500 - 3300 \text{ cm}^{-1}$.

(d) 3,5-Difluoro-2,4,6-Trichlorobiphenyl

This was prepared by a similar method to that previously described (p.45)

The product from the oxidation was isolated after column chromatography (alumina column (and n-hexane as eluent and recrystallisation from ethanol. This gave *3,5-difluoro-2,4,6-trichlorobiphenyl* (35%), m.p. $66^{\circ}-68^{\circ}\text{C}^{110}$. (Found: C, 49.8; H, 0.05; Cl, 38.5; F, 10.6%. $\text{C}_{12}\text{H}_5\text{Cl}_3\text{F}_2$ requires C, 49.1; H, 0.12; Cl, 36.3; F, 12.9%)

2.3.3. Polyfluoroaromatic Compounds

(a) Pentafluorophenylhydrazine

This synthesis was adapted from that described by Haszeldine *et.al.*⁷⁰

Hexafluorobenzene (40.0 g; 0.14 mole) was dissolved in ethanol (150 ml) and to this solution was added hydrazine hydrate (25 g; 0.5 mole) and the mixture boiled under reflux for twelve hours.

Removal of the solvent and unreacted hexafluorobenzene left a brown residue. Water was added to this residue and the product filtered. The pale yellow crystals were washed with water, dried and recrystallised from petroleum ether ($80^{\circ}-100^{\circ}$) to give pentafluorophenylhydrazine (68%), m.p. $75^{\circ}-76^{\circ}\text{C}$. (Lit. m.p. $77^{\circ}-78^{\circ}\text{C}$).⁷⁰

(b) 2,3,4,5,6-Pentafluorobiphenyl

This was prepared by the oxidation of the corresponding hydrazine by the method previously described (d).

This gave 2,3,4,5,6-pentafluorobiphenyl, m.p. $108^{\circ}-110^{\circ}\text{C}$. (Lit. m.p. $111^{\circ}-112^{\circ}\text{C}$)⁷⁰ in 64% yield. After recrystallisation and upon passing through an alumina column in n-hexane gave a sample m.p. $110^{\circ}-112^{\circ}\text{C}$.

2.3.4. Miscellaneous

(a) 4-Benzoyloxybiphenyl

This was prepared using the Schotten-Baumann method for benzoyloxylation.

4-Hydroxybiphenyl (3.4 g; 0.02 mole) was suspended in sodium hydroxide (50 ml) in a thick walled glass vessel. To this suspension was added benzoyl chloride (3.5 ml; 0.027 mole). This mixture was then shaken vigorously for $\frac{1}{2}$ hour during which time a white solid appeared. This precipitation was filtered off and washed thoroughly with water, dried at the pump and recrystallised from ethanol (twice).

This gave a 57% yield of 4-benzoyloxybiphenyl, m.p. 149° - 150° C. (Lit. m.p. 150° C)⁹⁵.

The infrared spectrum showed the presence of the (C=O) stretching frequencies in the region $1600 - 1450 \text{ cm}^{-1}$.

2.4. The Decomposition of Pentachloroaniline in Various Solvents using Amyl Nitrite.

2.4.1. General Procedure

Unless otherwise stated the procedure described here was adopted for all experiments.

Pentachloroaniline (10 m.mole; 2.65 g) was dissolved in the redistilled solvent (100 ml) in a 250 ml, two necked flask, fitted with a dropping funnel. To this solution was slowly added, by means of the dropping funnel, redistilled amyl nitrite (10-15 m.mole) and the solution was shaken periodically.

The reaction was slightly exothermic and proceeded with the evolution of gas.

When the evolution of gas ceased, the solution was heated under reflux for two hours.

When the reaction had cooled to room temperature the solvent was removed by distillation under reduced pressure and retained for analysis by g.l.c. In all reactions the presence of amyl alcohol was detected by comparison with an authentic sample.

The residue was dissolved in chloroform (50 ml) and extracted with water and sodium hydroxide ($2 \times 30 \text{ cm}^3$), respectively. The aqueous extracts

were separated and the organic layer dried over calcium chloride.

The water extracts were examined for chloride ions by acidification with nitric acid (2 M) followed by the addition of a few drops of silver nitrate (0.1 M) - the formation of a cloudy precipitate indicates the presence of chloride ions, which were detected in all reactions.

Thin layer chromatography of the acidified alkaline extracts, using alumina plates and a mixture of acetone:toluene (1:9), as eluent, provided evidence for the presence of phenols¹¹¹, using ultraviolet light as the developer.

The chloroform solution was filtered, and the solvent removed on a rotary evaporator. The residue was dissolved in chloroform (30 ml) and analysed by g.l.c. (15% Apiezon:240°C).

The results from the g.l.c. analysis are summarised in Table 7. Yields of products are expressed as mole per mole % of *pentachloroaniline*.

The only solvent to produce a biaryl apart from benzene, was chlorobenzene. The main products isolated from the majority of arenes were penta- and hexachlorobenzenes. The following procedure was used to isolate these compounds.

Removal of the chloroform on the rotary evaporator was followed by co-distillation of the residue with triethylene glycol (trigol). The initial stages of the distillation produced a thick white solid material that was shown to consist of a mixture of hexachlorobenzene and pentachlorobenzene, identified by g.l.c. and mass spectrometry.

Dilution of the trigol distillate with water gave a white solid, shown to be pentachlorobenzene. Extraction with ether only produced biaryl in one case, the products isolated being the polychlorobenzenes.

Using benzene as the substrate the following procedures were used for the isolation of 2,3,4,5,6-pentachlorobiphenyl.

(i) The reaction work-up was the same as that described in the general procedure. After removal of the solvent from the reaction mixture, the residue was dissolved in *n*-hexane and passed through an alumina column. The total volume of eluent was 300 ml. Evaporation of the solvent upon a rotary evaporator, produced a white crystalline solid, which upon recrystallisation from ethanol gave a 67.5% yield of 2,3,4,5,6-pentachlorobiphenyl, m.p. 111°-113°C. (Lit. m.p. 123°-124°C)¹⁰⁶. Analysis of this specimen by g.l.c. (OV-1; 210°C) showed the sample to contain ca 2% of hexachlorobenzene. The main component having the same retention time as an authentic sample of 2,3,4,5,6-pentachlorobiphenyl, identified from its mass spectral fragmentation pattern, and from g.l.c. analysis.

Calc. for $C_{12}H_5Cl_5$; C, 44.1; H, 1.5; Cl, 54.4%; found: C, 43.7; H, 1.5; Cl, 54.7%.

(ii) A second method of isolating 2,3,4,5,6-pentachlorobiphenyl was attempted. After evaporation of the solvent from the reaction mixture the residue was steam distilled. The steam distillate was extracted with ether (3 x 50 ml). The organic layer was separated from the aqueous layer, ^{and} dried (calcium chloride). The pale yellow crystalline solid was recrystallised from ethanol (twice) to give a white solid, m.p. 93°-95°C. Gas-liquid chromatography (15%, Apiezon, 230°C) showed the product to consist of hexachlorobenzene, pentachlorobenzene and 2,3,4,5,6-pentachlorobiphenyl, all identified by a comparison of their retention times with authentic samples.

The residue from the steam distillation was then extracted with ether (3 x 50 ml) the organic layer removed, dried (calcium chloride) and filtered into a distillation apparatus. The solvent was carefully removed by warming

the distillation flask on a water-bath, and the residue distilled under reduced pressure. During the course of the distillation the product sublimed in the condenser, temperature 220°C (15 mmHg), producing a white crystalline solid. Recrystallisation of this material produced a solid, m.p. 111°C-113°C in 54% yield.

G.l.c. analysis (15% Apiezon; 220°C) showed the solid to consist of 2,3,4,5,6-pentachlorobiphenyl as the major component together with hexachlorobenzene.

Table 7

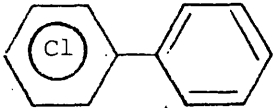
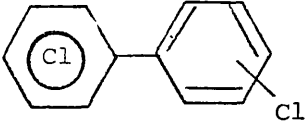
Product yields from pentachlorophenyl radicals in various substrates

Substrate	$C_6Cl_5NH_2-C_5H_{11}ONO$	$C_6Cl_5NHNH_2-CaOCl_2$
	C_6Cl_6 C_6Cl_5H	C_6Cl_5H
Benzene (a)	< 0.2 5.3	< 0.2
Fluorobenzene	< 0.2 5.4	< 0.2
Chlorobenzene	< 0.2 5.3	< 0.2
Bromobenzene	< 0.2 5.4	< 0.2
Toluene	< 0.2 15.9	8.9
Cumene	1.8 6.5	1.8
<u>p</u> -Xylene	1.8 5.6	13.9
Anisole	21.2 1.7	4.1

(a) 2,3,4,5,6-pentachlorobiphenyl was the major product. Yields are expressed in mole per mole % of pentachloroaniline and mole per mole % of pentachlorophenylhydrazine respectively.

Table 8

Biaryl products isolated from pentachloroaniline-amyI nitrite mixtures using benzene and chlorobenzene

Biaryl	m.p. (°C)	m/e	Found (%)			Calc. (%)		
			C	H	Cl	C	H	Cl
	111-113	324 ^(a)	43.7	1.5	54.7	44.1	1.5	54.4
	71-73	358-370 ^(b)	39.4	1.2	58.7	39.9	1.1	59.0

(a) isotope splitting pattern: $[\text{Cl}]^{35}$;
 Relative intensity (x 100) calc. 60 : 100 : 67 : 20 : 37
 Relative intensity (x 100) found: 60 : 100 : 68 : 21 : 35

(b) isotope splitting pattern $[\text{Cl}^{35}]$;
 Relative intensity (x 100) calc. 50 : 100 : 83 : 37 : 9
 Relative intensity (x 100) found: 51 : 100 : 81 : 36 : 7

2.4.2 Iodomethane

The same general procedure was adopted. (2.4.1.). Removal of the solvent from the reaction mixture by vacuum distillation resulted in a crystalline residue, which was dissolved in chloroform (30 ml) and analysed by g.l.c.; the results are tabulated in Table 9. The components were identified by the addition of known quantities of authentic samples.

Removal of the solvent after g.l.c. analysis, and steam-distillation of the resulting crystalline solid, produced two types of distillate. The first consisted of a dark brown oily liquid immiscible with water, followed by a light yellow liquid.

The heavy oil was separated from the aqueous distillate and retained; the aqueous distillate was extracted with ether (3 x 50 ml). The ethereal layer being separated, dried (calcium chloride), filtered and the solvent removed. A residue was left. Further characterisation of this material was not carried out.

The residue from the steam distillation was extracted with ether (2 x 100 ml). Removal of the solvent and elution from an alumina column with n-hexane produced a white crystalline solid. Recrystallisation of this from ethanol, and then from petroleum ether (80°-100°) produced 2,3,4,5,6-pentachloriodobenzene (12%), m.p. 206°-207°C. Mix. m.p. 205°-208°C; (Lit. m.p. 209°-210°C)¹⁰³

G.l.c. (15% Apiezon:column temp. 240°C) confirmed the identity of this specimen as pentachloriodobenzene by a comparison of its retention time with an authentic sample.

2.4.3. Bromotrichloromethane

After the same general work-up previously described (p. 59), the solution was analysed by g.l.c. (15% Apiezon, column temp. 240°C.) and the results are shown in Table 10.

Table 9

Decomposition of pentachloroaniline by amyl nitrite in iodomethane

Expt. No.	C_6Cl_5I %	C_6Cl_5H %	$C_6Cl_5NH_2$ %
17	26.1	54.46	3.1
18	26.8	54.8	3.0

Yields are expressed as a percentage of total amine consumed.

Table 10

Decomposition of pentachloroaniline by amyl nitrite in bromotrichloromethane

Expt. No.	C_6Cl_5Br %	C_6Cl_6 %	$C_6Cl_5NH_2$ %
19	17.0	20.0	7.4
20	17.5	19.6	7.3

Yields are expressed as a percentage of total amine consumed.

2.5. The Oxidation of Pentachlorophenylhydrazine in Various Solvents

2.5.1. General Procedure

Oxidation of polyfluorohydrazines has been carried out using silver oxide and bleaching powder as the oxidising agents. Preliminary experiments using these two oxidising agents have shown that bleaching powder gives better results and in general is easier to handle.

The following procedure was used.

The hydrazine (5-10 m.mole) was dissolved in redistilled solvent (100 ml) and to this suspension was slowly added portions of bleaching powder (25-30 g). After an induction period of 5-10 mins gas was quickly evolved and the reaction vessel became warm. When the evolution of gas

had ceased, the reaction vessel was charged with a further quantity of bleaching powder (5 g) and the suspension heated under reflux for a two hour period.

The reaction mixture was then cooled, filtered and concentrated by evaporation.

The residue, dissolved in chloroform (30 ml), was analysed by g.l.c. (15% Apiezon; 232°C). The results are tabulated in Table 11.

Removal of the solvent from the reaction mixture and co-distillation of the residue with trigol, produced mixtures of polychlorobenzenes initially on dilution with water. Dilution of the later trigol distillates with water produced biaryls in only two cases, chlorobenzene and toluene (Table 12). Both of these products were recrystallised from ethanol.

When benzene had been used as the substrate, the isolation of 2,3,4,5,6-pentachlorobiphenyl was attempted in separate experiments using the following procedures.

(i) The standard work-up procedure (2.5.1) was used for this reaction.

After filtering off the inorganic solids, the solution was transferred to a distillation apparatus. The solvent was carefully removed and the residue distilled under reduced pressure. This produced a pale yellow solid (b.p. 210°C/10 mmHg) which collected in the condenser and receiver. The whole apparatus was washed through with ethanol and crystallisation from this solvent produced a white crystalline solid, m.p. 109°C-111.5°C, in 50% yield.

G.l.c. (OV1; 180°C) showed the major product to consist of 2,3,4,5,6-pentachlorobiphenyl, together with pentachlorobenzene as a minor impurity.

Calc. for $C_{12}H_5Cl_5$; C, 44.10; H, 1.53; Cl, 54.40%; found: C, 43.98; H, 1.52; Cl, 54.36%.

(ii) After removal of the inorganic solids from the reaction mixture, the solvent was removed and the residue recrystallised from ethanol (three times) to produce 2,3,4,5,6-pentachlorobiphenyl (72%), m.p. 111° - 113° C. The identification of this solid was confirmed by g.l.c. (15% Apiezon; 240° C), by a comparison of its retention time with that of an authentic sample. Pentachlorobenzene was also present in the isolated sample, which successive recrystallisations failed to remove.

Table 11

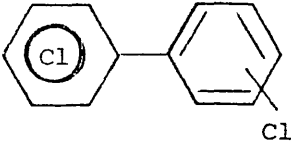
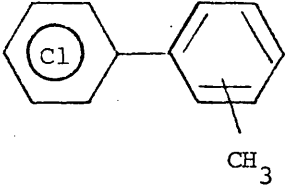
Oxidation products from pentachlorophenylhydrazine by bleaching powder. (Yields are mole per mole % of pentachlorohydrazine)

Solvent	Expt.21 C_6Cl_5H	Expt.22 C_6Cl_5H
Benzene (a)	0.19	0.20
Fluorobenzene	0.16	0.24
Chlorobenzene	0.27	0.24
Bromobenzene	0.14	0.10
Toluene	8.97	8.69
Cumene	1.76	1.82
<u>p</u> -Xylene	13.97	13.61
Anisole	4.00	4.37

(a) 2,3,4,5,6-Pentachlorobiphenyl is the main isolated reaction product.

Table 12

Isomer mixtures of biaryls from the oxidation of pentachlorophenylhydrazine using bleaching powder

Biaryl mixture	m.p.	m/e	Found			Calculated		
			C	H	Cl	C	H	Cl
	73-75°	(a) 358-370	39.1	1.1	60.2	39.9	1.1	59.0
	71-75°	(b) 338-348	43.2	2.2	51.8	45.8	2.1	52.1

(a) Isotope splitting pattern: $[\text{Cl}]^{35}$;

Relative intensity (x 100) calc. 50 : 100 : 83 : 37 : 9

Relative intensity (x 100) found: 51 : 100 : 82 : 39 : 11

(b) Isotope splitting pattern $[\text{Cl}]^{35}$

Relative intensity (x 100) calc. 60 : 100 : 67 : 20 : 3.7

Relative intensity (x 100) found: 61 : 100 : 67 : 23 : 3.5

2.6. Alternative Methods for the Generation of the Pentachlorophenyl Radical

2.6.1. Photolysis of Pentachloriodobenzene

The photolytic decompositions were carried out in a 1 litre photochemical reactor using a Hanovia water-cooled mercury arc-lamp.

The apparatus was flushed through with oxygen-free nitrogen prior to use, and was charged with 500 ml of redistilled benzene into which was dissolved pentachloriodobenzene. A continuous stream of nitrogen was allowed to pass through the apparatus during the course of the photolysis.

