HOMOLYTIC PATHWAYS TO AROMATIC BROMO-COMPOUNDS

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

by

MUHAMMAD IQBAL BHANGAR

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To

Baba and Amma
Acknowledgements

I wish to express by sincere gratitude to my supervisors Professor G.H. Williams and Dr. R. Bolton for suggesting the topic of research, and for their advice and constant enthusiasm throughout the period of this work.

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Abstract

The reactions of some polybromoanilines with pentyl nitrite in benzene at $80^\circ$ has been studied. 2,3,4,5,6-Pentabromobiphenyl was prepared by this method and also by the Ullmann reaction between iodobenzene, pentabromiodobenzene, and copper powder. The yield of biaryl formed from homolytic arylation of benzene decreases as o-bromoaniline, 2,4,6-tribromoaniline or pentabromoaniline are the sources of the aryl radicals. This decrease is paralleled by an increase in the yield of the benzene derivative arising from the formal protodeamination of the parent aniline derivative. Evidence was also found of a heterolytic reaction accompanying the main homolytic arylation reaction which gives hexabromobenzene as a side-product in the reaction of pentabromoaniline and pentyl nitrite in benzene.

Photochemical bromination reactions of some benzene derivatives, using molecular bromine as the source of bromine atoms, were performed. Both nuclear addition and nuclear substitution products were formed, the relative amounts of which vary with the benzene derivative since both polar and steric factors influence these reactions. However, it was found that the ratio of nuclear substitution to nuclear addition increased with increase in temperature from ca. 25 to ca. 50°. Evidence (i.e. the photochemical decomposition of benzene hexabromide and of 1,2,3,4,5,6-hexabromochlorocyclohexane to give some di-halo-arenes) was adduced which suggests an addition-elimination mechanism as an interpretation of the formation of bromo-arenes in the photochemical bromination of benzene derivatives. Direct abstraction of hydrogen from a species such as $\text{C}_6\text{H}_6\cdot\text{Br}^*$ seems unlikely by $\text{Br}_2$ on thermochemical grounds, but possible by $\text{Br}^*$ or by a photochemically excited species $\text{Br}_2^*$. 
Partial rate factors for free radical bromination of biphenyl have been determined and discussed, although it is unlikely that they are capable of simple interpretation. The isomer distribution of bromo-arenes found here was quite different from the corresponding ratio reported for heterolytic reactions. The meta-positions of certain benzene derivatives, which are deactivated towards electrophiles in ionic reactions, were found to be readily attacked by bromine atoms.
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1. **Introduction**

A free radical may be defined as an atom or group of atoms having an unpaired electron, formed as a result of a homolytic cleavage of a bond i.e. cleavage in which each group retains one of the bonding electrons.

\[ A - B \rightarrow A^* + B^* \]

This homolytic cleavage could happen spontaneously or could be induced by heat or light depending upon the strength of the bond present.

Carbon radicals i.e. radicals in which the unpaired electron is on a carbon atom, may have an intermediate structure between the carbonium ions and carbanions. Carbonium ions (I) are planar with the central carbon atom sp\(^2\) hybridized and a vacant p\(^z\) orbital. Carbanions (IV) are pyramidal with the carbon centre sp\(^3\) hybridized. Carbon radicals (II) are generally planar with the unpaired electron in a p\(^z\) orbital. This may have a certain degree of s character according to the nature of the substituent attached to the carbon (III).

The generally accepted theory that free radicals are electrically neutral does not prevent them being more reactive than ions. The high reactivity usually associated with free radicals is due to the unpaired electron, the driving force being the tendency to satisfy normal valency requirements. A radical reaction initiated by heat or light produces free radicals which may set up a chain process by reacting with other molecules.
in different ways, thus propagating reaction by any of the processes of abstraction, addition and fragmentation, eq. (1), (2) and (3) respectively.

\[
\begin{align*}
R^* + XY & \rightarrow RY + X^* \quad \ldots \ldots \quad (1) \\
R^* + \cdot\!C=\!C\cdot & \rightarrow R\cdot\!\!\!\cdot\!C\cdot\!\!\!\!\cdot \quad \ldots \ldots \quad (2) \\
Ph-O' & \rightarrow Ph^* + CO_2 \quad \ldots \ldots \quad (3)
\end{align*}
\]

This chain then ends by certain radical-destroying process such as radical coupling or disproportionation, eq. (4) and (5) respectively,

\[
\begin{align*}
R^* + R^* & \rightarrow R-R \quad \ldots \ldots \quad (4) \\
R^* + R^* & \rightarrow RH + R^-\!H \quad \ldots \ldots \quad (5)
\end{align*}
\]

for example, chlorination of methane is a chain reaction,

\[
\begin{align*}
Cl_2 \overset{hv}{\rightarrow} 2Cl \quad \ldots \ldots \quad (6) \, \text{Initiation} \\
Cl^* + CH_4 & \rightarrow CH_3^* + HCl \quad \ldots \ldots \quad (7) \\
CH_3^* + Cl_2 & \rightarrow CH_3Cl + Cl^* \quad \ldots \ldots \quad (8) \\
Cl^* + Cl^* & \rightarrow Cl_2 \quad \ldots \ldots \quad (9) \\
CH_3^* + Cl^* & \rightarrow CH_2Cl \quad \ldots \ldots \quad (10) \, \text{Termination} \\
CH_3^* + CH_3^* & \rightarrow H_3C-CH_3 \quad \ldots \ldots \quad (11)
\end{align*}
\]

Free radicals are usually more reactive and hence less selective, than ions. Their reactions are fast and of low activation energy and so often tend to give side-products, in contrast to most heterolytic reactions. Radicals being electrically neutral, are expected to be less sensitive to polar effects either in the solvent or at the reaction site. However, in some cases polar influences do in fact affect radical reactions. Such effects are, however, smaller than those operating in ionic reactions.
It is often difficult to decide whether a reaction is actually a free radical process or not. The change from a radical to an ionic mechanism can be easy; it may occur upon change of substituents, addition of a polar catalyst or use of a polar solvent. In some cases reactions can involve both radical and ionic processes in different stages. For instance, in allylic bromination with N-bromosuccinimide, the effective brominating agent is molecular bromine, at low stationary concentration, which operates by a homolytic mechanism.

\[
\begin{align*}
\text{Br}^\cdot + \text{RH} & \rightarrow \text{R}^\cdot + \text{HBr} \quad \ldots \ldots \quad (12) \\
\text{R}^\cdot + \text{Br}_2 & \rightarrow \text{RBr} + \text{Br}^\cdot \quad \ldots \ldots \quad (13)
\end{align*}
\]

The source of bromine is the fast ionic reaction between the N-bromosuccinimide and hydrogen bromide liberated in step 12.

\[
\begin{align*}
\text{N-Br} + \text{HBr} & \rightarrow \text{NH} + \text{Br}_2 \quad \ldots \ldots \quad (14)
\end{align*}
\]

The presence of transient radicals may be deduced from their effects often by a departure from the rules of activation and orientation for heterolytic processes, or by the high sensitivity of free radical initiators or light.

1.1. Stability of free radicals

The stability of the product radical is generally related inversely to the activation energy of the reaction leading to its formation. Table 1 illustrates the well known consequences of relative stabilities of allyl
radicals (primary < secondary < tertiary) namely that the rates of hydrogen abstraction reactions leading to these radicals vary in the same order. The magnitude of these rate differences, however, depend upon the reactivities of the abstracting radicals. Thus the selectivity of these radicals increases with their decreasing reactivity (or increasing stability). Thus the relative rates of these reactions are influenced by the stabilities of the attacking and product radicals.

Table 1
Relative reactivities (per active hydrogen) of alkanes and arylalkanes towards radicals.

<table>
<thead>
<tr>
<th>X (°C)</th>
<th>-CH₂</th>
<th>&gt;CH₂</th>
<th>&gt;CH</th>
<th>Ea⁺ (kcal mole⁻¹)</th>
<th>D(H-X) (kcal mole⁻¹)</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F· (25)</td>
<td>1</td>
<td>1.2</td>
<td>1.4</td>
<td>1.21</td>
<td>136</td>
</tr>
<tr>
<td>OH· (17.5)</td>
<td>1</td>
<td>4.7</td>
<td>9.8</td>
<td>3.83</td>
<td>103</td>
</tr>
<tr>
<td>Cl· (25)</td>
<td>1</td>
<td>4.6</td>
<td>8.9</td>
<td>119</td>
<td></td>
</tr>
<tr>
<td>MeO· (230)</td>
<td>1</td>
<td>8.5</td>
<td>27</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td>F₃C· (182)</td>
<td>1</td>
<td>6.0</td>
<td>36</td>
<td>11.7</td>
<td>104</td>
</tr>
<tr>
<td>Bu'O· (40)</td>
<td>1</td>
<td>10</td>
<td>44</td>
<td>106</td>
<td></td>
</tr>
<tr>
<td>Ph· (60)</td>
<td>1</td>
<td>9.3</td>
<td>44</td>
<td>7.5</td>
<td>112</td>
</tr>
<tr>
<td>Me· (182)</td>
<td>1</td>
<td>7</td>
<td>50</td>
<td>104</td>
<td></td>
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<tr>
<td>Cl₃C· (190)</td>
<td>1</td>
<td>80</td>
<td>6300</td>
<td>104</td>
<td></td>
</tr>
<tr>
<td>Br· (90)</td>
<td>1</td>
<td>250</td>
<td>6300</td>
<td>18.5</td>
<td>87</td>
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<table>
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<tr>
<th></th>
<th>PhCH₃</th>
<th>PhCH₂Me</th>
<th>PhCMe₂</th>
<th>Ph₂CH₂</th>
<th>Ph₃CH</th>
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<tr>
<td>Cl· (40)</td>
<td>1</td>
<td>2.5</td>
<td>5.5</td>
<td>2.0</td>
<td>7.2</td>
</tr>
<tr>
<td>Bu'O· (40)</td>
<td>1</td>
<td>3.2</td>
<td>6.8</td>
<td>4.7</td>
<td>9.6</td>
</tr>
<tr>
<td>Ph· (60)</td>
<td>1</td>
<td>4.6</td>
<td>9.7</td>
<td>7.5</td>
<td>39</td>
</tr>
<tr>
<td>Me· (65)</td>
<td>1</td>
<td>4</td>
<td>13</td>
<td>-</td>
<td>-</td>
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<tr>
<td>RO· (90)</td>
<td>1</td>
<td>7.8</td>
<td>13</td>
<td>16</td>
<td>13</td>
</tr>
<tr>
<td>Br· (40)</td>
<td>1</td>
<td>17</td>
<td>37</td>
<td>10</td>
<td>18</td>
</tr>
<tr>
<td>Cl₃C· (40)</td>
<td>1</td>
<td>50</td>
<td>260</td>
<td>50</td>
<td>160</td>
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† For hydrogen abstractions from methane.
Free radical stability is influenced by the ability of the group adjacent to the radical centre to delocalize the unpaired electron, as the phenyl group does in the benzyl radical (V). E.s.r. measurements indicate that the spin density on the methyl carbon is decreased from 1 to 0.77 by the replacement of a hydrogen by a phenyl group.

\[
\begin{align*}
\text{CH}_2 - & - \text{CH}_2 \\
| & | \\
\text{[V]} & \text{[V]}
\end{align*}
\]

A study of the reactivity of various radicals reveals that among halogens, fluorine is the most reactive and its reactions are very exothermic and often difficult to control. However, recently, certain methods have been reported in which all carbon-hydrogen bonds can be converted into carbon-fluorine bonds. Chlorine is less reactive than fluorine, but more reactive than bromine. Bromine, being mildly electrophilic, is selective in nature and hence been widely used as a brominating agent for both alkyl and aryl hydrocarbons. It is quite possible to brominate even tertiary positions selectively with bromine. Iodine is seldom used as a source of halogen radicals, partly because the hydrogen iodide formed reduces the alkyl iodide and also because the iodine atom is insufficiently reactive. The phenyl radical is similar in reactivity to the methyl radical (at 65°); it is more selective than chlorine or t-butoxy-radicals, and less so than bromine or the trichloromethyl radical (at 40°).

From a study of the dissociation energies of primary, secondary and tertiary carbon-hydrogen bonds, shown in Table 2, and from the relative
reactivities of primary, secondary and tertiary hydrogen atoms towards radicals (Table 3), it has been found that the order of the stability of the alkyl radicals is tertiary > secondary > primary, because of the different abilities of the alkyl groups to stabilize the radicals by hyperconjugation. This difference in relative stabilities of primary, secondary and tertiary radicals is, however, much less than that of the corresponding carbonium ions.

Table 2
Dissociation energies of C-H bonds in different environments  

<table>
<thead>
<tr>
<th>R-H</th>
<th>Bond dissociation energy k cal mole$^{-1}$</th>
</tr>
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<tbody>
<tr>
<td>Ph-H</td>
<td>103</td>
</tr>
<tr>
<td>CH$_3$-H</td>
<td>104</td>
</tr>
<tr>
<td>C$_2$H$_5$-H</td>
<td>98</td>
</tr>
<tr>
<td>Me$_2$CH-H</td>
<td>94.5</td>
</tr>
<tr>
<td>Me$_3$C-H</td>
<td>91</td>
</tr>
<tr>
<td>CH$_2$=CHCH$_2$-H</td>
<td>85</td>
</tr>
<tr>
<td>Ph-CH$_2$-H</td>
<td>85</td>
</tr>
<tr>
<td>HO-CH$_2$-H</td>
<td>92</td>
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<td>F$_3$C-H</td>
<td>105</td>
</tr>
<tr>
<td>Cl$_3$C-H</td>
<td>96</td>
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Table 3

Relative selectivities in hydrogen abstraction by halogen atoms at 300 K

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<thead>
<tr>
<th>Halogen</th>
<th>$\text{-CH}_3$</th>
<th>$\text{CH}_2$</th>
<th>$\text{CH}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>1</td>
<td>1.3</td>
<td>1.8</td>
<td>7</td>
</tr>
<tr>
<td>Cl</td>
<td>1</td>
<td>4.4</td>
<td>6.7</td>
<td>8</td>
</tr>
<tr>
<td>Br</td>
<td>1</td>
<td>80</td>
<td>1,600</td>
<td>9</td>
</tr>
<tr>
<td>I</td>
<td>1</td>
<td>1,850</td>
<td>210,000</td>
<td>10</td>
</tr>
</tbody>
</table>

The addition of hydrogen bromide to olefin proceeds by the addition of Br· to the terminal carbon atom because the intermediate (VIa) is more stable, due to hyperconjugation, than the (VIb). The abstraction of hydrogen from ethylbenzene by the methyl radical would be expected to occur at the α-position rather than the β-position as the radical (VIIa) is more stabilised than (VIIb) due to resonance involving the benzene ring. Groups such as carbonyl, carboalkoxy-, cyano- or methyl can also stabilise the intermediate radical in a similar way.
A comparison of the reactivities of carbon-hydrogen bonds towards chlorine and bromine radicals, reported by Russell and De Boer, is summarised in Table 4.

Table 4

Effect of structure on the relative reactivities of C-H bonds towards radicals.

<table>
<thead>
<tr>
<th>Bond</th>
<th>D(&gt;C-H)</th>
<th>Br(^{-})(40^\circ)</th>
<th>Cl(^{-})(40^\circ)</th>
<th>Ph(^{-})(60^\circ)</th>
<th>Bu(^{t})O(^{-})(40^\circ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me-H</td>
<td>104</td>
<td>0.0007</td>
<td>0.004</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Et-H</td>
<td>98</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
</tr>
<tr>
<td>Pr-H</td>
<td>95</td>
<td>220</td>
<td>4.3</td>
<td>9.2</td>
<td>10</td>
</tr>
<tr>
<td>Bu(^{t})-H</td>
<td>91</td>
<td>19,400</td>
<td>6.0</td>
<td>40</td>
<td>44</td>
</tr>
<tr>
<td>Ph-CH(_2)-H</td>
<td>85</td>
<td>64,000</td>
<td>1.3</td>
<td>9.2</td>
<td>10</td>
</tr>
<tr>
<td>PhCH(Me)-H</td>
<td>-</td>
<td>1,000,000</td>
<td>3.3</td>
<td>37</td>
<td>32</td>
</tr>
<tr>
<td>PhC(Me)(_2)-H</td>
<td>-</td>
<td>2,330,000</td>
<td>7.3</td>
<td>81</td>
<td>68</td>
</tr>
<tr>
<td>Ph(_2)CH-H</td>
<td>-</td>
<td>620,000</td>
<td>2.6</td>
<td>62</td>
<td>47</td>
</tr>
<tr>
<td>Ph(_2)CMe-H</td>
<td>-</td>
<td>2,700,000</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ph(_3)C-H</td>
<td>75</td>
<td>1,140,000</td>
<td>9.5</td>
<td>330</td>
<td>96</td>
</tr>
</tbody>
</table>

In cumene, the α-hydrogen is two millions times more reactive than the hydrogen in ethane towards bromine, while towards chlorine atoms the relative reactivity is only seven times judging by the appropriate rate coefficients. It could be seen that on the basis of Hammond's postulate where there is a considerable bond rupture the transition state resembles the product, as is evident from (VIIIa), when there is very little carbon-hydrogen bond breaking in the transition state it resembles with the reactant (VIIIb). Hence the transition state (VIIIa) is more stable than...
Thus as shown, bromine atom reactions involve a larger extent of bond breaking than do the reaction of chlorine atoms. For instance, in hydrogen abstractions from ring substituted toluenes, the substituents will be more effective in influencing the relative stabilities of the transition states (and, hence, the rates) of bromine than chlorine atom reactions. For bromine and chlorine $\rho$ values are found to be $-1.36$ (at $80^\circ$) and $-0.66$ respectively. This shows that the resonance hybrid for bromine atom reactions is analogous to that for chlorine but with a significantly larger amount of charge separation and positive charge on benzyl carbon.