After the required decomposition time the blood-red solution was analysed for its free iodine content by titration with sodium thiosulphate (0.0984 M).

The benzene portions taken for titration were separated from the aqueous solution, dried (magnesium sulphate) and returned to the bulk of the solution.

Gas-liquid chromatography (15% Apiezon; 220°C) showed the presence of the following components; pentachloriodobenzene, 2,3,4,5,6-pentachlorobiphenyl and a small peak corresponding to hexachlorobenzene. The results are given in Table 13.

Table 13

Products from the photolytic decomposition of pentachloriodobenzene

Wt. of C_6Cl_5I (g)	Photolytic Period (hr)	C_6Cl_5I %	C_6Cl_5Ph %	C_6Cl_6 %	I_2 %
0.27	10	49.3	12.7	3.1	24.6
0.56	30	56.9	22.0	3.6	37.37

2.6.2. Photolysis of Bis(Pentachlorophenyl)Mercury

The same photolytic apparatus was used as above.

Bis(pentachlorophenyl)mercury (1.0 g; 1.4 m.mole) was suspended in sodium-dried benzene (500 ml). The sample did not completely dissolve. This solution was then photolysed for a ten hour period.

At the end of the reaction no metallic deposit was seen on the walls of the reactor.

The solvent was distilled off (b.p. 79° - 80° C/758 mmHg) and a sample retained for g.l.c. analysis.

The solid residue was recrystallised from ethanol and the insoluble material filtered off from the hot ethanolic solution.

From the crystallisation a white solid (0.26 g; m.p. 194° - 196° C) was obtained. Thin-layer chromatography of this solid, using alumina plates and an acetone/toluene eluting mixture, showed the sample to contain hexachlorobenzene together with some of the starting material. Infrared analysis of this product also confirmed its identity as hexachlorobenzene.

2.6.3. The Thermal Decomposition of Pentachlorophenylazotriphenylmethane in Various Solvents

2.6.3.1. Benzene

Pentachlorophenylazotriphenylmethane (0.5 g; 1.0 m.mole) was dissolved in sodium-dried benzene (150 ml). The pale-yellow solution was placed in a thermostated oil-bath at 80° C for 1 hour. The decomposition of the solid observed by the evolution of gas.

Gas-liquid chromatography (15 Apiezon, 220° C) of the reaction mixture showed the presence of pentachlorobenzene (28%) and 2,3,4,5,6-pentachlorobiphenyl (46%), identified by a comparison of their retention times with authentic samples.

2.6.3.2. Bromotrichloromethane

The work-up was similar to that previously described, (page 70)

Gas-liquid chromatography of the reaction mixture (15% Apiezon: column temperature 240°C) showed the presence of the following components: pentachlorobromobenzene (15%) hexachlorobenzene (53%) and pentachlorobenzene (31%).

2.7. The Decomposition of Some Polychloroanilines by Amyl Nitrite in Benzene

2.7.1. General Procedure

The polychloroanilines used for this study were, 2,4- and 2,6-dichloroaniline and 2,4,6-trichloroaniline.

The polychloroaniline (20 m.mole) was suspended in redistilled sodium-dried benzene (100 ml). To this suspension was slowly added, at room temperature amyl nitrite (20-22 m.mole). With the exception of 2,4,6-trichloroaniline, no immediate reaction was observed only the precipitation of a fine yellow solid. In the case of the trichloroaniline an immediate reaction ensued producing an exothermic evolution of gas.

When the addition of the amyl nitrite was complete the solution was heated under reflux for two hours, during which time the solids deposited at room temperature decomposed.

When the solution had cooled to room temperature the solvent was removed under reduced pressure and retained for g.l.c. analysis. The presence of amyl alcohol was detected in all cases. The residue was dissolved in chloroform (30 ml) and analysed by g.l.c. (OV1; 85° and 155°C). The results are shown in Table 14.

Table 14

Amine	Expt. No.	Unreacted Amine (%)	$C_6H_xCl^{1}_{6-x}$ (%)	2 Biaryl (%)
2,4-Dichloro x = 4	23	11.53	1.18	57.30
	24	11.97	1.32	56.74
	Mean	11.80	1.25	57.00
2,6-Dichloro x = 4	25	29.04	24.87	39.71
	26	29.44	24.97	39.86
	Mean	29.24	24.92	39.73
2,4,6-Trichloro x = 3	27	40.37	31.02	10.01
	28	41.86	30.09	9.27
	Mean	41.11	30.55	9.64

1. Determined by internal standardisation using authentic sample.
2. Determined using Ph.Ph as marker, assuming linear response for all isomers.

After analysis the solution was washed with;

- (a) 2 x 25 ml 2M NaOH
- (b) 2 x 25 ml water
- (c) 2 x 25 ml 6M HCl
- (d) 2 x 25 ml sat. $NaHCO_3$
- (e) 2 x 50 ml water

Extracts from (a) and (b) were tested for chloride ion using silver nitrate and the presence of this ion was shown in the reactions of 2,6-dichloroaniline and 2,4,6-trichloroaniline.

The chloroform layer was separated from the aqueous layer, dried (calcium chloride) and concentrated. The residues were eluted through a

silica-gel column using petroleum ether (40° - 60°), portions of the eluent (50 ml) were collected. The solvent evaporated and the melting point of any solid material taken. The course of the chromatography was followed by using t.l.c.

Biaryl fractions were obtained as oils from the 2,4- and 2,6-dichloroaniline solutions.

2,4,6-Trichloroaniline produced a pale yellow oil, which upon trituration with ethanol produced a crystalline solid, m.p. 60° - 61° C. (Lit. m.p. 2,4,6-trichlorobiphenyl, 62° - 63° C)⁹⁵.

G.l.c. analysis (OV.1; 150°) showed the solutions to contain 2,4,6-trichlorobiphenyl and 1,3,5-trichlorobenzene, and the relative amounts of these components was calculated using g.l.c.

2.8. The Thermal Decomposition of Benzoyl Peroxide in Some Polychloropolyfluorobenzenes

2.8.1. General Procedure - Decomposition in Single Solvents

Benzoyl peroxide (5 m.moles) was placed in a 50 ml round-bottomed flask together with the substrate (10 m.mole) and the flask equipped with a reflux condenser. The reaction vessel was then placed in a thermostatted oil-bath (80° C) for a period of 72 hours. After which time the flask was removed, allowed to cool to room temperature and the reaction mixture dissolved in ether (40 ml). The solution was then extracted with sodium bicarbonate (2 x 50 ml) and water (2 x 50 ml). The aqueous extracts were combined and extracted with ether (2 x 50 ml) and these ethereal washings were then combined with the organic layer from above and dried (CaCl_2).

The solution was filtered into a 100 ml round-bottomed flask, the solution was concentrated and the residue dissolved in chloroform (30 ml). This solution was then analysed using the following g.l.c. conditions;

- 1,3,5-trichlorotrifluorobenzene, 15% Apiezon, column temperature 220°C;
 * chloropentafluorobenzene; 15% Apiezon, column temperature, 155°C.

Table 15

Decomposition of benzoyl peroxide in 1,3,5-trichloro-
trifluorobenzene. (Yields in mole per mole % of peroxide)

Expt. No.	$C_6H_5 \cdot C_6F_3Cl_2$	$C_6H_5 \cdot C_6F_2Cl_3$	Ph.Ph
1	1.30	1.4	4.0
2	1.30	1.4	4.0
Mean	1.30	1.4	4.0
Relative Yield(%)	48.2	51.8	-

Table 16

Decomposition of benzoyl peroxide in pentafluoro-
chlorobenzene. (Yields in mole per mole % of peroxide)

Expt. No.	Ph. C_6F_5	$C_6H_5 \cdot C_6F_4Cl$			Ph.Ph
		<u>o</u> -	<u>m</u> -	<u>p</u> -	
3	0.7	11.30	7.80	6.00	2.00
4	0.8	11.40	8.0	6.30	1.50
Mean	0.75	11.35	7.90	6.20	1.75
Relative Yield(%)	-	44.8	31.2	24.2	-
Literature Values ⁷¹	-	44.1	35.0	20.9	-

2.8.2. Decomposition of Benzoyl Peroxide in Single Substrates in the Presence of Trichloroacetic Acid

The procedure previously described in part 2.8.1. was used. The only modification being that trichloroacetic acid (1.5 m.mole) was added to the reaction. The reaction flask was equipped with a reflux condenser and the flask placed in a thermostatted oil-bath (80°C) for a 72 hour period. The flask was removed at the end of this time, allowed to cool to room temperature and the reaction mixture taken up in ether (40 ml). The ethereal solution was then extracted with sodium bicarbonate (2 x 50 ml) and water (2 x 50 ml) the aqueous extracts were then combined and extracted with ether (2 x 50 ml). After this all the ethereal washings were combined with the organic layer and dried (CaCl₂).

The solution was filtered into a 100 ml round-bottomed flask, concentrated and the residue dissolved in chloroform (30 ml). The solution was then analysed by g.l.c. as previously described. The results are given in Tables 17 and 18.

Table 17

Decomposition of benzoyl peroxide in 1,3,5-trichlorotrifluoro benzene in the presence of trichloroacetic acid. (Mole per mole % of benzoyl peroxide)

Expt. No.	$C_6H_5 \cdot C_6F_3Cl_2$	$C_6H_5 \cdot C_6F_2Cl_3$	Ph.Ph
5	1.9	2.0	1.4
6	1.6	1.8	1.3
Mean	1.8	1.9	1.4
Relative Yield (%)	49	51	-

Table 18

Decomposition of benzoyl peroxide in chloropentafluorobenzene in the presence of trichloroacetic acid. (Mole per mole % of benzoyl peroxide.)

Expt. No.	Ph.C ₆ F ₅	C ₆ H ₅ .C ₆ F ₄ Cl			Ph.Ph
		o-	m-	p-	
7	1.4	19.4	18.4	14.9	1.3
8	1.3	19.6	18.3	14.8	1.3
Mean	1.4	19.5	18.4	14.9	1.3
Relative Yield (%)	-	37.1	34.7	28.2	-
Literature Value (%) ⁷¹	-	44.1	35.0	20.9	-

2.8.3. Decomposition of Benzoyl Peroxide in Mixed Solvents - Competition Experiments

Into a 50 ml round-bottomed flask was placed benzoyl peroxide (5 m.mole), the substrate (10 m.mole) and hexafluorobenzene (10.m.mole) together with a small quantity of trichloroacetic acid (1.5 m.mole). The runs were duplicated. The reaction vessels equipped with reflux condensers were then placed in a thermostated oil-bath (80°C) for a period of 72 hours. At the end of this time the flasks were removed from the oil-bath and allowed to cool to room temperature. Acidic material was removed from the reaction mixtures by the procedure previously outlined.

The organic material was then analysed by gas-liquid chromatography under the conditions described in page 74. The results are given in Tables 19 and 20.

Table 19

Decomposition of benzoyl peroxide in 1,3,5-trichloro-trifluorobenzene and hexafluorobenzene. (Mole per mole % of benzoyl peroxide).

Expt. No.	Ph.C ₆ F ₅	Ph.C ₆ F ₃ Cl ₂	Ph.C ₆ F ₂ Cl ₃	Ph.Ph
9	27.6	5.4	22.9	0.6
10	28.0	5.1	22.5	0.7
Mean	27.8	5.3	22.7	0.7
Relative Yield(%)		20.7	79.3	

Table 20

Decomposition of benzoyl peroxide in chloropentafluorobenzene and hexafluorobenzene. (Mole per mole % of benzoyl peroxide).

Expt. No.	Ph.C ₆ F ₅	Ph.C ₆ F ₄ Cl			Ph.Ph
		<u>o-</u>	<u>m-</u>	<u>p-</u>	
11	13.6	9.1	7.2	5.3	0.9
12	13.3	8.9	6.8	4.8	0.9
Mean	13.5	9.0	7.0	5.1	0.9
Relative Yield (%)		42.8	33.3	23.8	-

Chapter 3 - DISCUSSION

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3.1. The Pentachlorophenyl Radical

The interest in this radical intermediate follows on from the discovery and subsequent investigation into the properties of the pentafluorophenyl radical. The primary aim of this work has been to show that by using reactions analogous to those used for the generation of the pentafluorophenyl radical^{65,70}, products derived from the pentachlorophenyl radical could be isolated.

3.1.1. Pentachloroaniline-Amyl Nitrite Reaction

The evidence for the participation of pentachlorophenyl radicals, generated by the action of amyl nitrite on pentachloroaniline in a wide range of substrates, comes from two sources.

(i) Formation of derivatives of 2,3,4,5,6-pentachlorobiaryls derived from attack of the pentachlorophenyl radical on an aromatic nucleus followed by subsequent dehydrogenation.

(ii) Abstraction reactions, leading to products e.g. pentachlorobenzene, derived from the pentachlorophenyl radical.

The formation of biaryls from the decomposition of aromatic amines by amyl nitrite in aromatic solvents was first utilised by Shu Huang in 1959⁵⁴ and further developed by Cadogan in 1962⁵⁵. Application of this reaction to pentafluoroaniline^{65,112} has enabled the reactions of the pentafluorophenyl radical to be examined, and the formation of biaryls derived from this radical is the preferred reaction in aromatic substrates. Products arising from abstraction reactions involving the pentafluorophenyl radical have also been investigated¹¹³. The pentachlorophenyl radical showed the following peculiarities when compared to similar reactions involving the pentafluorophenyl radical:

(i) Formation of biaryls by radical attack on an aromatic nucleus appears to be an unfavoured reaction route.

(ii) The predominance of pentachlorobenzene as the major reaction

product in these reactions suggests that the pentachlorophenyl radical is participating in a hydrogen abstraction reaction.

Decomposition of pentachloroaniline in benzene by amyl nitrite resulted in the formation of 2,3,4,5,6-pentachlorobiphenyl (60-70%) together with pentachlorobenzene (5.3%). The only other substrate to produce a biaryl from this method was chlorobenzene.

This gave an isomeric mixture of hexachlorobiphenyls together with pentachlorobenzene (5.3%). Decomposition of pentachloroaniline by amyl nitrite in the solvents listed in Table 21, resulted in products derived from abstraction reactions of pentachlorophenyl radicals. The formation of hexachlorobenzene is discussed in Section 3.3

Table 21

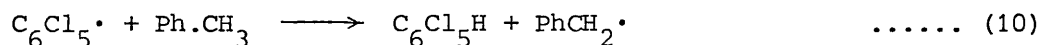
Product yields from pentachlorophenyl radicals in various solvents. (Mole per mole % of pentachloroaniline and mole per mole % of pentachlorophenylhydrazine)

Solvent	Radical Source		
	$C_6Cl_5NH_2-C_5H_{11}ONO$		$C_6Cl_5NHNH_2-CaOCl_2$
	C_6Cl_6	C_6Cl_5H	C_6Cl_5H
Fluorobenzene	<0.2	5.4	<0.2
Bromobenzene	<0.2	5.4	<0.2
Chlorobenzene	<0.2	5.3	<0.2
Toluene	<0.2	15.9	8.9
Cumene	1.8	6.5	1.8
<u>p</u> -Xylene	1.8	5.6	13.9
Anisole	21.3	1.7	4.1

Table 11 shows that the amount of pentachlorobenzene formed when the reaction is carried out in benzene and the monohalogenobenzenes is the same. This "residual" amount of pentachlorobenzene seems to originate from a source more rich in abstractable hydrogen atoms than the solvent. The most likely source of these abstractable hydrogen atoms would be the pentyl fragment of pentyl nitrite.

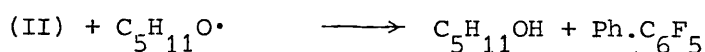
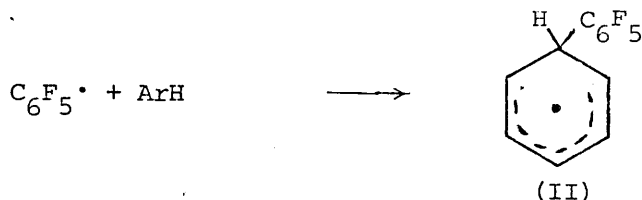
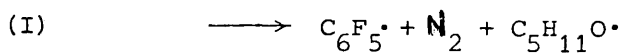
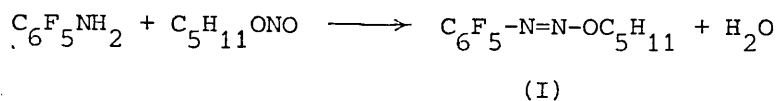
The type of process involved is postulated as an intramolecular hydrogen abstraction process, involving the diazo-ester, $C_6Cl_5-N=N-OC_5H_{11}$, fig (xi). The abstraction process involves the α -hydrogen atoms of the diazo-ether as these would be preferentially removed to produce the ^{most stable} radical, as has been found in other types of homolytic abstraction reactions¹¹⁴.

Solvents which possess side-chains such as toluene, cumene and p-xylene show increased yields of pentachlorobenzene, and this is consistent with an abstraction reaction of the type (10);



Products derived from the benzyl radical were not detected by g.l.c.

A mechanism for the decomposition of pentafluoroaniline by amyl nitrite in aromatic solvents has been proposed. Although each step in the mechanism has not been fully investigated, the mechanism does explain the experimental findings.



Scheme 19

The mechanism involves the formation of a diazo-ether (I), followed by its homolysis, in a manner similar to a number of related species⁵⁷, resulting in the formation of the pentafluorophenyl radical. Scheme 19 accounts for the following experimental observations;

(a) There is an evolution of nitrogen during the initial stages of the reaction.

(b) Upon addition of amyl nitrite to the reaction solution a cloudiness appears due to the formation of water.

(c) The presence of amyl alcohol was found in the solvent fractions of all the reactions.

These observations are also seen in the pentachloroaniline-amyl nitrite system, and therefore a similar reaction scheme is proposed for the generation of the pentachlorophenyl radical. The existence of the diazo-ether intermediate Fig. (xi) has no experimental foundation but it seems to be a plausible intermediate as similar intermediates have been shown to exist in alternative reactions of diazo-intermediates.

Table 22

Products from the abstraction reactions of pentachlorophenyl radicals in iodomethane and bromotrichloromethane.

Substrate Product	CH ₃ I	BrCCl ₃
[†] C ₆ Cl ₅ NH ₂	21.5	31.2
C ₆ Cl ₅ H	67.4	-
C ₆ Cl ₆	-	53.0
C ₆ Cl ₅ I	32.5	-
C ₆ Cl ₅ Br	-	46.9

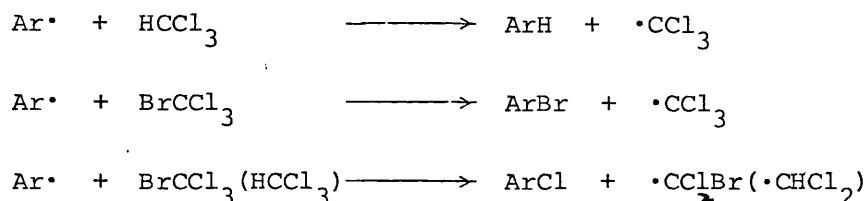
[†] Percentage of unreacted amine.

Yields of products are expressed as percentage of amine consumed.

The abstraction reactions of the pentachlorophenyl radical were further illustrated by the decomposition of pentachloroaniline using amyl nitrite in iodomethane and bromotrichloromethane. The products of these reactions have been interpreted in terms of the intermediacy of the pentachlorophenyl radical and its subsequent abstraction reactions. Table 22 summarises the results.

The abstraction reactions of the pentafluorophenyl radical using substrates of the type XCl₃ have been studied¹¹³ and the ease of removal of X found to decrease in the order X = Br, H, > Cl. Hydrogen is removed more readily than chlorine from chloroform and bromine is similarly

preferred over chlorine in abstraction from BrCCl_3 . Scheme (20) shows the two types of abstraction reaction which take place from bromotrichloromethane and chloroform.



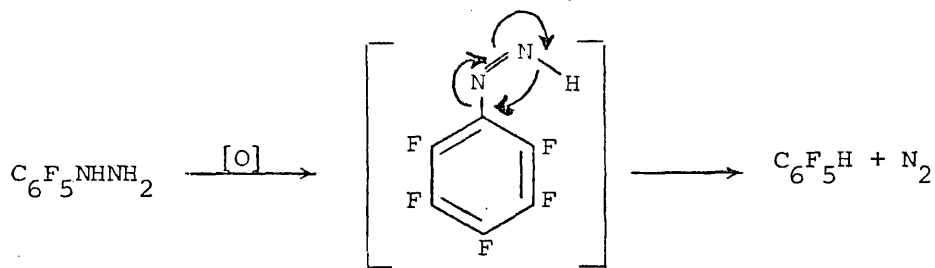
Scheme 20

The above equations represent the two types of abstraction reaction which compete with each other for radicals. Thus, the relative yields of each of these products reflect the relative rates of the abstraction reactions.

The selectivity of the radicals is evidently dependent upon the type of bond being broken, although the relative extents of reaction have also been found to involve the polar properties of the attacking radical. However, a series for the ease of abstraction of hydrogen and halogen atoms from iodomethane and bromotrichloromethane could not be obtained for the pentachlorophenyl radical.

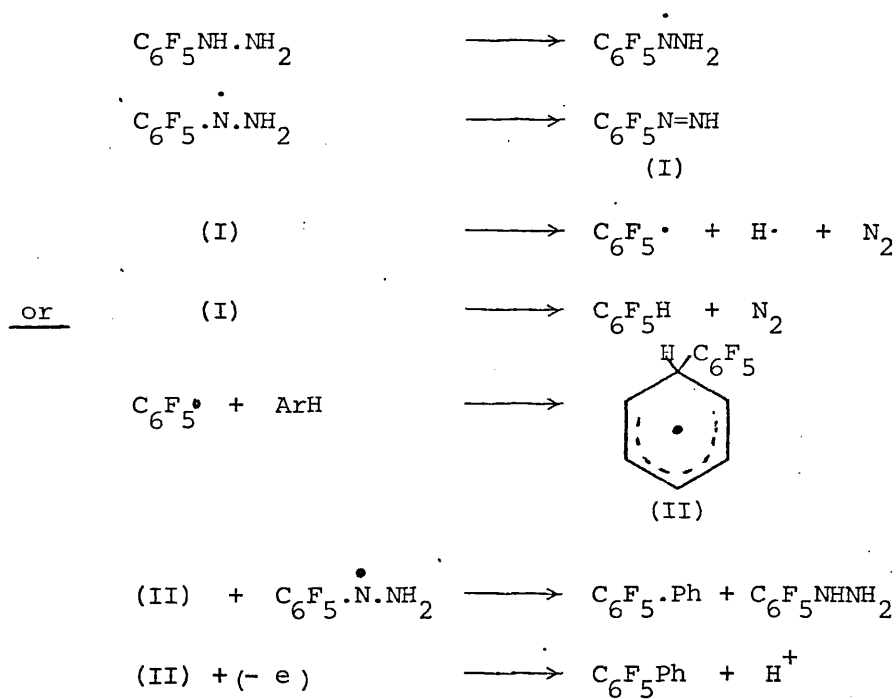
3.1.2 Oxidation of Pentachlorophenylhydrazine

The oxidation of the arylhydrazines by silver-oxide or bleaching powder in aromatic substrates, has been successfully used in the synthesis of a number of polyfluoroaromatic compounds^{70,115,116}. The main side reaction involved is the formation of products arising from protiodehydrazination, thought to result from the collapse of a diazene intermediate; Scheme (21).



Scheme 21

When this reaction did not interfere with the arylation process, good yields of biaryl products were obtained (60-70%). Oxidation of pentafluorophenyl hydrazine is thought to involve the following reaction steps, Scheme (22), although this reaction scheme has not been entirely clarified⁷⁰.



Scheme 22

The oxidation of pentachlorophenylhydrazine in benzene and in a range of aromatic substrates, using ^ebleaching powder, has shown that the pentachlorophenyl radical is generated in this reaction, presumably by a process similar to that outlined in Scheme (22). The evidence to support the existence of the pentachlorophenyl radical comes from two sources;

(i) The formation of biaryls arising from the attack of pentachlorophenyl radicals on an aromatic nucleus followed by dehydrogenation.

(ii) The formation of products arising from abstraction reactions of the pentachlorophenyl radical.

As previously mentioned in part 2.4 the isolation and detection of the polychlorobiaryls was found extremely difficult using ordinary analytical procedures, except in the case of the parent 2,3,4,5,6-pentachlorobiphenyl which could be isolated from the oxidation of the hydrazine by bleaching powder in benzene.

Oxidation of the hydrazine in benzene and the monohalogenobenzenes showed the absence of pentachlorobenzene, an indication that collapse of the diazene intermediate (Scheme 21) is not a significant reaction step. This absence of pentachlorobenzene (Table 11) shows that there is no source of abstractable hydrogen atoms in the pentachlorophenylhydrazine system, comparable with the pentyl (C_5H_{11} -) fragment in the pentachloroaniline/amyl nitrite system. Formation of pentachlorobenzene arises only from side-chain hydrogen abstraction in the alkylbenzenes, e.g. toluene, cumene and *p*-xylene. The presence of products derived from the benzyl radical e.g. $(Ph.CH_2^*)$ were shown to be absent by gas liquid chromatography.

The biaryl products which have been identified from the oxidation of pentachlorophenylhydrazine arise from the following solvents: benzene giving 2,3,4,5,6-pentachlorobiphenyl, chlorobenzene giving a biaryl mixture which analyses to a hexachlorobiphenyl, and toluene giving a mixture of methylpentachlorobiphenyls. The only other product identified from the remaining substrates was pentachlorobenzene.

Decomposition of pentafluorophenylhydrazine in halomethanes has not been studied, so the abstraction reactions of the pentafluorophenyl radical generated by this radical precursor have not been so closely examined as have other sources of the radical. The oxidation of pentachlorophenylhydrazine in iodomethane produced pentachlorobenzene (65%) and pentachloriodobenzene (24%). As in the pentachloroaniline-*o*-methyl nitrite system no distinct order of abstraction is apparent.

3.1.3. Photolysis of Pentachloriodobenzene

Photolysis of pentafluoroaryl iodides in aromatic solvents by ultraviolet light^{78,117} has been shown to result in the generation of free radicals by the isolation of biaryl products arising from homolytic arylation of the solvent.

Table 23

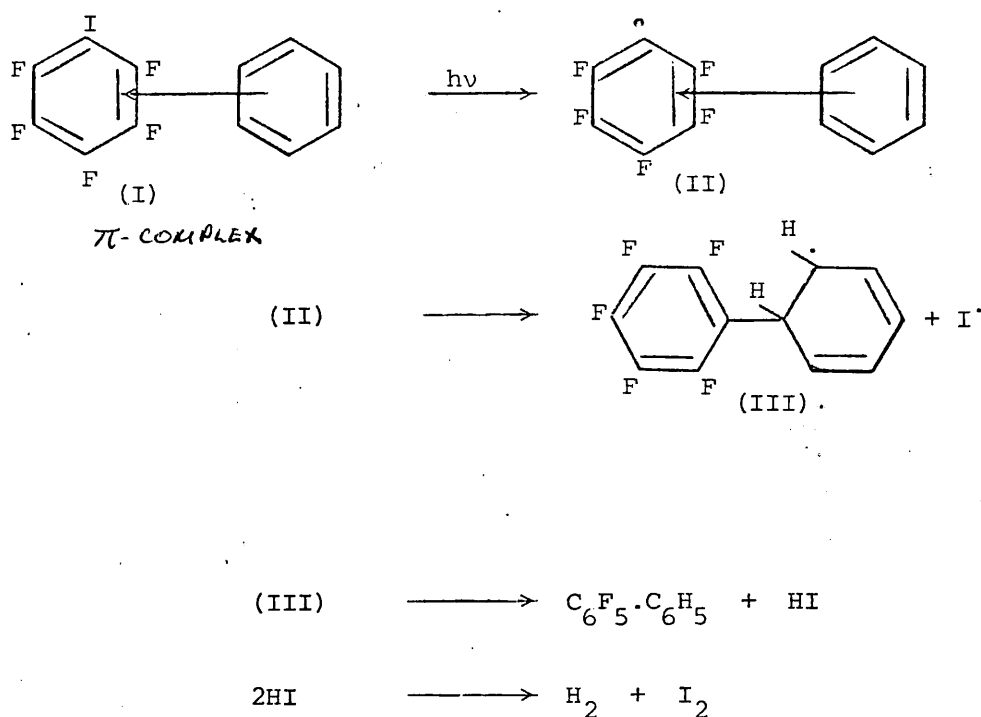
Product yields from the photolysis of pentafluoroiodobenzene in aromatic solvents

Solvent	$C_6F_5 \cdot C_6H_5$	C_6F_5H	$Me \cdot C_6H_4 \cdot C_6F_5$ [†]		
	%	%	<u>o</u> -	<u>m</u> -	<u>p</u> -
Benzene	89	<0.05	-	-	-
Toluene	-	7	48	25	26

[†] Yields of $(Me \cdot C_6H_4 \cdot C_6F_5)$ ^{isomers} are relative yields, expressed as percentage of total $(Me \cdot C_6H_4 \cdot C_6F_5)$ yield.

Table 23 shows the results, the yields of biaryl material are relative yields.

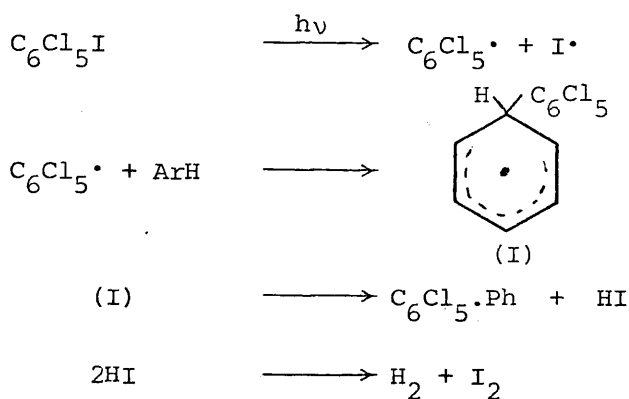
The mechanism suggested for the photolysis of pentafluoriodobenzene⁷⁸ involves a primary association of the type (I) Scheme 23, which assists the photochemical decomposition of the aryl iodide. Evidence for such an association comes from freezing point composition curves for mixtures of pentafluoriodobenzene with benzene and toluene, respectively⁷⁷. The facts reveal that appreciable association occurs between the iodo-compound and the solvent, particularly at molar compositions ranging from 1:2 of aryl iodide:benzene through to 2:1. Scheme 23 outlines the mechanism proposed.



Scheme 23

Photolysis of pentachloriodobenzene in benzene produced 2,3,4,5,6-pentachlorobiphenyl (22%), the mechanism for the photolysis of pentachloriodobenzene is probably very similar to that of the corresponding

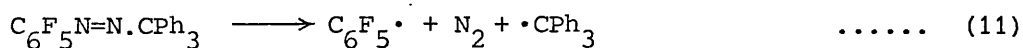
fluoro-compound. The existence of an associated complex between pentachloriodobenzene and benzene similar to that reported for pentafluoriodobenzene and benzene has not been reported in the literature. Scheme 24 shows a process for the decomposition of pentachloriodobenzene which accounts for all the experimental observations.



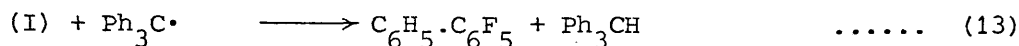
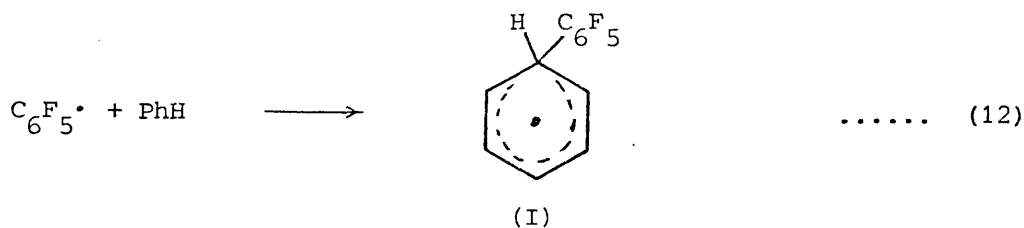
Scheme 24

3.1.4. Decomposition of Pentachlorophenylazotriphenylmethane

Pentafluorophenylazotriphenylmethane has been prepared¹¹⁸ and its decomposition in a range of aromatic substrates has been carried out. The thermal decomposition of this compound in benzene gives 2,3,4,5,6-pentafluorobiphenyl, triphenylmethane and nitrogen. The decomposition obeys first-order kinetics and this is consistent with a one-step decomposition into pentafluorophenyl and triphenylmethyl radicals¹¹⁸ eq. (11);



The second step in the mechanism involves attack of the pentafluorophenyl radical on an aromatic nucleus giving a σ -complex, eq.(12) and termination (eq. 13) involves the removal of a hydrogen atom from the σ -complex by triphenylmethyl radicals.



This termination step contrasts with the dimerisation and disproportionation of the σ -complexes which predominate in other systems and is due to the high stability of the triphenylmethyl radical. A stationary concentration of these long-lived radicals builds up and all intermediate radicals which are formed are scavenged by them with the exception of the extremely reactive pentafluorophenyl radical.