Thus a greater degree of selectivity is expected in the reaction of bromine.

1.2 Polar effects

Although the course of a homolytic reaction may be controlled by the relative stability of the radical intermediate in most of the reactions, the participation of effects of a polar nature cannot be ignored. Davidson suggested that in free-radical processes both the polar and stability factors made important contributions. In a highly exothermic
reaction (A), (figure 1) the transition state will resemble the reactants, where as for a less exothermic reaction (B) it would resemble the product. (Hammond's postulate). Thus polar effects with the substrate molecule, which effect the stability of the incipient radical are expected to be more important in reactions of high activation energy. This has been shown in the abstraction of hydrogen from benzylic carbon-hydrogen bonds. The order of reactivity of carbon-hydrogen bonds has already been shown to be tertiary > secondary > primary (c.f. page 14). This difference in reactivity depends upon the stability of their incipient radicals. Radicals like Cl* and CH₃* are less selective in their attack on the various types of bonds, but less reactive radicals (e.g. Br* and CCl₃*) show greater selectivity in their attack.

Free-radicals show a wide range of polarity, although they are found to be neutral when compared with negative and positive ions. The terms acceptors and donors have been suggested. A donor radical has a high tendency to form a stable cation rather than an anion.
Less stable than Donor radical More stable than
R^+

R^+ + e^- \rightarrow R^-

Less stable than Acceptor radical More stable than
R^-

R^- + e^- \rightarrow R^+

The donor/acceptor properties are expected from a consideration of the relative stabilities of the appropriate carbonium ion and carbanion.

A majority of radicals such as halogens, alkoxy- and appropriately substituted phenyl radicals are classified as acceptor, or electrophilic in nature. The preferred direction of electron transfer is particularly relevant to the type of polar structure which can be written as contributing to the transition state (IX) in which R^* is an acceptor

\[ X - R + R^* \rightarrow [X \cdots \cdots H \cdots \cdots R \leftarrow XHR] \rightarrow X^+ + R - H \]

(IX)

The extent to which polar effects influence radical reactions is much smaller than in ionic reactions in which charged particles participate. For instance, in the hydrogen abstraction reaction from the methyl group of toluene by bromine atom, the transition state has a polar character in which there is a charge separation such as (X)

\[ \text{CH}_2 \cdots \cdots \text{H} \cdots \cdots \text{Br} \quad \text{or} \quad \text{CH}_2 \cdot \text{H} \cdot \text{Br}^* \]

(X)
Evidence for such polar characteristics of the transition state is mentioned on page 19. Substituents have a smaller effect ($\rho \sim -1.36$) than they do in ionic reactions. For instance, in $S_N$ reactions the $\rho$ values are generally about $-4$ as considerable positive charge is created in the transition state.  

A range of work in aromatic substitution has revealed the polar characteristics of free radicals. Detailed study of the reactivities of substituted phenyl radicals was done by Hey and co-workers $^{17a-c}$ who found that electron-withdrawing substituents activate substrates towards donor radical reactions while electron-donating substituents activate the molecule towards attack by acceptor radicals. For instance, the para-nitrophenyl radical is an electrophile due to the $-I$ effect of the nitro-group and the para-tolyl radical is a nucleophilic radical due to the $+I$ effect of the methyl group. Thus the value found for the relative rates of arylation with para-nitro-phenyl radical $^{\text{PhNO}_2}$ is 0.94 and that with para-tolyl $^{\text{PhH}}$ radical is 3.4. These values indicate the polar influence of the substituents.

An interesting contrast between the radical and the ionic mechanism is also observed in the halogenation of alkanes. It has been found that the presence of an electron-withdrawing substituent deactivates the adjacent position towards halogen atom attack e.g. (XI):

```
H O

H--C--C--R

H

(XI)
```

Compounds of the type $X-\text{CH}_2-\text{CH}_3$ are attacked by the halogen predominantly at the $\beta$-position when $X$ is $\text{CO}_2\text{H}$, $\text{CO}.\text{Cl}$, $\text{CN}$, $\text{CO.\text{OR}}$ etc. This is in
contrast to electrophilic halogenation where only the $\alpha$-position is substituted, eq.(16)

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{H}
\end{array}
\xrightarrow{\text{Br}_2} 
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{Br}
\end{array}
\]

The deactivation of $\alpha$-positions is also at variance with the expected stability of the resultant radicals, since they would be expected to be stabilized by resonance similar to that for allylic and benzylic radicals. This behaviour is a result of a polar transition state discussed on page 19.

Halogen atoms are electrophilic and look for position of high electron density. Positions next to electron-withdrawing groups being electron deficient are therefore not preferred. Radicals which are not electrophilic do not display this behaviour. For example, the methyl radical is formally non-polar and does not avoid positions next to the electron-withdrawing groups: relative rates of abstraction of hydrogen at the $\alpha$- and $\beta$-carbons of propionic acid are\(^{18}\)

\[
\begin{array}{c|c|c}
\text{Me}^* & 1 & 7.8 \\
\text{Cl}^* & 1 & 0.03
\end{array}
\]

Hence, the free radical reactions are affected by the polar characteristics of the substituents present in a molecule. The ideal case in which free radicals, being formally neutral species, are free from the effect of any electrical characteristics either of charge distribution or of polarisability of the molecule attacked, can be realised very seldom.
In certain cases, depending upon the position of a polar group in a molecule, polar effects have been found to have comparatively little influence in determining the stability of the radical as Cadogan demonstrated in a study of the addition of bromotrichloromethane to some unsymmetrically substituted stilbenes. Substituents in the meta-position were found to have very little influence on the position of the attack of the electron-accepting trichloromethyl radical. This is due to the absence of any marked difference in stability between the two possible radicals in each case, since delocalisation of the benzylic free electron with the non-conjugated meta-substituent cannot occur. In contrast to this, in the case of para-substituted stilbenes a greater stability of radical (XIIa) than of (XIIb) might be expected as a result of possible additional delocalisation of the free electron.

\[\begin{align*}
\text{C} & \quad \text{C} \\
\text{CCl}_3 & \quad \text{CCl}_3 \\
\text{CH} & \quad \text{CH} \\
\text{C} & \quad \text{C} \\
\text{CH} & \quad \text{CH} \\
\text{H} & \quad \text{H} \\
\text{CH} & \quad \text{CH} \\
\text{CCl}_3 & \quad \text{CCl}_3 \\
\text{NO}_2 & \quad \text{NO}_2 \\
\text{NO}_2 & \quad \text{NO}_2 \\
\text{NO}_2 & \quad \text{NO}_2 \\
\text{NO}_2 & \quad \text{NO}_2 \\
\text{NO}_2 & \quad \text{NO}_2 \\
\text{NO}_2 & \quad \text{NO}_2 \\
\text{NO}_2 & \quad \text{NO}_2 \\
\text{NO}_2 & \quad \text{NO}_2 \\
\text{NO}_2 & \quad \text{NO}_2 \\
\end{align*}\]

This is probably the reason why the CCl\textsuperscript{3} radical attacks the carbon atom which is further away from the nitro-group, rather than any polar effect.

1.3. **Solvent polarity**

As compared to the heterolytic reactions, less work seems to have been reported regarding the influence of solvent polarity in free-radical reactions. Solvents have been found to affect rate, mechanisms or product
distributions in certain free radical reactions by different ways. The subject has been reviewed. A close comparison could be made with the ionic reactions in which the solvent effects could be predicted. More polar solvents increase the rate of nucleophilic substitution reactions in which there is charge formation in the transition state, by reducing the activation energy through greater solvation of the transition state.

\[
\text{RH} + Y \rightarrow \text{R}...\text{H}...\text{Y} \quad \text{SN}_2
\]

More polar solvents increase the rate of nucleophilic substitution reactions in which there is charge formation in the transition state, by reducing the activation energy through greater solvation of the transition state.

Peroxy-radicals (ROO*) which are intermediates in autoxidation reactions also show solvent dependence. Kinetic analysis of certain autoxidation reaction is reported to have shown that the rate of the reaction may be affected by the medium in which the reaction is performed. Complexing of the chain-carrying peroxy-radicals by the solvents is probably responsible for these rates of changes. It is suggested that peroxy-radicals being electron acceptors could give rise to a polar transition state in reactions of hydrocarbons e.g.

\[
\text{ROO}^* + \text{RH} \rightarrow \text{[R—O—O}...\text{H}...\text{R]}
\]

This transition state tends to undergo solvation with polar solvents.

Russell's classical example of the photochlorination of 2,3-dimethylbutane shows that various aromatic solvents can drastically alter the position of attack of chlorine atom. This effect is connected with the ability of aromatic hydrocarbon to form a complex with chlorine atom. The complexed chlorine atom is much more selective than free chlorine atoms. The relative reactivity ratio \(k_t/k_p\) of tertiary with respect to primary were calculated by the equation 17.
Rel. reactivity (tert/prim) = \( \frac{\text{Moles of tert-chloride}}{\text{Moles of prim-chloride}} \times 6 \) \hspace{1cm} (17)

The reaction is outlined in Scheme 1.

\[
\begin{align*}
\text{Cl}^* + \text{Me} - &\text{C} - \text{Me} \rightarrow \text{Me} - \text{C} - \text{Me} + \text{HCl} \\
&\text{(A)} \\
\text{Cl}^* + (\text{A}) &\rightarrow \text{CH}_2 - \text{C} - \text{Me} + \text{HCl} \\
&\text{(C)} \\
\text{Cl}_2 + (\text{B}) &\rightarrow \text{Cl}^* + \text{Me} - \text{C} - \text{Me} \\
&\text{(B)} \\
\text{Cl}_2 + (\text{C}) &\rightarrow \text{Cl}^* + \text{ClCH}_2 - \text{C} - \text{Me} \\
&\text{(C)}
\end{align*}
\]

Scheme 1

Table 5 gives some of the solvents used in this study with the corresponding tert/prim- ratios. This ratio becomes progressively large in certain aromatic solvents.
Table 5

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(Concentration, M)</th>
<th>Relative reactivities $k_t/k_p$</th>
<th>$25^\circ$</th>
<th>$55^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,3-Dimethylbutane</td>
<td>7.6</td>
<td>4.2</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>4.0</td>
<td></td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>Carbon disulphide</td>
<td>2.0</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>8.0</td>
<td>106</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>12.0</td>
<td>225</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>4.0</td>
<td>3.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t-butyl alcohol</td>
<td>4.0</td>
<td>4.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dioxan</td>
<td>4.0</td>
<td>5.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-butyl ether</td>
<td>4.0</td>
<td>7.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>4.0</td>
<td>4.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>2.0</td>
<td>11</td>
<td>8.0</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>4.0</td>
<td>20</td>
<td>14.6</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>8.0</td>
<td>49</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>4.0</td>
<td></td>
<td>15.4</td>
<td></td>
</tr>
<tr>
<td>Anisole</td>
<td>4.0</td>
<td></td>
<td>18.4</td>
<td></td>
</tr>
</tbody>
</table>

Changes of the selectivity with temperature are more pronounced with aromatic solvents than in the pure hydrocarbon. The very small solvent effects displayed by aliphatic solvents such as t-butyl alcohol, dioxan and ether may be due to the complexing of the electrophilic chlorine atom with the oxygen of these compounds. The comparatively small increase in selectivity caused by these solvents suggest that the equilibrium (18) in these cases, is probably on the side of the uncomplexed chlorine atom.
The higher degree of selectivity caused by carbon-disulphide is also thought to be due to some sort of π-complex between the chlorine atom and the sulphur.

Russell suggested two possible modes for complexing of the chlorine atom by an aromatic compound. One is the σ-complex and the other is a π-complex. Since there was no evidence of any addition or substitution products of aromatic compounds in the photochlorination reactions of 2,3-dimethylbutane when aromatic compounds were used as solvents, hence the intervention of a σ-complex is less likely.

The formation of a π-complex between the chlorine atom and the aromatic ring is possible. Table 5 shows that benzene derivatives having electron-donating groups (e.g. alkyl, ether) also increases the selectivity of the chlorine atom. On the other hand, electron withdrawing groups (e.g. nitro, halogen) decrease the selectivity relative to benzene.

1.4. Abstraction reactions by free radicals

Displacement of univalent atoms like hydrogen and halogens by free radical species are probably the simplest and most frequent reactions both in alkyl and aryl hydrocarbons. This happens to be in a more or less
analogous way to the $S_N$ reactions encountered in ionic species. A new radical is generated in a free radical abstraction reaction:

\[ X^* YZ \rightarrow XY + Z^* \]

1.4.1. **Hydrogen abstraction**: This has been the subject of much interest for many years since most of the free-radical substitution reactions reach to completion through hydrogen abstraction. The subject was reviewed by Trotman-Dickenson on the measurement of accurate rate constants in hydrogen abstraction reactions by several radicals, such as phenyl, alkyl, alkoxy-halogens etc. Of these the abstraction reactions by phenyl and halogen radicals being more relevant to this work are discussed here.

(a) **By halogen atoms**

The hydrogen abstraction reactions by different halogens are very common reactions when molecular halogen is used as a source of halogen atom. Substantial amount of work on the reactivity data, rate measurement etc., has been reviewed on the halogenation of aliphatic hydrocarbons compared with the aromatic compounds.

Halogens, among themselves, exhibit a great difference in their reactivity with hydrocarbons. The reactivity decreases in the order F $>$ Cl $>$ Br $>$ I. This is due to the difference in the bond strength of the corresponding halogen acids i.e. $H-F = 135$; $H-Cl = 103$; $H-Br = 87$ and $H-I = 71.5$ kcal mole$^{-1}$.

Studies of the polar effects were largely done in the liquid phase, using carbon tetrachloride as an inert medium. Table 6 shows some results on the halogenation of butanes.
Table 6
Halogenation of butanes\(^a\) 23

<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>H</th>
<th>F</th>
<th>Cl</th>
<th>H</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fluorination at 20(^o)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>Y</td>
<td>a</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
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<tr>
<td>Y</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha)</td>
<td>(XCH_2)</td>
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<td>0.3</td>
<td>(23.9)</td>
<td>(7.9)</td>
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</tr>
<tr>
<td>(\beta)</td>
<td>(YCH)</td>
<td>1.3</td>
<td>0.8</td>
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</tr>
<tr>
<td>(\gamma)</td>
<td>(CH_2)</td>
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<td>1.0</td>
<td>(31.9)</td>
<td>(25.5)</td>
<td></td>
</tr>
<tr>
<td>(\delta)</td>
<td>(CH_3)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>(44.2)</td>
<td>(66.6)</td>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>H</th>
<th>F</th>
<th>Cl</th>
<th>H</th>
<th>H</th>
<th>CF(_3)</th>
<th>H</th>
<th>H</th>
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<tr>
<td><strong>Chlorination at 75(^o)</strong></td>
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<tr>
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<td>a</td>
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<td>0.8</td>
<td>0.04</td>
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<tr>
<td>(\beta)</td>
<td>(YCH)</td>
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<td>1.7</td>
<td>2.1</td>
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<td>3.2</td>
<td>2.0</td>
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<tr>
<td>(\gamma)</td>
<td>(CH_2)</td>
<td>3.6</td>
<td>3.7</td>
<td>3.7</td>
<td>4.3</td>
<td>2.0</td>
<td>2.9</td>
<td></td>
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<tr>
<td>(\delta)</td>
<td>(CH_3)</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>0.7</td>
<td>0.8</td>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>H</th>
<th>F</th>
<th>Cl</th>
<th>CF(_3)</th>
<th>H</th>
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<tbody>
<tr>
<td><strong>Bromination at 150(^o)</strong></td>
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</tr>
<tr>
<td>X</td>
<td>Y</td>
<td>a</td>
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<tr>
<td>Y</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha)</td>
<td>(XCH_2)</td>
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<td>9</td>
<td>34</td>
<td>1 (^3)</td>
<td></td>
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</tr>
<tr>
<td>(\beta)</td>
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<td>80</td>
<td>7</td>
<td>32</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\gamma)</td>
<td>(CH_2)</td>
<td>80</td>
<td>90</td>
<td>82</td>
<td>90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\delta)</td>
<td>(CH_3)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Results are expressed per hydrogen atom relative to the rate of reaction of the terminal hydrogen which was assumed to be unaffected by substitution. When this assumption would not hold the results are given as percentage distribution of products in parentheses.
Selectivities have been tabulated at one temperature so that it reveals clearly the directional effect of substituents. In most of the cases, it can be seen, that the preferred site of substitution is the γ-carbon atom. The presence of a substituent generally lowers the strength of a C-H bond to which it is bonded, but the inductive effect will more than offset this activation.