Pentachlorophenylazotriphenylmethane has been prepared by the oxidation, using aqueous bromine, of pentachlorophenylhydrazotriphenylmethane which was prepared by reacting the hydrazine (2 moles) with triphenylmethyl chloride (1 mole) in ether.

Decomposition of pentachlorophenylazotriphenylmethane in benzene produced 2,3,4,5,6-pentachlorobiphenyl (46%), triphenylmethane (23%) and pentachlorobenzene (28%). The mechanism for the decomposition of this radical precursor in aromatic substrates is probably analogous to that proposed for the pentafluoro-analogue. However, more work needs to be carried out to establish the mechanism for the decomposition of this radical precursor.

3.1.5. Summary of the Reactions of the Pentachlorophenyl Radical

The pentachlorophenyl radical has been prepared by several independent routes, analogous to those used for the generation of the pentafluorophenyl radical^{65,70}. In comparison to its fluorine counterpart, the pentachlorophenyl

radical undergoes abstraction reactions rather than participate in aromatic substitution, *except in the case of benzene and chlorobenzene.*

The main products from the reaction of the pentachlorophenyl radical in several aromatic substrates are pentachlorobenzene and hexachlorobenzene: the formation of the latter is discussed elsewhere (Section 3.3, page 99). Pentachlorobenzene which is a dominant reaction product in the pentachloroaniline-amyl nitrite system, apparently arises from abstraction of a hydrogen atom from the pentyl fragment (Fig. xi).

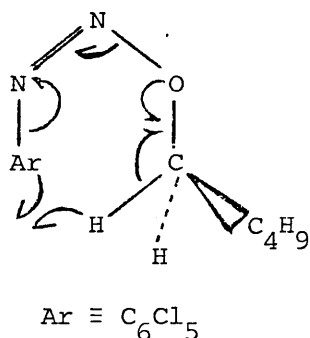


Fig. xi

This hypothesis is supported by evidence from the oxidation of pentachlorophenylhydrazine in aromatic substrates, where the lower yields of pentachlorobenzene are attributed to the absence of a suitable hydrogen donor possessing hydrogen atoms which are available for abstraction.

Biaryls have been detected and isolated in some of the reactions of the pentachlorophenyl radical. The most easily isolated is 2,3,4,5,6-pentachlorobiphenyl arising from the pentachlorophenylation of benzene. Decomposition of pentachlorophenyl radical precursors in chlorobenzene and toluene have also produced the respective biaryls, although the abstraction reactions of this radical appear to be dominant.

The order of hydrogen abstraction from toluene and cumene differs from that normally associated with hydrogen abstraction from alkylbenzenes (Table 21). The order of hydrogen removal would be such that the

most stable radical is formed, i.e. *tertiary hydrogens are preferentially removed over secondary and primary*. Thus cumene should show the highest yield of pentachlorobenzene. However, this trend is reversed, with two different sources of radical. Thus it seems that this observation is a result of the radical and can be explained in terms of a steric effect, and this is discussed later in Section 3.2.

Abstraction reactions of the pentachlorophenyl radical towards the halogens (Cl, Br, I) do not show any order of selectivity, in contrast to that found with the pentafluorophenyl radical. From the experimental data it appears that each of the halogens are removed to the same extent by the pentachlorophenyl radical.

3.2. Steric Effects in Polychlorophenyl Radical Systems


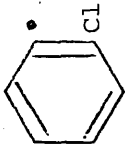
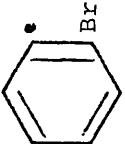
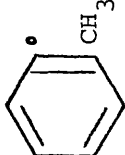
Steric effects in the Gomberg reaction have been investigated using radicals which possess a substituent ortho- to the radical site and their reactions with o- and m-dichlorobenzenes have been studied¹¹⁹. The results are summarised in Table 24.

These experiments indicate that while ortho-halogen substitution may give rise to unfavourable dipolar repulsions in the transition state, steric effects are relatively unimportant in the formation of the reaction products. However, a more detailed study on the effect of ortho-substituted radicals in arylation reactions has been carried out by Hey, Moulden and Williams¹²⁰.

These workers obtained the relative rates of arylation of chlorobenzene, nitrobenzene and toluene using o-nitro- and o-bromo-phenyl radicals. Table 25 shows the results of these experiments.

Table 24

Product isomer ratios from the phenylation of ortho- and meta-dichlorobenzenes¹¹⁹

Radical	o-Dichlorobenzene		Ratio	m-Dichlorobenzene		
	3-	4-		3-/4-	2-	4-
	67 ± 3	33 ± 3	2.0	46 ± 2	44 ± 2	10 ± 2
	55 ± 3	45 ± 3	1.2	25 ± 3	59 ± 3	16 ± 3
	54 ± 4	46 ± 4	1.2	-	-	-
	66 ± 3	34 ± 3	1.9	40 ± 3	48 ± 3	12 ± 3

Yields are relative, and are expressed as a % of amine consumed.

The relative rates of o-bromo- and o-nitro-phenylation of nitrobenzene are significantly lower than the corresponding rate of phenylation, and are consistent with the theory of polarised radicals, in that the changes in their values are in accord with the known properties of nitrobenzene towards electrophilic reagents.

Table 25

Radical	PhNO ₂ PhH ^K	PhCl PhH ^K	Ph.Me PhH ^K
<u>o</u> -NO ₂ .C ₆ H ₄ •	0.26	0.83	1.16
<u>p</u> -NO ₂ .C ₆ H ₄ •	0.94	1.30	2.50
<u>o</u> -Br.C ₆ H ₄ •	0.79	0.90	1.69
<u>p</u> -Br.C ₆ H ₄ •	1.76	-	-
C ₆ H ₅ •	4.0	1.44	1.68

A similar variation occurs in the relative rates of arylation of chlorobenzene, but here the differences are much smaller. All the relative rates of arylation with ortho-substituted aryl radicals are lower than the relative rates of arylation with the corresponding para-position, since the magnitude of the inductive effect is known to depend on the distance of the polarising field from the site of the reaction. This means that nitrobenzene will be less reactive towards o-nitrophenyl radicals than towards p-nitrophenyl radicals, since the former are the more electrophilic. This argument does not explain the decreased reactivity of toluene towards o-nitrophenyl radicals compared with its reactivity towards p-nitrophenyl radicals, since toluene would be expected to display a greater reactivity in

o-nitrophenylation than in p-nitrophenylation, the methyl group being activating towards electrophiles.

It was therefore considered probable that steric factors influence the reactivity of aromatic compounds towards arylation with ortho-substituted phenyl radicals. The reduced reactivities of nitrobenzene and chlorobenzene for o-nitro- and o-bromo-phenylation may be due to a steric effect as well as to the enhancement of the polar properties of the radicals arising from the presence of the nitro- and bromo-substituents.

Changes in the size of the attacking radical must have their greatest influence on the reactivity of the ortho-positions of the substrate molecules. The reactivity of the para-positions should be least affected. Thus it is possible to consider the effect of changes in the polar characteristics of the radical by reference to the partial rate factors for substitution at the para-position, and the influence of the effective size of the radical by reference to the partial rate factors for substitution at the ortho-positions. Table 26 shows the partial rate factors for arylation of nitrobenzene.

For o-bromophenylation the reactivity of the ortho-position in nitrobenzene is much less than that of the para-position, and the f_o/f_m ratio for p-bromophenylation is more than three times as great as for o-bromophenylation. The implication of these results is that there is a definite hindrance to substitution at the ortho-position of nitrobenzene arising from the increased effective size of the o-bromophenyl radical.

Table 26

Partial rate factors for arylation of nitrobenzene (80°C)

Radical	f_o	f_m	f_p	f_o/f_m	f_p/f_m
$o\text{-Br}\cdot\text{C}_6\text{H}_4$	0.83	0.59	1.90	1.41	3.22
$p\text{-Br}\cdot\text{C}_6\text{H}_4$	3.10	0.7	2.9	4.43	4.14
$o\text{-NO}_2\cdot\text{C}_6\text{H}_4$	0.43	0.14	0.42	3.07	3.00
$p\text{-NO}_2\cdot\text{C}_6\text{H}_4$	1.64	0.43	1.56	3.81	3.63
$\text{C}_6\text{H}_5\cdot$	7.5	1.2	6.6	6.25	5.50

From studies carried out using suitably substituted polychlorophenyl radicals a steric effect influencing the yield of biaryls was examined.

The species used for this investigation were 2,4- and 2,6-dichlorophenyl and 2,4,6-trichlorophenyl radicals. These species were generated by allowing the respective anilines to react with amyl nitrite in benzene and measuring, by gas-liquid chromatography, the relative amounts of biaryls and abstraction product formed. The abstraction product $\text{C}_6\text{H}_4\text{Cl}_{2-y}$, results from hydrogen abstraction by the radical from the pentyl fragment of an intermediate diazo-ether (fig. xi) page 91. The results are summarised in Table 27.

Table 27

Relative yields of the products derived from the reaction of polychlorophenyl radicals in benzene

Polychlorophenyl Radical	$C_6H_yCl_{6-y}$ %	Biaryl %
$2,4-Cl_2-C_6H_3\cdot$	2	98
$2,6-Cl_2-C_6H_3\cdot$	38	62
$2,4,6-Cl_3-C_6H_2\cdot$	76	24

The incidence of hydrogen abstraction to produce $C_6H_yCl_{6-y}$ increases as the number of ortho-substituents to the radical site increases. This is accompanied by a corresponding decrease in the yield of biaryl.

This result has been interpreted in terms of a steric effect associated with the two chlorine atoms adjacent to the radical site. This is evident from a comparison of the biaryl: $C_6H_yCl_{6-y}$ ratio obtained with 2,4-dichlorophenyl radicals (49:1) to that with 2,6-dichlorophenyl radicals (2:1), showing that the inclusion of a second chlorine atom adjacent to the radical site produces a decrease in the amount of biaryl. These results can be fully explained using steric arguments without the need to invoke any polar properties of the radical. The magnitude and influence of this steric effect can be seen in the following discussion.

A comparison of the relative yields of $C_6H_yCl_{6-y}$ obtained from the 2,6-dichlorophenyl and 2,4,6-trichlorophenyl radicals show that the more heavily substituted radical increases the yield of $C_6H_yCl_{6-y}$ over that obtained for the 2,6-dichlorophenyl radical, by a factor of ca.2. This

increase is entirely due to the presence of a chlorine atom in the 4-position of the tri-substituted radical. However, from a comparison of the relative yields of $C_6H_4Cl_2$ obtained from 2,4- and 2,6-dichlorophenyl radicals the influence of a chlorine atom in the 6-position can be determined. The yield of $C_6H_4Cl_2$ obtained from 2,6-dichlorophenyl radicals is increased by a factor of ca. 19 over that obtained using 2,4-dichlorophenyl radicals. This implies that it is the radical with the chlorine atom in the 6-position which is contributing more to the increase in the yield of abstraction product ($C_6H_4Cl_2$) than the radical with a chlorine atom in the 4-position.

This means that it is the steric influences of the two chlorine atoms flanking the radical site which is the predominating factor in determining the yields of the products formed in this reaction.

Molecular models show that there is a high degree of steric hindrance for carbon atom attack in benzene by the 2,6-dichlorophenyl radical. The transition state proposed by Weingarten for attack of an ortho-substituted phenyl radical on o-dichlorobenzene is shown in fig. (xii). The plane of the radical approximately bisects the o-dichlorobenzene at the carbon atom to which it is becoming attached.

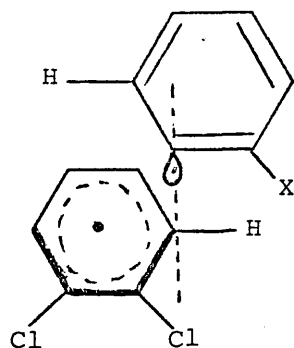


Fig. (xii)

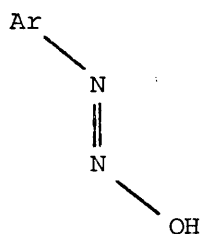
A similar line of attack for the 2,6-dichlorophenyl radical across the plane of the benzene ring causes a high degree of steric interaction between the two ortho-chlorine atoms contained in the radical and the carbon atoms of the benzene ring.

The presence of five chlorine atoms in the pentachlorophenyl radical has been shown to favour abstraction reactions at the expense of aromatic substitution. From this result the presence of a steric effect has been inferred. From the previous discussion it has been shown that two ortho-chlorine atoms flanking a radical site are responsible for a substantial steric effect in the transition state, thus affecting the products of the reaction. The pentachlorophenyl radical possesses a similar steric effect to that found in the reactions of these di- and tri-chlorophenyl radicals, in that the radical site is flanked by two chlorine atoms, and this can be used to explain some of the unexpected results arising from the reactions of the pentachlorophenyl radical.

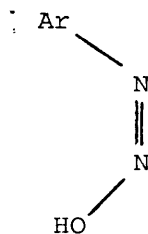
3.3 The Origin of the Hexachlorobenzene from the Decomposition of Pentachloroaniline by Amyl Nitrite in Aromatic Substrates

The origin of pentachlorobenzene as a reaction product in the decomposition of pentachloroaniline by amyl nitrite in aromatic solvents has been explained by a free-radical abstraction process involving the pentachlorophenyl radical. The aim of this section is to show how hexachlorobenzene arises as another reaction product, by means of a heterolytic mechanism involving nucleophilic attack on the pentachlorophenyldiazonium ion. However, it is necessary briefly to review some of the work which has been carried out on the equilibrium between covalent diazo-compounds and the diazonium ion¹²¹.

Hantzsch^{122,123} was the first to investigate the equilibria which existed between a covalent diazo-compound and a diazonium ion. Hantzsch's theory was that on addition of alkali to an acid diazo-solution, a "diazonium hydroxide" ($\text{Ar-N=N}^+\text{OH}^-$) was formed and this subsequently rearranges to the diazo-hydroxide or diazoic acid (Ar-N=N-OH). He then proposed, on the basis of analogy with the oximes¹²⁴, that the diazo-hydroxides could exist as two geometrical isomers; fig (xiii),



trans(~~anti~~)-diazo-hydroxide

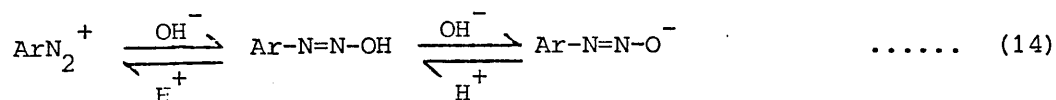


cis(~~syn~~)-diazo-hydroxide

Fig. (xiii)

and attempted, but failed, to prepare those diazo-hydroxides, which in the light of more recent data is hardly surprising, as the work of Wittwer and Zollinger¹²⁵ has shown that in aqueous solution the diazo-hydroxide accounts for only a very small fraction of the total diazo-compounds present.

The equilibrium can be represented by eq. (14);



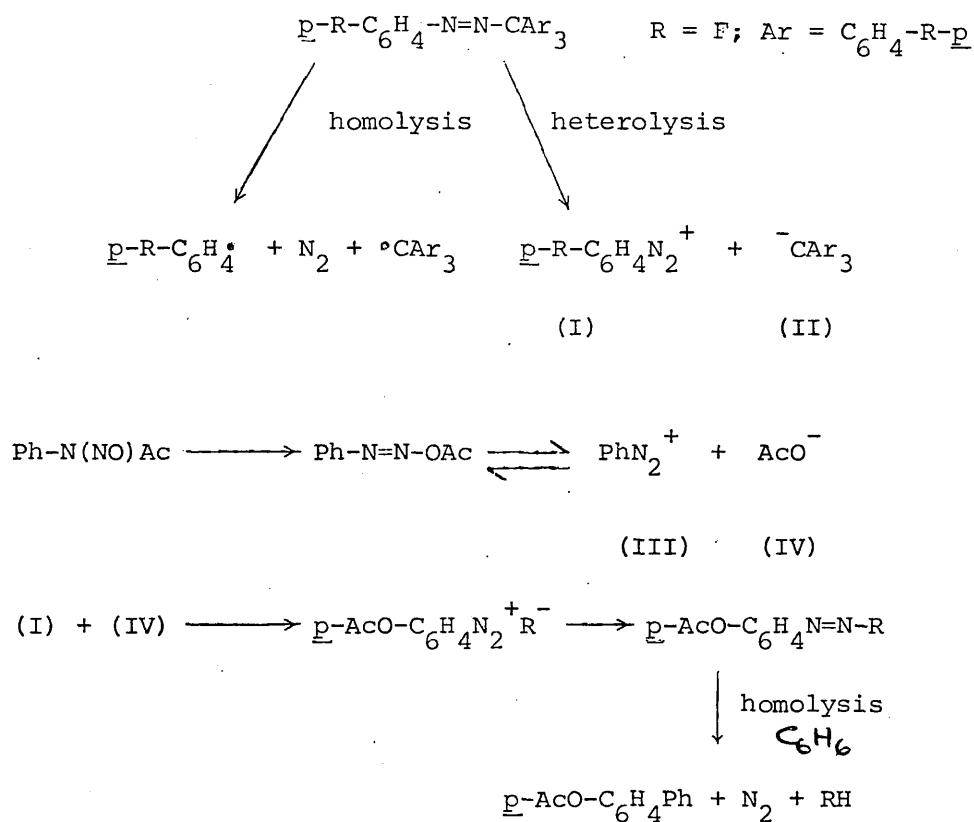
Hantzsch deduced from conductivity measurements the dissociation constants for the diazo-hydroxides, but it is now known that his assumption concerning the equilibrium (14) was incorrect. In the neutralisation of

diazonium ion solutions one hydroxyl group is taken up to give the diazohydroxide, which loses a proton to yield the diazotate, a second hydroxyl group acting as proton acceptor. Hence the covalent diazohydroxide is not a stable intermediate and does not exist in aqueous solution in any detectable concentration. This diazonium-diazotate equilibrium can also be measured spectroscopically¹²⁶.