The product of radical halogenation of alkenes is usually an alkyl halide which may undergo further reaction resulting in the elimination of halogen acid to give an olefin A, e.g.

\[
RX \xrightarrow{\text{HX}} A + \text{HX}
\]

(b) By phenyl radicals

Hydrogen abstraction by phenyl radicals has been found to take place both in gas and liquid phases. Much of the work was by Russell and co-workers⁵ who studied the reaction of phenyl radicals with a wide variety of C-H bonds by measuring the amounts of benzene and chlorobenzene formed as products of the competing reactions, eq (19) and (20) respectively.

\[
\begin{align*}
\text{C}_6\text{H}_5^* + \text{RH} & \xrightarrow{k_H} \text{C}_6\text{H}_6^* + \text{R}^* & \cdots \cdots \cdots (19) \\
\text{C}_6\text{H}_5^* + \text{CCl}_4 & \xrightarrow{k_{Cl}} \text{C}_6\text{H}_5\text{Cl} + \text{CCl}_3^* & \cdots \cdots \cdots (20)
\end{align*}
\]

Phenyl radicals were generated by thermal decomposition of phenylazo-triphenylmethane (PAT) at 60⁰; as suggested by Russell and Garst²⁴, separately, PAT mainly produces free phenyl radicals. Reactivities of a single carbon-hydrogen bond relative to the carbon tetrachloride molecule were calculated from the expression

\[
\frac{k_H}{k_{Cl}} = \frac{[\text{C}_6\text{H}_6^*][\text{CCl}_4]}{[\text{C}_6\text{H}_5\text{Cl}][\text{RH}]}
\]

For primary, secondary and tertiary hydrogens in alkanes relative reactivities
have been found to be 0.0098: 0.091: 0.43, for alkene it is 0.145, 0.30: 1.20 for aralkyl hydrocarbons 1: 4.6: 9.7. Phenyl radicals have been found to be similar in reactivity to methyl radicals (at 65°) but more selective than chlorine and t-butoxy-radicals and less so than bromine and trichloromethyl radicals.

1.4.2. **Abstraction of halogen atoms**: Halogen atoms are known to be abstracted by alkyl, phenyl or hydrogen atoms. From the kinetic information and other abstraction\(^{25a}\) and displacement\(^{25b}\) data, the ease of hydrogen abstraction is suggested to be,

\[
I > Br > H > Cl > F
\]

the order of abstraction following the strength of the C-X bonds being broken with the exception of hydrogen abstraction. Haszeldine\(^{25c}\) demonstrated some radical chain addition of polyhalomethanes, principally bromotrichloromethane and trifluoriodomethane, to olefins where halogen abstraction by alkyl radicals is part of the chain transfer processes.

\[
R_3C^+ + CX_4 \rightarrow R_3CX + CX_3^-
\]

Wayne\(^{26}\) reported some aspects of the abstraction of iodide from a series of substituted iodobenzenes by phenyl radicals generated from phenylazotriphenylmethane (PAT) at 60° and noted that the process contrasts with hydrogen abstraction in that a positive \(\rho\) value is observed in the Hammett correlation which indicates that in these systems the polarisation of the transition state is different from that of the hydrogen abstractions. The two transition states are represented in eq (21) and (22).

\[
\begin{align*}
R-I + \text{Rad.} & \rightarrow [R\ldots I\ldots \text{Rad}] \rightarrow R^+ + \text{Rad-I} & (21) \\
R-H + \text{Rad.} & \rightarrow [R\ldots H\ldots \text{Rad}] \rightarrow R^+ + \text{Rad-H} & (22)
\end{align*}
\]
1.5 **Dimerization and disproportionation**

Free radicals generated as a result of a chain process have a tendency to end up by either coupling or disproportionating in order to attain a stable state. The process of dimerization is, unlike the chain-propagating step, a bimolecular reaction. The amount of product formed as a result of dimerization is necessarily low if the chain is long.

Atoms, owing to the lack of vibrational and rotational freedom, usually require a third body for a combination process to occur. The energy released appears in the form of vibrational or rotational energy of this third body. The reaction is usually represented as eq. (23) and (24),

\[
\begin{align*}
A^* + B^* & \xrightarrow{k_1} AB^* \quad \ldots \ldots \quad (23) \\
AB^* + T & \xrightarrow{k_3} AB + T \quad \ldots \ldots \quad (24)
\end{align*}
\]

where \(T\) is a third body. Kinetically the reaction is represented as

\[
\frac{d(AB)}{dt} = \frac{k_1 k_3 (A^*)(B^*)(T)}{k_2 + k_3 (T)}
\]

At low concentration of the third body \(T\), when \(k_2 > k_3 (T)\)

\[
\frac{d(AB)}{dt} = \frac{k_1 k_3 (A^*)(B^*)(T)}{k_2}
\]

At high concentration of \(T\) when \(k_3 > k_2 (T)\)

\[
\frac{d(AB)}{dt} = \frac{k_1 (A^*)(B^*)}{k_3}
\]

i.e. independent of \(T\).

Simple examples of combination reactions are met within common reactions involving species such as trichloromethyl, benzyl and ethyl radicals, eq. (25-28).
In solutions, radicals are most likely to first encounter a solvent molecule as a substrate for reaction. To avoid this, relatively "inert" solvents are used. Resonance stabilisation and steric factors may also affect the reactions of radicals. Thus diphenylmethyl radicals readily undergo "head to head" dimerization, e.g.,

\[ 2\text{Ph}_2\text{CH}^« \longrightarrow \text{Ph}_2\text{CH} \cdot \text{CH. Ph}_2 \]

whereas triphenylmethyl radicals undergoes "head to tail" dimerisation in a reaction which is reversible at room temperature. e.g.

\[ \text{Ph}_3\text{C}^+ + \text{CPh}_2 \rightleftharpoons \text{H} \text{Ph}_3\text{C} = \text{CPh}_2 \]

The process of dimerization has received considerable attention as a synthetic route for many organic compounds. The coupling of phenoxy-radicals, formed readily from oxidation of phenols, is the most elegant and simple synthesis of rather complex organic molecules.

A process which usually competes with dimerization is disproportionation. A radical could undergo chain termination by way of disproportionation with the aid of another like radical giving olefins and saturated compounds, e.g.

\[ 2\text{CH}_3\text{CH}^« \longrightarrow \text{CH}_2=\text{CH}_2 + \text{CH}_3-\text{CH}_3 \]

The ratio of rate of disproportionation to that of combination has been studied by analysis of the products from a number of alkyl radicals.
at various temperatures$^{29a,b}$. For unbranched radicals coupling is favoured over disproportionation while with branched radicals the process of disproportionation becomes more and more important, possibly for steric reasons.

1.6 Electrophilic aromatic substitution reactions

The history of electrophilic aromatic substitution reactions is long and has been reviewed by many workers$^{30a,b}$. Much of the early work was related to the problems of orientation and rate of substitution. The so-called "normal laws" of orientation have been established mainly as the result of studies of nitration by Ingold and collaborators$^{30c-h}$. The contribution made by these workers is of the highest importance in providing quantitative data to ascribe the phenomena.

Studies about the nature of the substitution process, i.e. the detailed approach of aromatic substrate and substituting agent, and the formation of product by expulsion of proton, began seriously after 1950. The subject has been reviewed by Berliner$^{31}$. Pfeiffer and Wizinger$^{32a}$ proposed the geometry of the intermediate in nitration of an aromatic substrate - this idea was later supported by Wheland$^{32b}$.

\[
\begin{align*}
\text{ benzene + H} & \leftrightarrow \text{ benzene + H} \\
\text{NO}_2 & \leftrightarrow \text{NO}_2
\end{align*}
\]

Much of the pioneering studies were done by Melander following the use of$^{33}$ isotopes in organic reactions. In principle, there seems to be two possibilities for the replacement of a proton during the substitution process which could be represented as (a) and (b).
The route (a) is a one-step process involving an intermediate in which the aromatic character of the molecule is maintained throughout. The route (b) is a two-step process which proceeds through the intermediate in which the aromaticity of the molecule is disturbed as the molecule formed a cyclohexadienate cationic system. In this system a primary isotope effect could arise if the carbon-hydrogen bond is broken in the rate-determining step. Melander proposed that nitration and, in all likelihood, bromination proceeds by a two-step mechanism with the first step (the formation of intermediate) as rate-determining as no isotope effect was found to be present.

An evidence supporting the Σ-complexes intermediate was given by Olah and co-workers\(^{34}\). In a reaction of mesitylene with ethyl fluoride and the catalyst boron trifluoride at -80°, a solid (XIIIA) was obtained m.p. -15°. This on heating gave the normal substitution product (XIIIB)

There is a considerable amount of evidence like this in support of a Σ-complex route in the electrophilic aromatic substitution but an alternative scheme has been proposed.\(^{35a}\) This requires the interconversion of the two π complexes through an intermediate Σ complex.
The formation of a non-localised π complex was at first considered to be the rate determining step so that the rate should be nearly independent of the nature of the substituent in the ring; although this is not true. Later it was suggested \(^{35b}\) that the slow step is the conversion of a localised π complex into the σ complex. Now both the rate and products would be dependent on the substituent in a manner similar to that of the σ complex and distinguishable from it.

Support in favour of the π complex mechanism comes mostly from physical evidence. A change in the u.v. spectrum when the two components were mixed and from their solubility measurements was taken as an indication for their existence\(^{31}\).

Brown and co-workers studied the role of two types of complexes in electrophilic aromatic substitution reactions\(^{36}\). They studied the differences of aromatic-hydrogen halide complexes in the absence and presence of aluminium halides. The solubility of hydrogen chloride in several hydrocarbons at \(-78^\circ\) was studied, both in heptane and in toluene as the solvent. The physical data is known to support the formation of 1:1 complex between ArH and hydrogen chloride. These complexes are colourless, non-conductors of electricity, and when deuterium chloride, instead of hydrogen chloride, is used no exchange of deuterium for the aromatic protons take place\(^{31}\). Brown and co-workers concluded that these physical properties are in agreement with a structure in which the aromatic character is relatively undisturbed, i.e. a π-complex,
shown below, best fit into these requirements.

\[ \overset{\text{HCl}}{\overset{\text{C}}{\text{C}}} \]

The subject of \( \pi \)-complex participation has also been reviewed by Banthorpe\(^{37} \).

The total substitution process can be kinetically represented as a two stage reaction:

\[
\begin{align*}
\text{ArH} + Y^+ & \xrightleftharpoons[k_1]{k_{-1}} \text{Ar}^+\text{HY} \\
\text{Ar}^+\text{HY} & \xrightarrow[k_2]{k_2} \text{ArY}
\end{align*}
\]

Isotope effects could arise if the second step has a rate comparable or less than the first \( (k_2[Ar^+HY] \leq k_1[ArH][Y^+] \)). Since the first step is a reversible one, the rate at which \( \text{Ar}^+\text{HY} \) reverts to \( \text{ArH} \) should be the same as that at which \( \text{Ar}^+\text{DY} \) reverts to \( \text{ArD} \) since no carbon-hydrogen bond is broken in this step. However, \( \text{Ar}^+\text{HY} \) should go to \( \text{ArY} \) faster than \( \text{Ar}^+\text{DY} \), since carbon-hydrogen bond is broken in this step. If \( k_2 < k_{-1} \) (or equal) then reversion to starting material is important. If \( k_2 \) for \( \text{Ar}^+\text{DY} \) is less than \( k_2 \) for \( \text{Ar}^+\text{HY} \), but \( k_{-1} \) is the same, then a larger proportion of \( \text{Ar}^+\text{DY} \) reverts to the starting material, i.e. \( k_2/k_{-1} \) (the partition factor) for \( \text{Ar}^+\text{DY} \) is less than that for \( \text{Ar}^+\text{HY} \) hence causing an isotope effect. This apparently happens in sulphonation. Melander\(^{33} \) suggested that the intermediate in sulphonation has a neutral character, in contrast to nitration and bromination. The negative charge on the sulphonic acid group adjacent to the proton will make it more difficult for the proton to leave,
thus $k_2$ will be decreased relative to $k_{-1}$ and the relation $k_2 > k_{-1}$ does not hold any more, and this leads to the observed isotope effect.

Many workers recognised that the absence or presence of an isotope effect does not prove the existence of a particular intermediate in aromatic substitutions. It gives information about how much C-H bond stretching has occurred in the transition state. From the observation that in such types of reactions hydrogen cannot be loosened appreciably in the activated state of addition, the existence of a relatively stable intermediate seems more likely. The absence of an isotope effect serves as a simple and attractive way to explain the results.

1.7. Some less common routes of electrophilic aromatic substitution reactions.

Addition-elimination mechanism

This is a less common but a well recognised mechanism encountered not only in aromatic but also in open chain unsaturated compounds. A summary of the relevant history is given by Fieser. As the title indicates, the substitution occurs initially by an addition across the carbon-carbon double bond followed by elimination sequence thus reverting to the carbon $sp^2$ state. Kinetics and orientational information have been used to determine whether the reaction involves electrophilic attack by any dominant species.

Most of the early work of Price and co-workers on electrophilic aromatic substitution has explained this phenomena. In the bromination of phenanthrene it is proposed that the formation of the addition and substitution products could take place through a common intermediate (XIVb).
This shows that addition accompanies substitution in the reactions of quite simple aromatic compounds under heterolytic conditions. It also involves a reversible equilibrium (XIVb) $\rightleftharpoons$ (XIVc).

Chlorination of phenanthrene in acetic acid\textsuperscript{40a} proceeds as follows:

The adduct (XVa) is mostly the trans isomer. De la Mare suggested that the formation of (XVc) may be through the intermediate (XVI) (see below). The substitution is completed through proton loss. The nucleophile whether from the reagent or from the medium solvent can complete addition to the aromatic system by combining to the carbonium ionic centre. The formation
of the adduct (XVa) (mostly trans) comes about through the diversion of
the intermediate (XVI) by reaction with the solvent. The chlorination of
phenanthrene to form chlorophenanthrene (XVc) therefore, must not proceed
exclusively through an addition-elimination mechanism. The accompanying
acetoxylation on the other hand, necessarily must go through such a path.
A corresponding conclusion is given by Price in the bromination and
methoxylation of phenanthrene \(^{39}\).

Acid-catalysed chlorination of naphthalene was studied by de la Mare
and co-workers \(^{40b}\). The occurrence of both the substitution and the addition
products has been reported. Different isomers of 1,2,3,4-tetrachloro-1,2,3,4-
tetrahydronaphthalene have been isolated. The reactions are heterolytic since
light catalysed (homolytic) reactions give isomers of different stereochemistry \(^{40}\).
Alkaline dehydrochlorination of these addition products has been found to
give substitution products such as mono-chloronaphthalene and dichloro-
naphthalene \(^{40c}\).

Bromination of quinoline with molecular bromine
gives 3-bromoquinoline, 3,6-dibromoquinoline and 3,6,8-tribromoquinoline.
The exact mechanism is not clear but Johnson and Ridd \(^{41}\) proposed an addition-
elimination sequence to these products, Scheme 2.
Substitution in the 3-position arises by addition followed by elimination. The substitution in 6- and also in 8-position has occurred by the conversion of the quinoline nucleus into a derivative of di- or tetra-hydroquinoline, in which the lone pair of electrons of nitrogen is able to conjugate with the remaining aromatic ring. Thus it activates the position ortho- and para- to itself.
1.8. **Electrophilic aromatic halogenation reactions**

Among halogens, chlorine and bromine have been widely used as halogenating species.

1.8.1. Chlorination: Chlorine affords a great deal of substitution both in molecular and non-molecular form. The general pattern of the reaction is the conventional two-stage process involving the carbenium or σ-complex intermediate which could undergo many possible reactions depending upon the reaction conditions, to give the final product \(^{42}\).

Theories of aromatic substitution which use free energy relationships have been extended to the reactions of polycyclic aromatic hydrocarbons with chlorine as electrophile. It has been generally observed that whereas benzene, because of its resonance stabilisation, is less reactive bi- and poly-cyclic hydrocarbons become progressively more activated \(^{40c}\) as illustrated in Scheme 3.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Relative rates of chlorination ( \text{PhH} = 1 \text{ Cl}_2, \text{ COH, 25°C} )</th>
<th>Main position of attack</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Substrate 1" /></td>
<td>( 6.6 \times 10^4 )</td>
<td>1</td>
</tr>
<tr>
<td><img src="image2.png" alt="Substrate 2" /></td>
<td>( 1.1 \times 10^5 )</td>
<td>2</td>
</tr>
<tr>
<td><img src="image3.png" alt="Substrate 3" /></td>
<td>( 3.0 \times 10^5 )</td>
<td>9</td>
</tr>
<tr>
<td><img src="image4.png" alt="Substrate 4" /></td>
<td>( &gt;10^8 )</td>
<td>9</td>
</tr>
<tr>
<td><img src="image5.png" alt="Substrate 5" /></td>
<td>-</td>
<td>Mainly 4 accompanied by 2</td>
</tr>
</tbody>
</table>

*Scheme 3*
These chlorination reactions are also complicated by addition which accompanies substitution. Different isomers of the addition products are formed and in some cases these adducts are reported to have decomposed to give the normal substitution products, as shown in Scheme 4.