The stability of diazo-compounds depends on the pH of the solution and upon the type of substituents present in the aryl nucleus, the diazonium ions tending to be more stable in the pH range 0 - 3.5. The general rule regarding stability is that substituents which increase the double-bond nature of the (C-N) bond will increase the stability of the diazonium species.

Work by Miles and Suschitzky¹²⁷, on the decomposition of the following aryl radical precursors in non-polar solvents has shown that they result in the formation of diazonium ions, i.e. p-fluorophenylazotriphenylmethane, p-fluorophenyldiazoaminobenzene. Decomposition of these radical precursors was carried out in the presence of N-nitrosoacetanilide in benzene, which provides acetate ions for nucleophilic substitution. In the subsequent product analysis fluoride ions were detected together with products arising from nucleophilic substitution of fluorine atoms by acetate ions.

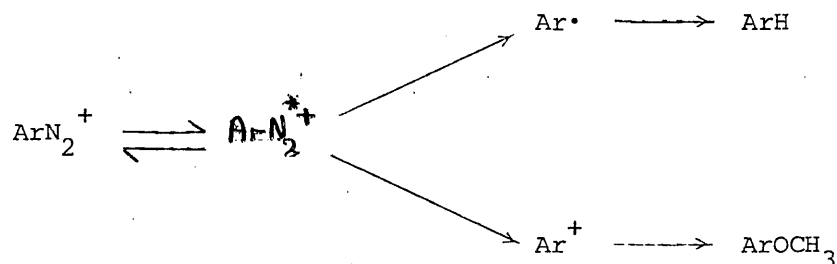
The results have been interpreted by these workers as involving a heterolytic dissociation of the diazo-intermediate followed by interaction between the p-fluorobenzene diazonium cation and the acetate anion from N-nitrosoacetanilide. Scheme 25 shows the proposed reaction mechanism for the decomposition of p-fluorophenylazotriphenylmethane.



Scheme 25

The above reaction scheme involves heterolytic dissociation of the diazo-compound to provide the diazonium ion similar to the reactions investigated by Hantzsch, although the application of this principle to some of the radical precursors used by Suschitzky remains questionable.

The decomposition of arenediazonium ions in acidic methanol¹²⁸ provides evidence that the radical and ionic pathways proceed via a common intermediate, and the type of intermediate postulated is an activated diazonium ion in a mechanism of the following type;



The formation of hexachlorobenzene in the decomposition of pentachloroaniline by amyl nitrite in aromatic solvents arises from a heterolytic mechanism occurring in this system, involving nucleophilic displacement of chlorine atoms.

Nucleophilic displacement of halogen during diazonium reactions has been found in polyhaloaryl systems by Tatlow¹²⁸ and co-workers from studies involving pentafluoroaniline. Diazotisation of pentafluoroaniline in aqueous media¹²⁹ leads to nucleophilic replacement of a para-fluorine atom by a hydroxyl group, providing intermediates of the type shown in fig.(xiv), which lead ultimately to the formation of phenolic material.

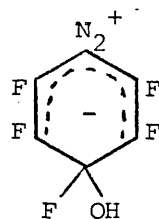
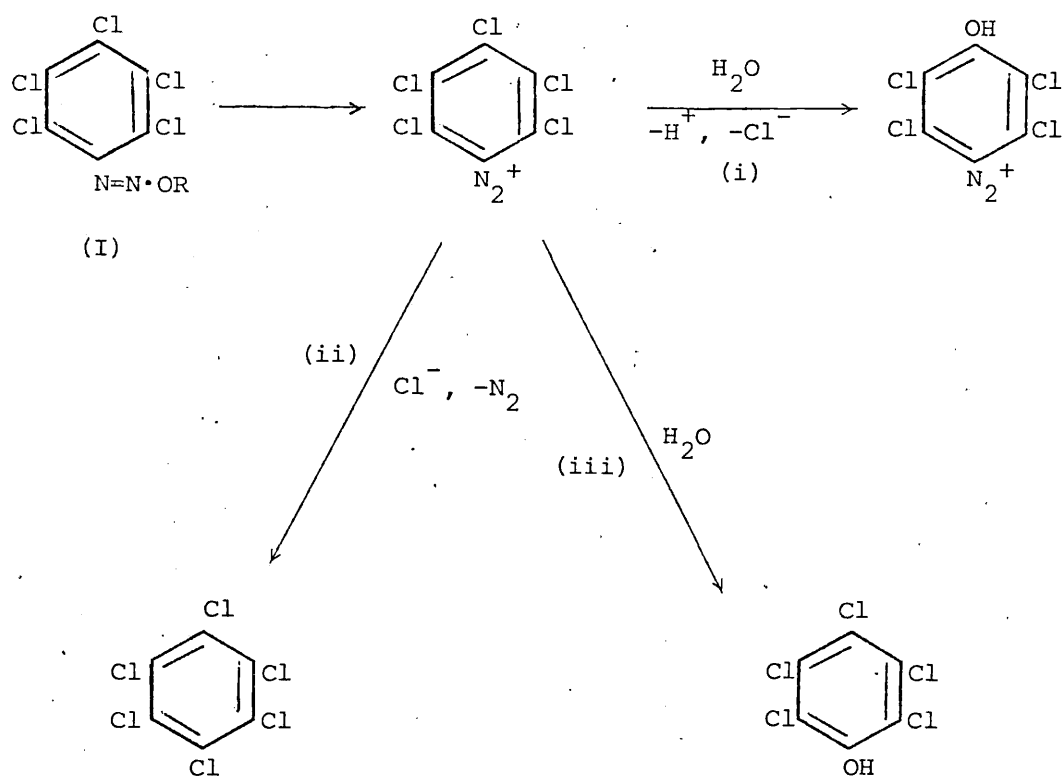


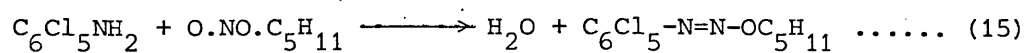
Fig. (xiv)

Formation of water during the diazotisation of pentachloroaniline using amyl nitrite gives species which can take part in nucleophilic substitution of the polychlorophenyl system, Scheme 26.



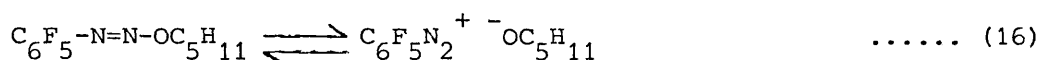
Scheme 26

Ionisation of the diazo-ether (I), Scheme 26, produces the pentachlorophenyldiazonium ion, a process which is favoured by the generation of water during the reaction and the acidity of the reaction media (eq. 15);

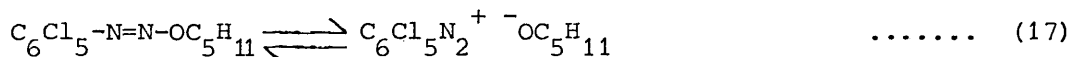


The pentachlorophenyldiazonium ion then undergoes nucleophilic attack at the para-chlorine atom, route (i), Scheme 26, displacing chloride ion to give a phenol. This process occurs to a greater extent in the polychloro-system than with the fluoro-analogues. This means that the

extent of ionisation of (I) to give the species $C_6Cl_5N_2^+$, must be greater in the pentachloroaniline/amyl nitrite system than it is in the pentafluoroaniline/amyl nitrite system although no evidence has been found to support the formation of hexafluorobenzene in this system⁶⁵. This can therefore be interpreted as an equilibrium between the covalent diazo-ether (I) and the ionic diazonium ion, i.e. in the pentafluoroaniline/amyl nitrite system the diazo-ether ($C_6F_5-N=N-OC_5H_{11}$) is the predominant species in the equilibrium represented in (eq. 16), thus providing



an opportunity for greater homolytic dissociation into pentafluorophenyl radicals. However, in comparison, if the equilibrium (16) lies over to the right the amount of diazo-ether available for homolysis will be reduced thus leading to a lower concentration of pentachlorophenyl radicals, (eq. 17).



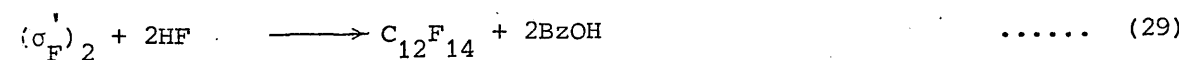
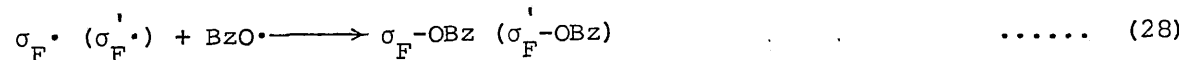
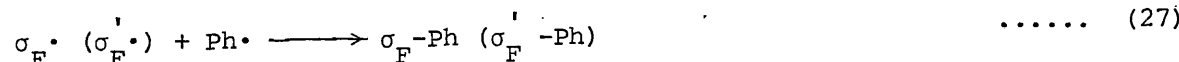
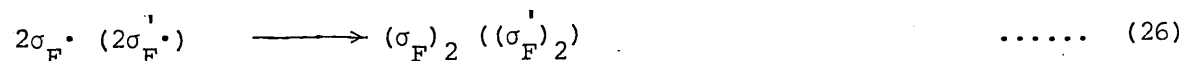
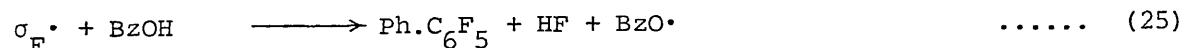
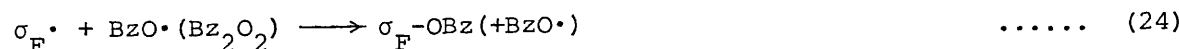
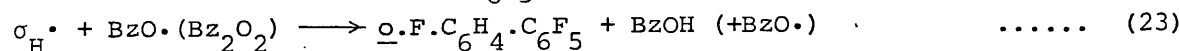
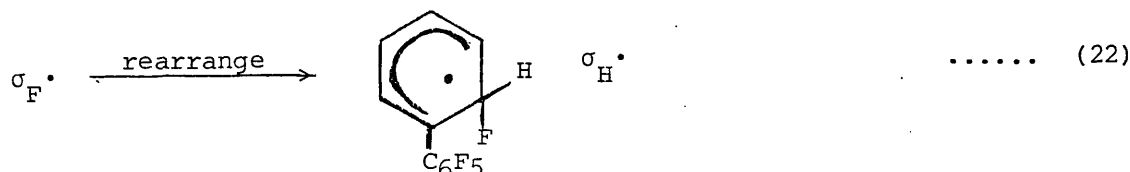
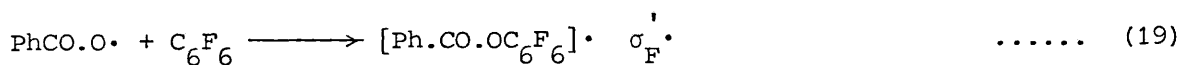
Two possible explanations for this preferred dissociation can be put forward; firstly, steric effects in the pentachlorophenyl system may help to reduce the stability of the diazo-ether, and secondly, the pentachlorophenyl group has been found to withdraw electrons from an electron-centre more powerfully than the pentafluorophenyl group¹³⁰, a factor which may affect the stability of the diazo-ether ($C_6Cl_5-N=N-OC_5H_{11}$).

3.4. Homolytic Aromatic Substitution Reactions in Polychloropolyfluorobenzenes using Benzoyl Peroxide

3.4.1. Decomposition of Benzoyl Peroxide in Polyfluoroarenes

The decomposition of benzoyl peroxide in hexafluorobenzene^{85,87,90} decafluorobiphenyl¹³¹, pentafluorobenzene⁷⁵ and octafluorotoluene⁷⁵ has been reported.

The mechanism for the formation of the observed products of the decomposition of benzoyl peroxide in hexafluorobenzene has been established^{90,87}, leading to aryldefluorination accompanied by a little fluorine atom migration. The reaction scheme is given below;



(where $\text{R}_\text{F} = \text{C}_6\text{F}_5$)

Phenylation of C_6F_5X (where X, H, Br, CF_3) substrates has been examined by Bolton, Sandall and Williams⁷⁵ and the yields of the isomeric phenylation products for these substrates including those for chloropentafluorobenzene are given in fig.(xv).¹³⁹



Fig. (xv)

The isomer distribution found in the above compounds can be explained by examining the relative stabilities of the σ -complexes formed by attack of phenyl radicals in the substrates. This is examined in Section 3.4.2.1. (page 121) where a series for the stabilisation of the σ -complexes is determined and the results of this study are shown to be consistent with this proposed series.

3.4.1.1. Decomposition of Benzoyl Peroxide in Chloropentafluorobenzene

The results obtained from the thermal decomposition of benzoyl peroxide in chloropentafluorobenzene are given in Table 28 together with the previously reported isomer distribution of the derived chlorotetrafluorobiphenyls¹³⁹. From a comparison of the reported isomer distribution and those obtained in this work, it can be seen that there are differences in the yields of all three isomeric chlorotetrafluorobiphenyls. This difference may have arisen from the different methods employed in treating the reaction mixture prior to determining the yield of the chlorotetrafluorobiphenyl isomers.

In the work of Oldham, Williams and Wilson¹³⁹ the biaryl fraction was distilled out from the reaction mixture and then subjected to gas liquid chromatographic analysis, whereas in the present study, after removal of acid material from the reaction mixture and removal of the solvent by distillation, the crude organic residue was used for analysis.

In the paper by Oldham et.al.¹³⁹ 2,3,4,5,6-pentafluorobiphenyl was not reported, but in this study it has been found.

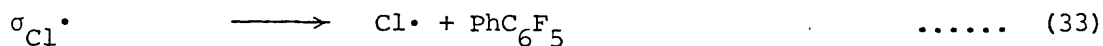
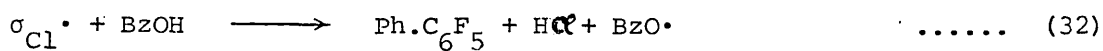
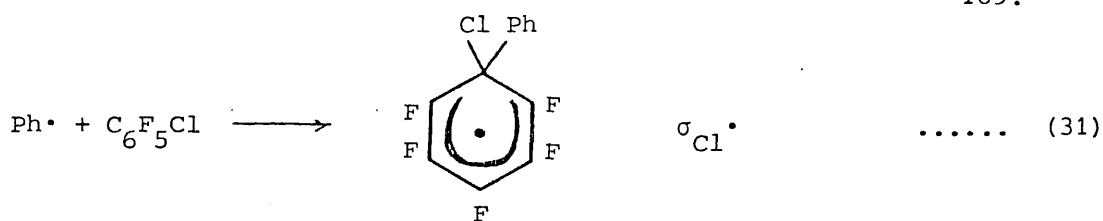
Table 28

Products from the thermal decomposition of benzoyl peroxide
in chloropentafluorobenzene

	Yield (mole per mole % of benzoyl peroxide)	Relative yield (%)
Ph.Ph	0.8	-
Ph.C ₆ F ₅	1.5	6.0
<u>o</u> -Cl.C ₆ F ₄ .Ph	11.4	42.0 (44.1)
<u>m</u> -Cl.C ₆ F ₄ .Ph	7.9	29.0 (35.0)
<u>p</u> -Cl.C ₆ F ₄ .Ph	6.1	23.0 (20.9)
PhCO ₂ H	20.0	-

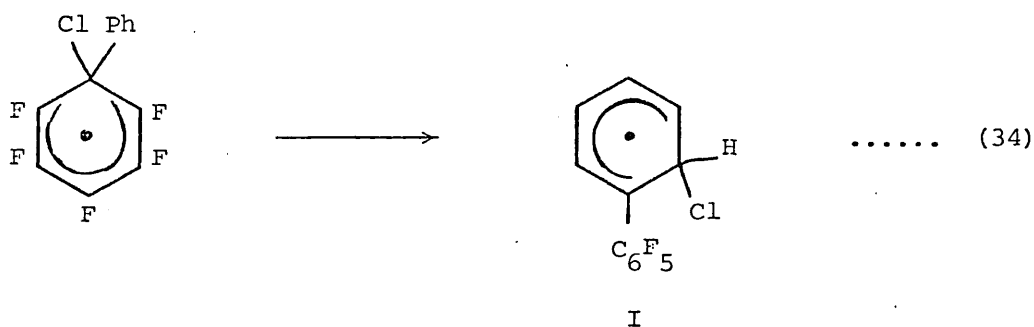
Values in parenthesis are from ref. 139.

The 2,3,4,5,6-pentafluorobiphenyl probably originates from attack of a phenyl radical on the carbon bearing chlorine in the substrate molecule, followed by subsequent dechlorination of the resulting σ -complex. Two types of process are possible for the dechlorination of the σ -complex formed by phenyl radical attack on a carbon bearing chlorine atom in the substrate. These two processes are outlined in Scheme 28.

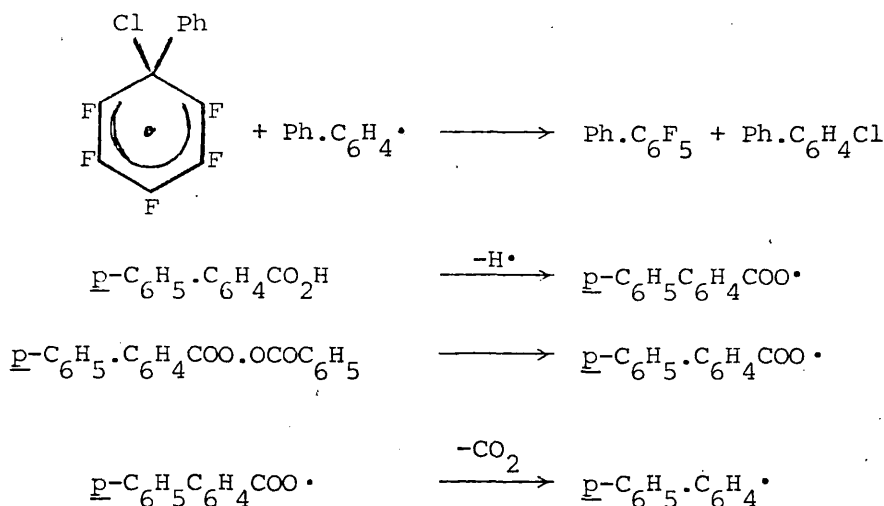


Scheme 28

Reaction (32) is similar to the defluorination of the σ -complex arising from phenyl radical attack on hexafluorobenzene. As no product arising from rearrangement of $\sigma_{\text{Cl}}\cdot$ to give I reaction (34), was found in the reaction products, the origin of the benzoic acid may not be so easily explained. Although evidence has been found that aroic acids are formed in the arylation of Bz_2O_2 ^{140,93}.



An alternative to this process may be found in the results obtained by Bolton, Williams, Sandall and Moss⁹³. In the decomposition of benzoyl peroxide in hexafluorobenzene evidence was found for the existence of biphenyl radicals arising from the arylation of the peroxide or from the derived aroic acids. If $\text{Ph}\cdot\text{C}_6\text{H}_4\cdot$ radicals are obtained in this reaction then they could also participate in the dehalogenation of $\sigma_{\text{Cl}}\cdot$ Scheme 29.



Scheme 29

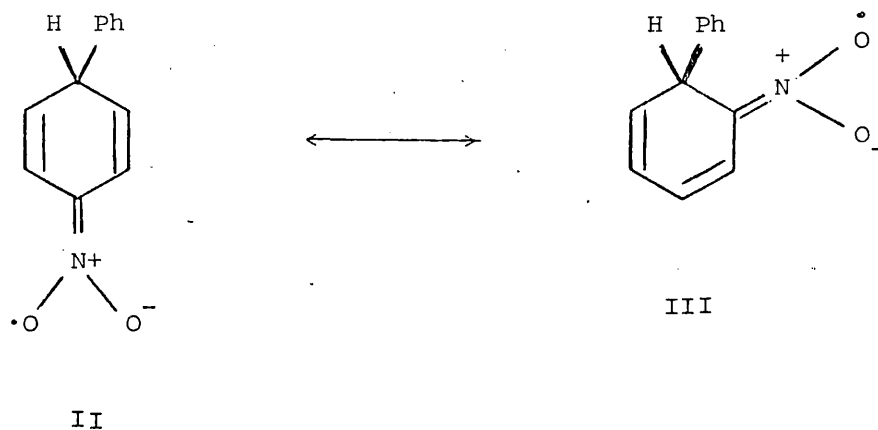
The process described in reaction (33) Scheme 28 involves the homolysis of the carbon-chlorine bond to give 2,3,4,5,6-pentafluorobiphenyl and chlorine radicals. A similar process was initially envisaged as a route for the defluorination of the σ -complex arising from phenyl radical attack on hexafluorobenzene⁸⁵. Although this defluorination route was later dismissed on the grounds that as the C-F bond was very strong an endothermic process would be needed to initiate the reaction. Although the C-Cl bond is much weaker than the C-F bond ($\Delta H_{\text{C-X}}$; C-F = 100; C-Cl = 73 k.cal mole⁻¹)²⁵ it is doubtful that such a homolysis will occur in this system.

It has been found that addition of a small quantity of a hydrogen donor to the reaction mixture produces an overall increase in the yield of biaryl material and in the yield of benzoic acid; this result is discussed in Section 3.4.2. Hence it would appear that the above result supports reactions involving aroic acids as participating in the dechlorination of the σ -complexes.

The decomposition of benzoyl peroxide in bromopentafluorobenzene has been reported⁷⁵ as giving 5% bromine replacement, although a mechanism was not proposed to account for this debromination step.

It is generally believed that attack of a phenyl radical on a substrate (C_6H_5X) to form a σ -complex is the product-determining step in homolytic aromatic substitution reactions. However, for systems containing two types of carbon atom, carbon bearing fluorine and carbon bearing X (X = H, Cl, Br) there are available two types of atom which can participate in stabilising the intermediate σ -complexes. This situation is not, therefore, as limited as in simple benzene systems of the type C_6H_5X where only one type of atom, i.e. the substituent (X) is available for stabilising the odd electron in the σ -complex. In the polyfluoroaromatic system (C_6F_5X) the choice lies between structures using fluorine or X as substituents for delocalisation. This may cause different isomer distributions to be found in the arylation of C_6F_5X substrates compared with those found for C_6H_5X . In the latter case the ortho-position (with respect to X) is often the most vulnerable site to arylation regardless of the electronic nature of X. This activation is usually ascribed to a specific interaction between the substituent and the reagent. Such interaction can only selectively activate a site if the substituents in the substrate do not all undergo such an activation; this is the case for C_6H_5X compounds but it is not true for C_6F_5X substrates.

For substituent groups which can accommodate an odd electron, resonance structures can be drawn resulting from phenyl radical attack on the substrate where the odd electron is delocalised through the group. The simplest example of this is in nitrobenzene, where structures of the type II and III can be drawn, showing greatest stabilisation in the ortho- and the para-positions. This is reflected in the isomer distribution and partial rate factors for phenylation of nitrobenzene. (Table 2 page 23).



For the halogenobenzenes a similar set of resonance structures, produced from phenylation, can be drawn, fig.(xvi).

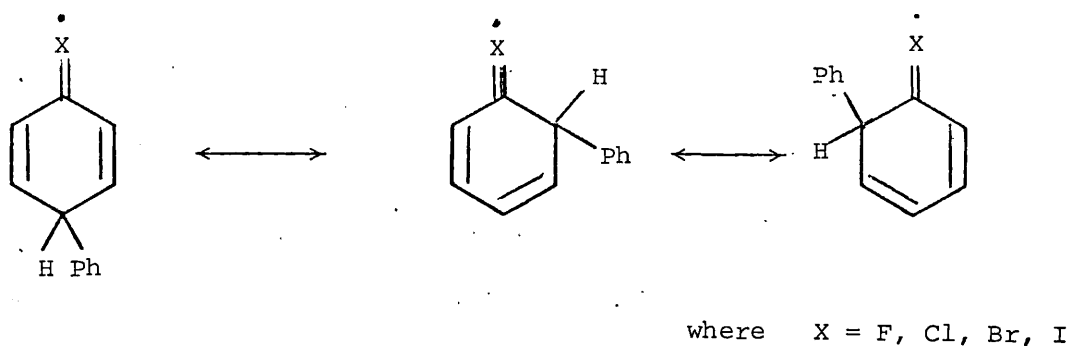


Fig. xvi

The stability of these resonance structures will depend upon the ability of the p-orbitals of the halogen atom X to overlap with the p-orbital on the carbon atom to which it is attached. As the size of the p-orbitals in the halogens is of the order $F > Cl > Br > I$, this will influence the

If the above resonance structures for these two substrates are compared, according to the series of stability previously given, their stability should be in the order, IV > VII; V > VIII; VI > IX. If the isomer distributions resulting from phenyl radical attack on these two substrates are examined (fig. xv) it is found that this trend is reflected in the magnitudes of the respective isomers. A similar confirmation of this order of the stabilities of the σ -complexes IV and VII is found if the partial rate factors obtained from competition studies of C_6F_5X/C_6F_6 systems⁷⁵ are examined (fig. xviii).

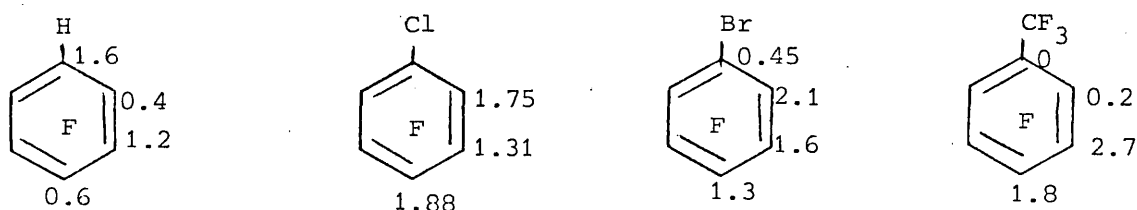


Fig. xviii

In the case of pentafluorobenzene it is the σ -complex which is stabilised by two ortho-fluorine atoms and a para-fluorine atom which is the most stable and shows the highest p.r.f., compared to the σ -intermediates which involve hydrogen as one of the stabilising atoms.

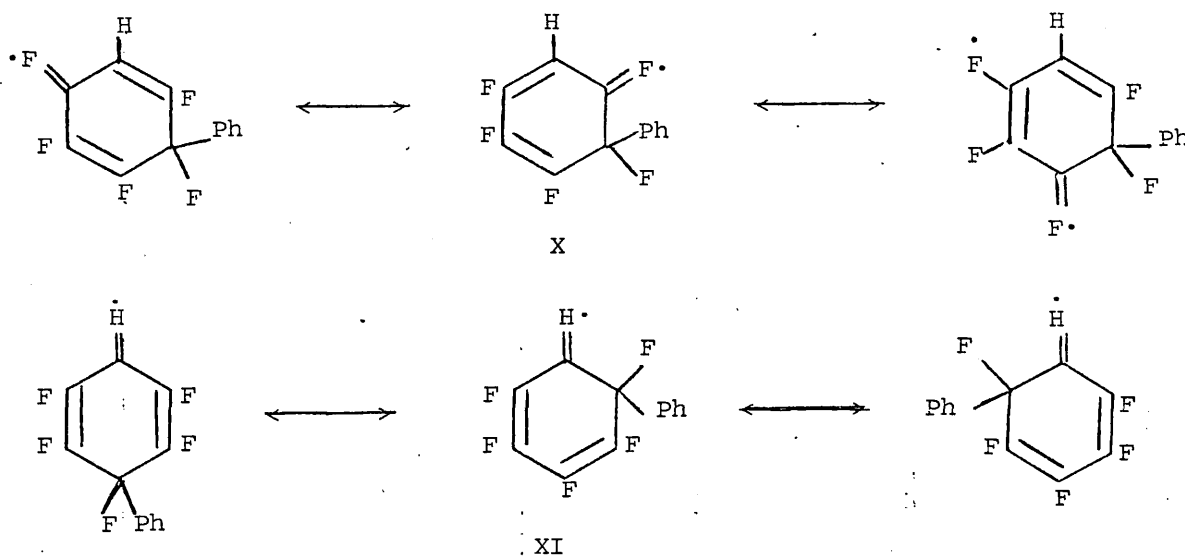


Fig. xix

Intermediates which involve resonance contributions from hydrogen as shown in XI are very unstable as hydrogen possesses no suitable p-orbitals with which conjugation can occur. If the resonance structures of the σ -complexes arising from phenylation of octafluorotoluene are drawn out, it can be seen that it is the structures in which fluorine participates as the major stabilising atom in the o- and p-positions that produce the sites of highest reactivity (Fig. XX). Structures such as XVII, XX, which involve delocalisation of the odd electron through the $(-\text{CF}_3)$ substituent would be very unstable due to the inability of the group to form double-bond structures, and would not participate in the stabilising mechanism. The structures which possess fluorine atoms in ortho- and para-positions relative to the site of attack would contribute most to the stability of the σ -complex, and this results in the activation observed for the meta-position with respect to the $(-\text{CF}_3)$ group.

Thus results obtained in this study for the phenylation of chloropentafluorobenzene are consistent with the series obtained for the effect a substituent X (where X = H, Cl, F, Br, CF_3) exhibits upon σ -complexes resulting from phenylation of $\text{C}_6\text{F}_5\text{X}$ compounds.

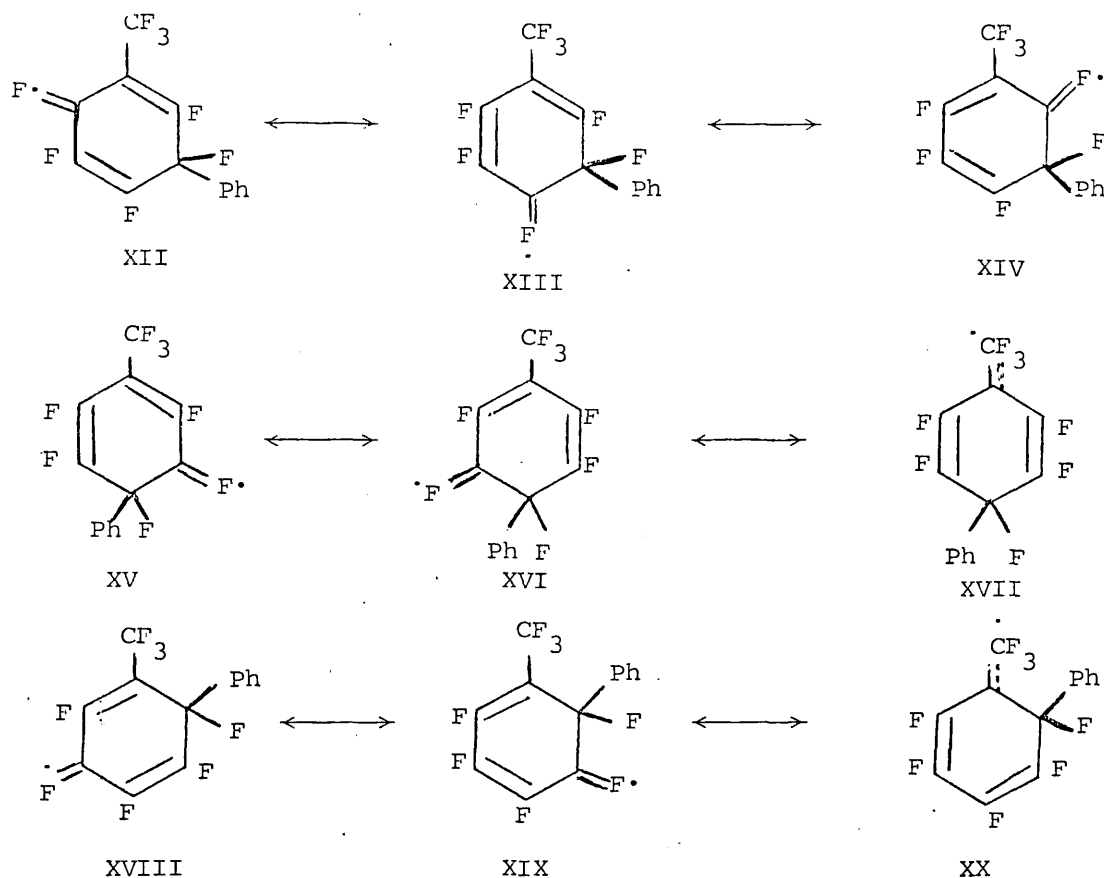
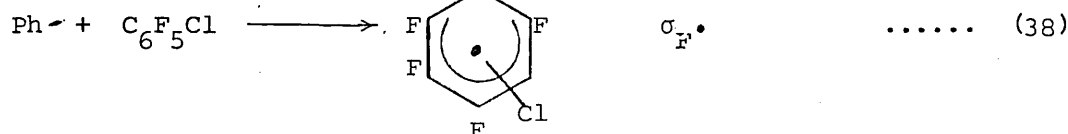
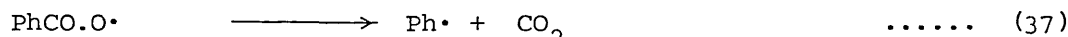
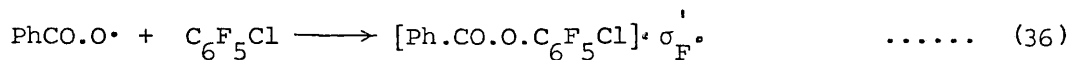


Fig. xx

The overall reaction mechanism for the decomposition of benzoyl peroxide in chloropentafluorobenzene is given in Scheme 30 . This mechanism is similar to that proposed by Bolton, Sandall and Williams⁹⁰ for the decomposition of benzoyl peroxide in hexafluorobenzene. The mechanism accounts for the following experimental observations;

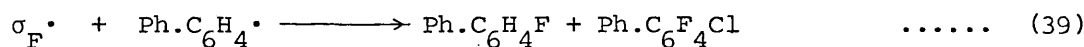
(a) Defluorination of the σ -complexes arising from attack of phenyl radicals on carbon bearing fluorine atoms and the dechlorination process of the intermediate σ -complexes which are produced by phenyl radical attack on carbon bearing chlorine.