Scheme 4
Nuclear chlorination of alkylbenzenes usually proceeds smoothly according to eq.(29);

\[ \text{RC}_6\text{H}_5 + n\text{Cl}_2 \rightarrow \text{RC}_6\text{H}_5-\text{Cl}^+ + n\text{HCl} \]  \hspace{1cm} \ldots \ldots \text{(29)}

However, chlorination of t-butylbenzene, promoted by ferric chloride gives a number of side-products as a result of secondary reactions accompanying the main reaction. These side-products include benzene, chlorobenzene, para-dichlorobenzene, meta- and para-di-t-butylbenzene and t-butylchloride.

The side-products arise as a result of the higher stability of the t-butyl group. Hence, the bond joining the tertiary carbon atom of the t-butyl group to the aromatic ring is weak relative to that in other alkyl benzenes (e.g. toluene, ethylbenzene) and thus the t-butyl group may be displaced by the chlorine. The mechanism in Scheme 5 has been suggested to be consistent with the observed side-products.
The meta/para-ratio of di-t-butylbenzenes was reported to be 1.27 at 30°, 1.5 at 60°. A corresponding ratio (1.04) has been found in the aluminium chloride catalysed isomerisation of di-t-butylbenzenes by Olah and co-workers.

Kinetic studies

The simplest kinetic form for molecular chlorine has been generally observed as,

\[ \text{Rate} = [\text{ArH}][\text{Cl}_2] \]

The transition state (XVII) thus involves the whole of the chlorine molecule and the unsaturated compound:

\[
\begin{align*}
\text{Cl}_2 \text{Cl}^- \\
\text{H} \\
\end{align*}
\]

(XVII)

this being more polar than the reagents becomes powerfully solvated in more polar solvents.

The kinetics of aqueous aromatic chlorination was investigated and the subject has been reviewed. In chlorination using acidified hypochloric acid and aromatic substrate, the reaction proceeds according to the following equation:

\[ \text{Rate} = k[\text{ArH}][\text{ClOH}][\text{H}^+] \]

According to these workers an increase of the rate with the acidity suggest the importance of the pre-equilibrium (30) and (31),

\[
\begin{align*}
\text{ClOH} + \text{H}_3\text{O}^+ & \rightleftharpoons \text{ClOH}_2^+ + \text{H}_2\text{O} & \quad \text{(30)} \\
\text{ClOH}_2^+ & \rightarrow \text{Cl}^+ + \text{H}_2\text{O} & \quad \text{(31)}
\end{align*}
\]

The small size of the chlorinium ion has been found to cause certain minimum steric requirements, as the partial rate factors for chlorination by molecular chlorine in toluene reveals that the ortho/para-ratio falls below unity. This is because the chloride ion associated in
the transition state hinders the ortho-substitution. In attack by "positive chlorine" this ratio rises above unity which shows that there is less hindrance, than molecular chlorine, at the ortho-position.

1.8.2. Bromination: Bromine generally resembles chlorine in its reactions with unsaturated and aromatic hydrocarbons, although certain differences are also observed which are due to the following reasons:
(a) bromine is larger than chlorine so the steric effects are more severe; (b) it is more easily polarisable, compared to chlorine, and so reactions involving positive bromine are more recognised; (c) it forms a weak carbon-bromine bond so that the reverse step might be easily apparent; as such the products are frequently determined by thermodynamic control, and (d) bromine is a mild electrophilic reagent hence the reactions are usually selective.

Kinetics and general mechanism of bromination

A general formulation of the reaction mechanism involving the formation of the complex ArH.Br₂ has been postulated by Robertson, de la Mare and their co-workers as a result of their kinetic studies involving molecular bromine, acetic acid and aromatic substrate. A general form is eq. (32-34),
\[ \text{ArH} + \text{Br}_2 \quad \leftrightarrow \quad \text{ArHBr}_2 \quad \ldots \quad (32) \]

\[ \text{ArHBr}_2 + \text{E} \quad \leftrightarrow \quad \left[ \text{ArBr}^{+} \right] + \text{EBr} \quad \ldots \quad (33) \]

\[ \text{Ar}^{+} + \text{Base} \quad \rightarrow \quad \text{ArBr}^{+} \quad \ldots \quad (34) \]

This was supported in subsequent studies by Andrew and Keefer\textsuperscript{48a,b}. The general kinetic form was

\[ \text{Rate} = k_2[\text{ArH}][\text{Br}_2] \]

and this rate is found to increase greatly with electron release from substituents present in the substrate. This confirms an electrophilic attack to give a positively charged transition state. A series of aromatic compounds for which this kinetic form has been obtained was studied by various other workers\textsuperscript{49a,b}.

Hypobromous acid, mineral acid and the aromatic substrate showed a kinetic form similar to that found with the chlorine analogue:

\[ \text{Rate} = k[\text{ArH}][\text{HOBr}][\text{H}^+] \]

A pre-equilibrium also exists, eq. (35) and (36)

\[ \text{BrOH} + \text{H}_3\text{O}^+ \quad \leftrightarrow \quad \text{BrO}^+\text{H}_2 + \text{H}_2\text{O} \quad \ldots \quad (35) \]

\[ \text{BrO}^+\text{H}_2 \quad \rightarrow \quad \text{Br}^+ + \text{H}_2\text{O} \quad \ldots \quad (36) \]

The bromonium ion has, like chloronium ion, relatively small steric requirements compared with molecular bromine. With t-butylbenzene nearly 38\% of ortho-isomer is obtained where as using molecular bromine this amount is reduced to 10\%\textsuperscript{50}. 
1.9. Homolytic aromatic substitution

This comprises substitution reactions of aromatic compounds in which the attacking species is a free radical. The vast subject of homolytic aromatic substitution has been frequently reviewed.\(^{17a, 51a,b}\)

The present reaction has been divided into two portions. In the first part, reactions involving the displacement of hydrogen from the benzene nucleus by phenyl or substituted phenyl radicals are given. In the second part, some free radical halogen displacements of hydrogen in aromatic compounds are described.

It should be mentioned here that these are not the only arylation or free radical halogenation reactions but being more relevant to this work have been discussed.

1.9.1. Arylation reactions:

Following the early work of Gomberg\(^{52a,b}\), Hey and Waters\(^{53}\), in 1944 Bachmann and Hoffeman\(^ {54}\) developed the synthetic utility of substitution of aromatic compounds by phenyl radicals. These types of reaction have also been used for many quantitative studies as the product could not be fitted into the established pattern of electrophilic or nucleophilic aromatic substitution reactions.

(a) Origin of phenyl radicals

The decomposition of benzoyl peroxides has remained one of the most traditional and useful sources of phenyl radicals; thermolysis or photolysis generates aroyloxy-radicals which subsequently lose carbon dioxide to give aryl radicals, e.g.

\[
(Ar.CO.O)_2 \rightarrow 2Ar.C0.0^*.
\]

\[
Ar.C0.0^* \rightarrow Ar^* + CO_2
\]
Decomposition of unsubstituted and many substituted benzoyl peroxides has received exhaustive attention by many workers. The results are well documented. Certain diazo-, azo- and related compounds have also been used for similar purposes. The decomposition of N-nitroso-acetanilide in benzene also provides a route for the synthesis of biaryls. The mechanism of this reaction is proposed recently to proceed as shown in Scheme 6.

\[
\begin{align*}
\text{PhN(NO)Ac} & \rightarrow \text{PhN=N-OAc} \rightleftharpoons \text{PhN}^+ + \text{AcO}^- \\
\text{PhN(NO)Ac} + \text{AcO}^- & \rightarrow \text{PhN=N-O}^- + \text{Ac}_2O \\
\text{PhN}^+ + \text{PhN=N-O}^- & \rightarrow (\text{PhN=N})_2O \\
(\text{PhN=N})_2O & \rightarrow \text{Ph}^+ + \text{N}_2 + \text{Ph-N=N-O}^- \\
\text{Ph}^+ + \text{PhH} & \rightarrow \text{Ph} \cdot + \text{N}_2 + \text{Ph-N=N-O}^- \\
[\text{Ph.C}_6\text{H}_{6}^-]^+ + \text{Ph-N=N-O}^- & \rightarrow \text{Ph-Ph} + \text{Ph-N=N-OH}
\end{align*}
\]

Scheme 6

Aryl radicals can also be generated by thermolysis of certain covalent diazo-compounds such as arylazotriphenyl methanes. These undergo decomposition at 80° to phenyl and triphenylmethyl radicals, the driving force for the reaction being the stability of the triphenylmethyl radicals:

\[
\begin{align*}
\text{PhN=NCP}^3\text{H} & \rightarrow \text{PhN}_2^- + \text{Ph}_3\text{C} \cdot \\
\text{PhN}_2^- & \rightarrow \text{Ph} \cdot + \text{N}_2
\end{align*}
\]

The earlier Gomberg and Gomberg-Hey procedure of generating phenyl radicals from diazonium salts and sodium hydroxide, or acetate was modified by the use of pentyl nitrite and non-aqueous conditions instead of sodium hydroxide or acetate. The general procedure is
The heat of formation of nitrogen (225 kcal mole\(^{-1}\)) supplies a strong driving force for the dissociation process.