(b) The formation of biphenyl from the combination of two phenyl radicals.

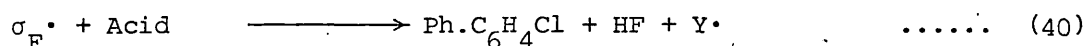


There are possibly a number of routes open for defluorination:

(a) Using biphenyl radicals;

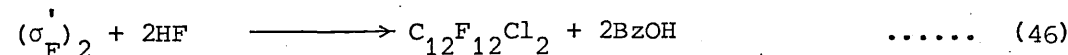
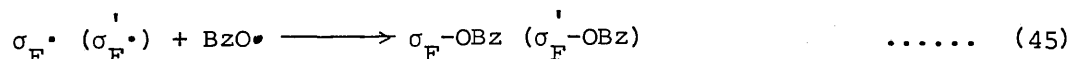
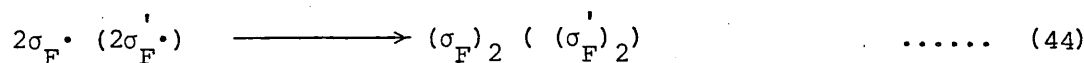
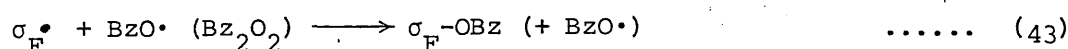
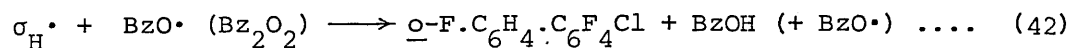
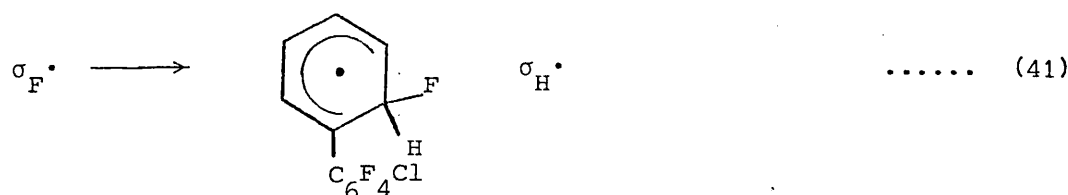


(b) Removal of fluorine by an aroic acid, (BzOH or \underline{p} -C₆H₅.C₆H₄CO₂H)



(where Y· ≡ BzO· or \underline{p} -C₆H₅.C₆H₄COO·)

(c) Or by rearrangement of $\sigma_{\text{F}}\cdot$ to $\sigma_{\text{H}}\cdot$, and dehydrogenation of $\sigma_{\text{H}}\cdot$, followed by subsequent defluorination by BzOH.



A similar mechanism can be proposed for phenyl radical attack on carbon bearing chlorine in chloropentafluorobenzene. Steps(35-38) would be similar and the three possible routes of dechlorination would be analogous to those proposed for defluorination, although the most likely route would be that involving $(\text{Ph.C}_6\text{H}_4\cdot)$ radicals, for the reasons already stated.

3.4.1.2. Decomposition of Benzoyl Peroxide in 1,3,5-Trichlorotrifluorobenzene

The results obtained from the thermal decomposition of benzoyl peroxide in 1,3,5-trichlorotrifluorobenzene are given in Table 29.

Table 29

Products from the thermal decomposition of benzoyl peroxide
in 1,3,5,-trichlorotrifluorobenzene

	Yield (mole per mole % of benzoyl peroxide)
Ph.Ph	4.00
$3,5\text{-F}_2\cdot\text{C}_6\text{Cl}_3\cdot\text{Ph}$	1.40
$3,5\text{-Cl}_2\text{C}_6\text{F}_3\cdot\text{Ph}$	1.30

The decomposition of benzoyl peroxide in this substrate has not been previously reported in the literature. If the resonance structures of the σ -complexes arising from phenyl radical attack on carbon bearing fluorine and carbon bearing chlorine are drawn the influence of the halogens upon the stability of the σ -complexes can be seen (Fig. xxi)

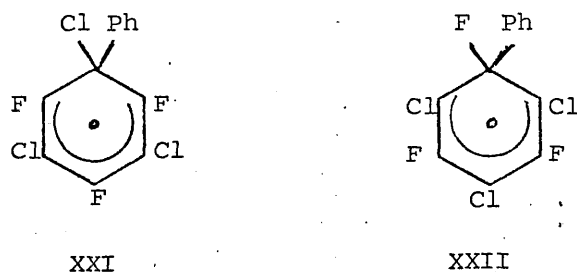


Fig. xxi

If the σ -complexes are stabilised by the halogen substituents in the order previously found, i.e. $F > Cl > Br > H$, then the relative stabilities of XXI and XXII (Fig. XXI) can be determined. Structure XXI is stabilised by two ortho-fluorine atoms and one para-fluorine atom. Structure XXII is stabilised by two ortho-chlorine atoms and one para-chlorine atom. Therefore as fluorine exhibits a stronger stabilising influence over chlorine in these σ -complexes, structure XXI will represent an *Stabilised* system compared to structure XXII. Hence attack by phenyl radicals at a carbon bearing chlorine atom in XI. will be just as effective, i.e. occur at a similar rate, as it does in chloropentafluorobenzene. The attack of phenyl radicals on a carbon bearing fluorine atom in XXII will occur at a slower rate compared to chloropentafluorobenzene because the σ -complex formed will be less stable due to the presence of chlorine atoms in the o- and p-positions, than the σ -complexes XXIII - XXV (Fig. xxii)

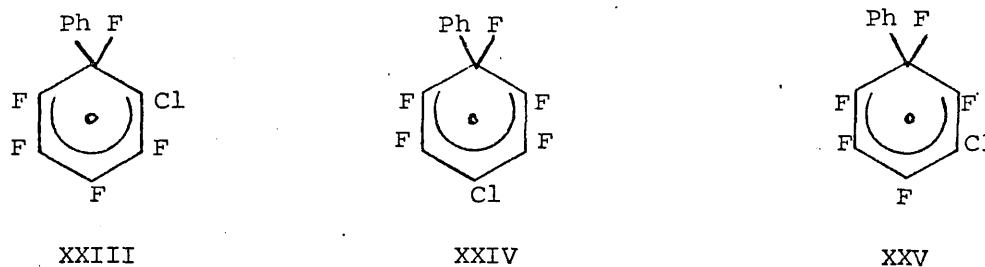


Fig. xxii

This result has been confirmed using competition reactions and is discussed in Section 3.4.4.

Another consequence of the stabilities of XXI and XXII (Fig. xxi), is reflected in the similar yields of biaryl products formed in this reaction. As the σ -complex XXI represents an activated system compared to the σ -complex XXII which is deactivated, the net result is that the yield of the biaryls formed from these two intermediates are approximately the same.

The low yield of products obtained in this reaction can also be explained in terms of the relative stabilities of the σ -complexes XXI and XXII. As the stabilities of XXI and XXII have been lowered compared to the σ -complexes formed from phenyl radical attack on chloropentafluorobenzene, by replacing fluorine atoms with chlorine atoms, the life-times of XXI and XXII will be extremely short. Hence they will not exist in solution long enough to undergo dehalogenation but will undergo some alternative fate, e.g. dimerisation to produce polyhalogenoquaterphenyls (fig. xxiii), by analogy with the σ -complexes formed in phenylation reactions of simple benzene systems³³.

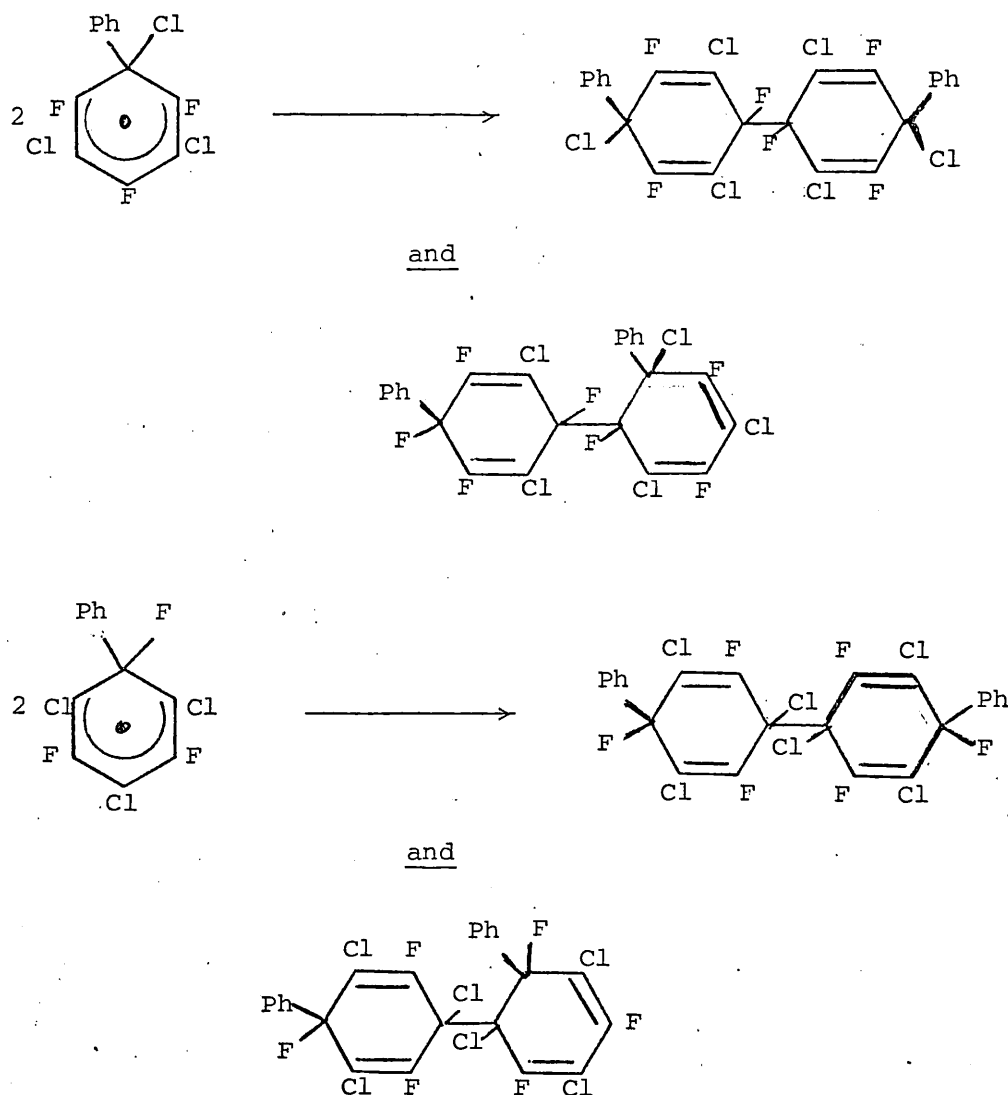


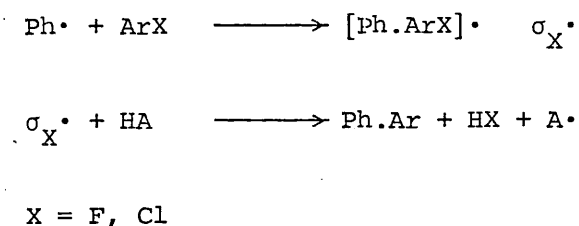
Fig. xxiii

3.4.2. The Effect of an Additive on the Decomposition of Benzoyl Peroxide in some Polychloropolyfluorobenzenes

3.4.2.1. The Effect of Trichloroacetic Acid on the Thermal Decomposition of Benzoyl Peroxide in Chloropentafluorobenzene

The addition of a number of additives which can act as hydrogen donors, on the decomposition of phenylazotriphenylmethane in hexafluorobenzene has been investigated by Williams and co-workers¹⁴. From their studies it was found that the presence of trichloroacetic acid in the reaction mixture gave the greatest increase in the yield of biaryl material, although no relationship was found between the acidity of the additive and the yield of biaryl.

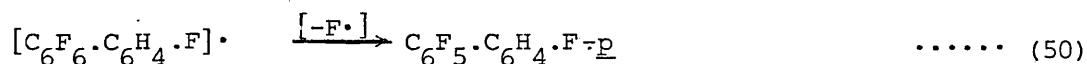
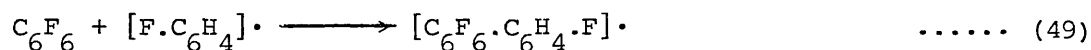
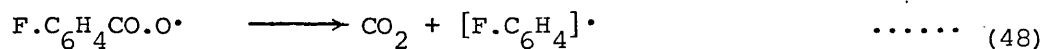
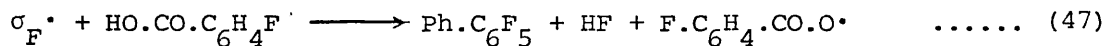
The additive provides hydrogen atoms that are required for the aromatisation of the σ -intermediates, probably by a mechanism similar to that outlined in Scheme 31, where HA represents the acid additive.



Scheme 31

A similar mechanism has been proposed by Bolton and Sandall⁸⁹ to explain the increase in the yield of 2,3,4,5,6-pentafluorobiphenyl. Arising from the decomposition of benzoyl peroxide in hexafluorobenzene in the presence of small quantities (0.1 - 0.4 mole) of p-fluorobenzoic acid. As removal of a hydrogen atom from p-fluorobenzoic acid, followed by subsequent decarboxylation, results in the formation of p-fluorophenyl radicals the influence of the additive on the reaction can be followed by monitoring the yield of 2,3,4,4',5,6-hexafluorobiphenyl. The proposed mechanism for the decomposition of benzoyl peroxide in hexafluorobenzene in the presence of p-fluorobenzoic acid is given in Scheme 32. Defluorination of the

σ -intermediate formed in eq. (49) is carried out by the mechanism previously described on page 106 Scheme 27 .



Scheme 32

As a result of this work it was decided to use trichloroacetic acid as the additive in the reactions under study here.

The results obtained from the decomposition of benzoyl peroxide in chloropentafluorobenzene in the presence of trichloroacetic acid, are presented in Table 30 . The yields of biaryls and benzoic acid are increased. These results suggest that mechanisms similar to those previously described illustrating the effect of additives on the yields of biaryls, are operating.

The results are also consistent with the interpretation given previously (pages 112-114) to explain the stabilities of the intermediate σ -complexes, and the view that the orientation-determining step is the attack of the phenyl radical on the substrate.

Table 30

Products from the decomposition of benzoyl peroxide in chloropentafluorobenzene in the presence of trichloroacetic acid (0.0015 mole)

	$[\text{CCl}_3\text{CO}_2\text{H}]=0$ (mole per mole % of benzoyl peroxide)	Yield (mole per mole % of benzoyl peroxide)	Relative Yield (%)
Ph.Ph.	0.8	1.3	
Ph.C ₆ F ₅	1.5	5.2	
<u>o</u> -Cl.C ₆ F ₄ .Ph	11.4	19.6	37.1
<u>m</u> -Cl.C ₆ F ₄ .Ph	7.9	18.3	34.7
<u>p</u> -Cl.C ₆ F ₄ .Ph	6.1	14.9	28.2
Ph.CO.OH	20.0	37.5	

3.4.2.2. The Effect of Trichloroacetic Acid on the Thermal Decomposition of Benzoyl Peroxide in 1,3,5-Trichlorotrifluorobenzene

The results for the phenylation of 1,3,5-trichlorotrifluorobenzene in the presence of trichloroacetic acid are given in Table 31 .

Table 31

	$[\text{CCl}_3\text{CO}_2\text{H}]=0$	Yield mole per mole % of benzoyl peroxide	Relative Yield (%)
Ph.Ph	4.0	5.7	
3,5-F ₂ C ₆ Cl ₃ .Ph	1.4	1.90	51.4
3,5-Cl ₂ C ₆ F ₃ .Ph	1.3	1.80	48.6

The influence of an additive such as trichloroacetic acid does not appear to have such a large effect in increasing the yield of biaryl in this reaction as it does in the phenylation of chloropentafluorobenzene. This probably reflects the fact that the life-times of the σ -complexes XXI, XXII, (fig. xxi) are much shorter than those produced in the phenylation of chloropentafluorobenzene and so have alternative fates other than dehalogenation to biaryls. Dimerisation has already been suggested (page 120) as an alternative reaction pathway.

The similarity in product yields of the biaryls obtained from this study seem to confirm the reactivity of this substrate suggested by the theoretical model discussed in part 3.4.1.2.

3.4.3 Summary

(1) Attack by phenyl radicals on chloropentafluorobenzene results in aryldefluorination and aryldechlorination.

(2) The results from this study are consistent with those previously obtained for C_6F_5X ($X = H, Br, CF_3$) substrates, and a series which reflects the ability of a substituent X in C_6F_5X to stabilise the intermediate σ -complexes has been determined and discussed.

(3) A mechanism has been proposed to account for the experimental findings by analogy with the decomposition of benzoyl peroxide in hexafluorobenzene, although further work is required to confirm this.

(4) Attack by phenyl radicals on 1,3,5-trichlorotrifluorobenzene results in the formation of biaryls arising from aryldefluorination and aryldechlorination.

(5) The relative stabilities of the σ -complexes XXI, XXII (fig.xxi) have

been discussed in terms of the results obtained in (2). From this discussion it has been found that the similarity in the yields of biaryl arising from aryldefluorination and aryldechlorination can be explained in terms of the stabilities of the σ -complexes involved.

(6) The low yield of biaryl product obtained in the phenylation of 1,3,5-trichlorotrifluorobenzene has been explained as being due to the short life-time of the σ -complexes leading to dimerisation reactions.

(7) Addition of trichloroacetic acid to the decomposition of benzoyl peroxide in chloropentafluorobenzene produces an increase in the yield of biaryl. This is consistent with previously reported work on the effect of additives in homolytic aromatic substitution. The results support the mechanism reached in (3), that the orientation determining step is attack of a phenyl radical on the substrate molecule.

(8) Decomposition of benzoyl peroxide in 1,3,5-trichlorotrifluorobenzene in the presence of trichloroacetic acid does not result in the increased yields of biaryls found in (7). This is consistent with the suggestion in (6) that the life-time of a σ -complex in this system is not sufficient to enable the additive to assist in its aromatisation.

(9) The order of radical displacement found in these experiments is consistent with the order of radical displacement determined by Oldham, Williams and Wilson¹³⁹ for $F > NO_2 > Cl, Br$.

3.4.4. The Thermal Decomposition of Benzoyl Peroxide in Mixed Solvents. Competition Reactions using Hexafluorobenzene and some Polychloropolyfluorobenzenes

3.4.4.1. Quantitative Studies of Phenylation

In 1951, Hey and his co-workers embarked upon a quantitative study of homolytic arylation using the competitive method which had been used extensively by Ingold and others to study electrophilic substitution. The

principle behind this technique is to allow two molecular species to compete for an insufficient quantity of reagent, and to determine the relative amounts of product formed from each compound. From this the ratio of the total reaction rates for the two compounds may be calculated, (the total rate factor): $\frac{\text{PhX}}{\text{PhY}}K =$ the ratio of the total rates of phenylation of PhX and of PhY. Combination of this total rate factor with the isomer ratio of the substituted biaryls gives a new set of reactivity indices called partial rate factors. This is an expression of the reactivity of any specific nuclear position in PhX with reference to that of any one position in benzene. Expressions leading to the partial rate factors for mono-substituted benzenes are given below:

$$f_o = 3 \cdot \omega \frac{\text{PhX}}{\text{PhH}}K$$

$$f_m = 3 \cdot \mu \frac{\text{PhX}}{\text{PhH}}K$$

$$f_p = 6 \cdot \pi \frac{\text{PhX}}{\text{PhH}}K$$

where ω , μ and π are the isomer ratios for the ortho-, meta- and para-position respectively.

In the formulation of partial rate factors, one assumption has been made, i.e. the rate of formation of binuclear products is directly related to the rate of formation of the various σ -complexes. If the σ -radicals are not all oxidised to biaryls but are selectively diverted, e.g. by dimerisation or disproportionation to other non-biaryl products this will render the derived partial rate factors invalid. On these grounds Pausacker and Lynch³³, Walling¹³² and Cade and Pilbeam¹³³ criticised the validity of such partial rate factors as true measures of the reactivity of the various positions in the aromatic nucleus. When competition reactions are conducted in the presence of an oxidising agent^{134,135}

the isomer ratios and the total rate factors are different from those obtained in similar reactions in the absence of such an additive. Therefore one of the requirements for the successful use of the competition reaction is that all of the σ -complexes, or nearly all, are converted into the analysed reaction products, or that the same proportion of the σ -complexes in each case is converted to product. A further requirement necessary for obtaining reliable data from competition reactions is that the differences in polar character between each of the substrates used in the competition reaction must be negligible. This is to avoid substrate - substrate complexation which may occur in systems where the polar properties of the substrates are different, as for example in the hexafluorobenzene - benzene systems. Similarly radical - substrate or radical precursor - substrate complexation may occur in systems where differences in the polar properties of the radical or its precursor are large, as for example in the pentafluorophenylation of mono-substituted benzenes. A third requirement necessary for obtaining reliable data from competition reactions is that both the mechanism of substitution and the atom displaced by phenyl radical attack should be the same for each of the reacting species.

Competition reactions in this study were carried out using hexafluorobenzene as the reference standard and used trichloroacetic acid to reduce reactions, such as dimerisation, which could divert σ -complexes away from biaryl formation, thereby fulfilling the requirements previously stated (page 126) for the successful use of the competition reaction. The data obtained from the decomposition of benzoyl peroxide in chloropentafluorobenzene - hexafluorobenzene and 1,3,5-trichlorotrifluorobenzene - hexafluorobenzene mixtures are given in the following Table 32 .

Table 32

		Yield (mole per mole % of benzoyl peroxide)	Relative Yield (%)*
C_6F_6/C_6F_5Cl 1:1 mole ratio	Ph.Ph	1.0	
	Ph. C_6F_5	14	
	<u>o</u> -Cl. C_6F_4 .Ph	9	43
	<u>m</u> -Cl. C_6F_4 .Ph.	7	33
	<u>p</u> -Cl. C_6F_4 .Ph.	5	24
$C_6F_6/C_6F_3Cl_3$ 1:1 mole ratio	Ph.Ph	0.7	
	Ph. C_6F_5	28	
	3,5- $F_2C_6Cl_3$ Ph	23	79
	3,5- $Cl_2C_6F_3$.Ph	6	21

* Isomer distribution of biaryl products.

The partial rate factors and relative rates of phenyl radical attack on a range of C_6F_5X ($X = H, Br, Cl$) substrates is given in Table 33 .

Table 33

Partial rate factors and relative rates of phenylation of some C_6F_5X substrates

Substrate	$\frac{C_6F_5X}{C_6F_6}$ K	f'_o	f'_m	f'_p	Reference
C_6F_5Cl	1.34	1.75	1.31	1.88	this work
C_6F_5Br	1.00	1.4	1.1	1.05	138
C_6F_5H	0.9	0.4	1.2	0.6	75
C_6F_5Br	1.50	2.1	1.6	1.3	75

The results obtained in this research are consistent with those obtained in other studies involving C_6F_5X derivatives¹³². The three positions (o-, m-, p-) with respect to the substituent X, in chloropentafluorobenzene show an increased activation over similar positions in the bromo-analogue, and this is consistent with the observed mesomeric effect found in the halogen series, i.e. $F > Cl > Br > I$. In the competitive phenylation of bromopentafluorobenzene, the rate of attack $\frac{C_6F_5Br}{C_6F_6} K = 1.5$, differs from that obtained when both of these substrates competed separately with benzene when a value of $\frac{C_6F_5Br}{C_6F_6} K = 1.00$ was obtained. The relative rate $\frac{C_6F_5Br}{C_6F_6} K$, was calculated using the relationship defined by Augood and Williams eq. (51) which is

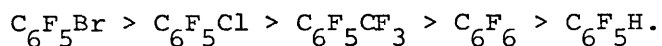
$$\frac{A}{B} K = \frac{A}{C} \cdot \frac{C}{B} \quad \dots\dots (51)$$

invalid as "free" intermolecular selection does not take place. Competition reactions in which bromopentafluorobenzene and hexafluorobenzene compete with octafluorotoluene for phenyl radicals produce a relative rate of $\frac{C_6F_5Br}{C_7F_8} K = 1.3$, thus confirming the higher value of 1.5 obtained for $\frac{C_6F_5Br}{C_6F_6} K$. Deviations in the Augood, Williams²² relationship given in (51)

have previously been observed in the phenylation of some pentafluorophenyl derivatives⁷⁶ and also in the reactions of mono- and di-substituted benzenes¹³⁶. These deviations can be used as evidence to support the idea of an "intra-molecular" selection process. This involves the formation of substrate - radical or substrate - radical precursor complexes by Van der Waals forces. If such complexing occurs between phenyl radical precursors and C_6F_5X molecules, the phenyl radicals subsequently generated may not show a random selectivity towards the competing substrate molecules,

and so the derived reactivities will reflect the stability of the complex, and will not represent the actual reactivities of the various sites in the substrate. This deduction also follows if phenyl radicals themselves complex in this way, which may be a further complication. This will mean that the phenyl radical will actively select more between sites outside the complex than within the complex itself, the consequence of this is that the phenyl radical will show greater discrimination as it attacks the substrate molecules.

The results obtained from the decomposition of benzoyl peroxide in the chloropentafluorobenzene - hexafluorobenzene system can be interpreted in a similar manner to the results obtained by Bolton, Sandall and Williams⁷⁵. These workers, using similar polyfluoroaromatic substrates, stated that the relative reactivities of substrate molecules towards phenylation are reflected in the different degrees of formation of the radical - substrates or radical precursor - substrate complexes, i.e.



In the decomposition of benzoyl peroxide in 1,3,5-trichlorotrifluorobenzene - hexafluorobenzene mixtures the following results have been observed.

(a) The yield of the two biaryl products from the competition reaction in the presence of trichloroacetic acid are greater than when the reaction was carried out in the single solvent.

(b) The total number of phenyl groups (C_6H_5) arising from the decomposition of benzoyl peroxide are not all accounted for in the biaryl products. This would suggest that the phenyl radicals find alternative destinies other than biaryl formation.

(c) The presence of trichloroacetic acid in the competition reaction increases the yield of 3,5-difluoro-2,4,6-trichlorobiphenyl over that of 3,5-dichloro-2,4,6-trifluorobiphenyl. If the results from the 1,3,5-trichlorotrifluorobenzene/trichloroacetic acid/benzoyl peroxide system (Table 31 page 123) are compared to the results obtained from the competition reaction (Table 32 page 128) it would appear that in the presence of hexafluorobenzene the dehalogenation process exhibits some type of selection, i.e. fluorine atoms are preferentially removed over chlorine atoms.

There are two possible lines of thought which could be used to explain the above experimental observations. The first is to interpret the results in terms of the relative stabilities of the resulting σ -complexes fluorine or carbon bearing chlorine, in a similar manner to that used by Bolton, Sandall and Williams⁷⁵. The second is to consider the role of complexation between the radical or radical precursor and substrate.

Phenylation of 1,3,5-trichlorotrifluorobenzene produces σ -complexes fig. (xxiv), XXVI and XXVII.



Fig. xxiv

The yields of the biaryls resulting from dehalogenation of the above σ -complexes will reflect the relative stabilities of XXVI and XXVII. In the presence of trichloroacetic acid in a non-competitive reaction it appears that the stabilities of XXVI and XXVII are equal, on the grounds that the yields of 3,5-difluoro-2,4,6-trichloro- and 3,5-dichloro-2,4,6-trifluoro-biphenyl are similar. However, in the competition reaction in the presence of trichloroacetic acid the yields of the two biaryl products are not equal, but the yield of 3,5-difluoro-2,4,6-trichlorobiphenyl exceeds that of the 3,5-dichloro-2,4,6-trifluorobiphenyl. Thus in this system it would appear that the phenyl radicals attack a carbon bearing fluorine atom in preference to a carbon bearing chlorine atom. In this case it is the σ -complex XXVI (fig. XXIV) which shows the greatest stability compared to the σ -complex XXVII.

An alternative way of rationalising the observed biaryl yields in the 1,3,5-trichlorotrifluorobenzene-hexafluorobenzene system is to envisage a situation in which the phenyl radical is not able to select among the sites in the substrates.

As previously mentioned (page 129) differences in the polar properties between the radical and the substrate have been shown to give erroneous results for the reactivities of substrate molecules towards homolytic arylation.

Phenyl radicals, benzoyloxy radicals and benzoyl peroxide itself show different polar properties to the substrates used in this study. Therefore we have present in this system a situation where complexing between radical/radical precursor and substrate is possible, as found in similar reactions⁷⁵, using polyfluoroaromatic compounds. If

complexation occurs between the radical (or radical precursor) and the substrate, the radical species is stabilised, and any radical entity subsequently generated from the complex, will not exhibit a random selectivity towards the sites of attack in the competing substrate molecules, but shows a certain degree of discrimination. As the difference in yields of the two biaryls arising from defluorination and dechlorination of XXVI and XXVII (fig.xxiv) only occur in the competition reaction it would appear that any complex formed derives from hexafluorobenzene. The type of complex envisaged, involves a specific arrangement of the radical precursor and the substrate molecules such that upon decomposition the phenyl radical would be in the vicinity of a carbon bearing fluorine atom, thereby giving σ -complexes of the type XXVI (fig.xxiv). The diagram below illustrates the type of "sandwich" complex which could be relevant.

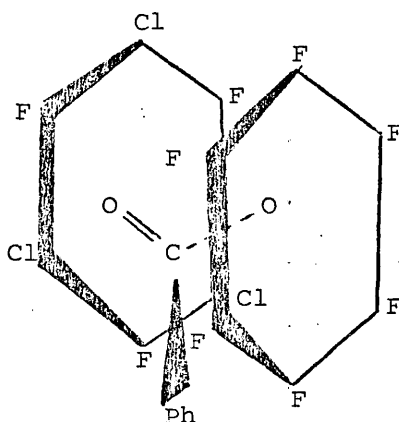


Fig. XXV

Evidence for the participation of complexes involving radical precursors and substrates has been documented, involving benzoyl peroxide - pyridine³⁹ and benzoyl peroxide - toluene systems¹³⁴.

In conclusion it must be pointed out that the postulate of complexes of the type illustrated in fig. (xxv) has not been confirmed directly

but they can be used to explain the anomalies observed in the yield of biaryls arising from the competitive phenylation of 1,3,5-trichlorotrifluorobenzene - hexafluorobenzene systems.

Summary

(a) Evidence for aryldefluorination and aryldechlorination has been found in the competitive phenylation of chloropentafluorobenzene - hexafluorobenzene and 1,3,5-trichlorotrifluorobenzene systems.

(b) Partial rate factors and the relative rate of attack were obtained for the phenylation of chloropentafluorobenzene - hexafluorobenzene mixtures and are consistent with the observed order of reactivities previously found for a range of polyfluoroaromatic substrates. The order of reactivities found for the sites in chloropentafluorobenzene are also consistent with the observed mesomeric effect in the halogen series, i.e. $F > Cl > Br > I$.

(c) Phenylation of 1,3,5-trichlorotrifluorobenzene - hexafluorobenzene mixtures in the presence of trichloroacetic acid results in an increase in the yield of 3,5-difluoro-2,4,6-trichlorobiphenyl compared to the yields obtained from the non-competitive experiment. This result is discussed in terms of complexation between the radical precursor and the substrate, thereby stabilising the radical species with the overall result that any radical intermediate produced from the decomposition of the complex will show greater discrimination in attacking the substrate molecules.

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