This method is used successfully for the synthesis of many substituted biaryls from appropriately substituted amines\(^{59,60}\).

Miscellaneous sources of phenyl radicals.

(i) Oxidation of phenylhydrazines with silver oxide in aromatic solvents gives biaryls.\(^{61}\)

(ii) Photolysis of aryl iodides and bromides has been shown to be an effective method for arylation. These reactions were developed by Kharasch and co-workers for synthesis of biaryls photochemically.\(^{62a,b}\)

\[ \text{e.g. } \text{PhI} + C_6H_6 \xrightarrow{\text{hv}} \text{PhPh} + \text{HI} \]

(iii) Phenyl iodosobenzoate decomposes at 125-130\(^{\circ}\) in aromatic solvents to give phenyl radicals which give rise to the phenylation of the aromatic substrate. The phenyl radical was thought to have come from...
the benzoate groups, but later it was proposed that it actually comes from iodobenzene, e.g.

$$\text{PhI}(\text{O.C.O.C}_6\text{H}_5)_2 \rightarrow \text{PhI} + 2\text{PhCO}_2$$

$$\text{PhI} \rightarrow \text{Ph}^* + \text{I}^*$$

(iv) Photolysis of diphenyl mercury, tetraphenyllead and triphenylbismuth have been used as sources of phenyl radicals in homolytic substitution reactions.

(b) Nature of phenyl radical. The application of quantitative methods to the arylation reactions has not only made the general nature of phenyl radicals clear but has substantially contributed towards describing the main features of homolytic aromatic substitution. The arylation is generally accepted as proceeding through the rate determining step of the addition of an aryl radical to the aromatic substrate giving an arylocyclohexadienyl radical followed by the elimination of $\text{H}^*$, to give biaryl,

$$\text{H} \quad \text{Ar} \quad \rightarrow \quad \text{Ar} + \text{RH} \quad \text{[37]}$$

The presence of substituent groups in the attacking phenyl radical or in the substrate may cause differences in reactivity and orientation of the homolytic arylation of benzene. A considerable amount of work has been reported. In most of the quantitative studies partial rate factors for a large number of arylation reactions have been determined which give a quantitative expression of the velocity of substitution at each nuclear position relative to one position in benzene. Some of the results are placed in Table 7.
### Table 7

Partial rate factors for homolytic phenylation with benzoyl peroxide at $80^\circ$C

<table>
<thead>
<tr>
<th></th>
<th>Rate ratio $\text{C}_6\text{H}_6 = 1$</th>
<th>Composition %</th>
<th>Partial Rate Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\sigma^-$</td>
<td>$m^-$</td>
</tr>
<tr>
<td>PhNO$_2$</td>
<td>2.94</td>
<td>62.5</td>
<td>9.8</td>
</tr>
<tr>
<td>PhF</td>
<td>1.03</td>
<td>54.1</td>
<td>30.7</td>
</tr>
<tr>
<td>PhCl</td>
<td>1.06</td>
<td>50.1</td>
<td>31.6</td>
</tr>
<tr>
<td>PhBr</td>
<td>1.29</td>
<td>49.3</td>
<td>33.3</td>
</tr>
<tr>
<td>PhI</td>
<td>1.32</td>
<td>51.7</td>
<td>31.6</td>
</tr>
<tr>
<td>PhMe</td>
<td>1.23</td>
<td>66.5</td>
<td>19.3</td>
</tr>
<tr>
<td>PhEt</td>
<td>0.90</td>
<td>53</td>
<td>28</td>
</tr>
<tr>
<td>PhPr$_t$</td>
<td>0.64</td>
<td>31</td>
<td>42</td>
</tr>
<tr>
<td>PhBu$_t$</td>
<td>0.64</td>
<td>24</td>
<td>49</td>
</tr>
<tr>
<td>PhCN</td>
<td>3.7</td>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td>PhCO$_2$Me</td>
<td>1.77</td>
<td>57.0</td>
<td>17.5</td>
</tr>
<tr>
<td>Ph$_2$</td>
<td>2.94</td>
<td>48.5</td>
<td>23.0</td>
</tr>
</tbody>
</table>
Most of the phenylation reactions are characterised here by ortho-para- orientation with less meta-substitution. t-Butylbenzene and isopropylbenzene show less reactivity at the ortho-position due to steric reasons. On the other hand, the presence of substituents in the attacking phenyl radical can give rise to polarisation and thus shows some measure of electrophilic or nucleophilic character. Table 8 shows the change in reactivity of the phenyl radical with the change in substituent.

Table 8
Relative rates and partial rate factors for the arylation of nitrobenzene

<table>
<thead>
<tr>
<th>Radical</th>
<th>PhNO&lt;sub&gt;2&lt;/sub&gt; K</th>
<th>F&lt;sub&gt;O&lt;/sub&gt;</th>
<th>F&lt;sub&gt;M&lt;/sub&gt;</th>
<th>F&lt;sub&gt;P&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-NO&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;H&lt;/sub&gt;&lt;sub&gt;6&lt;/sub&gt;·</td>
<td>0.26</td>
<td>0.42</td>
<td>0.14</td>
<td>0.42</td>
</tr>
<tr>
<td>m-NO&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;H&lt;/sub&gt;&lt;sub&gt;6&lt;/sub&gt;·</td>
<td>0.43</td>
<td>0.68</td>
<td>0.73</td>
<td>0.75</td>
</tr>
<tr>
<td>p-NO&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;H&lt;/sub&gt;&lt;sub&gt;6&lt;/sub&gt;·</td>
<td>0.94</td>
<td>1.64</td>
<td>0.43</td>
<td>1.6</td>
</tr>
<tr>
<td>o-ClC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;·</td>
<td>0.82</td>
<td>0.88</td>
<td>0.66</td>
<td>2.0</td>
</tr>
<tr>
<td>m-ClC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;·</td>
<td>1.3</td>
<td>2.2</td>
<td>0.58</td>
<td>2.2</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;·</td>
<td>2.9</td>
<td>5.5</td>
<td>0.86</td>
<td>4.9</td>
</tr>
<tr>
<td>o-MeC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;·</td>
<td>2.2</td>
<td>2.7</td>
<td>1.2</td>
<td>5.2</td>
</tr>
<tr>
<td>m-MeC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;·</td>
<td>3.0</td>
<td>5.5</td>
<td>1.2</td>
<td>4.7</td>
</tr>
<tr>
<td>p-MeC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;·</td>
<td>3.4</td>
<td>6.1</td>
<td>1.2</td>
<td>5.8</td>
</tr>
</tbody>
</table>

Nitrophenyl and halogenophenyl radicals show some electrophilic character in the sense that their rate ratio (PhNO<sub>2</sub> K) is much less than that shown in phenylation. On the other hand, tolyl radicals show some degree of nucleophilicity as they react with nitrobenzene more rapidly.
than benzene. The influence of the substituent group on the polarisation of phenyl radicals is also dependent on its proper location. Thus the magnitude of the effect in the attacking radical, increase in the order para < meta < ortho-. Similar studies have been made with para-chloro- and para-nitro-phenyl radicals derived from appropriately para- substituted nitrosoacetanilides. These results confirm that for most aromatic substrates the ortho- and para- positions are usually more reactive than the meta-position irrespective of the polar nature of the phenyl radicals.

The widely observed ortho-para-orientation suggests that the major factor controlling the orientation of the entering group ought to be the varying degree of stabilisation due to the delocalisation of the odd electron, of the various transition states leading to the respective isomeric arylcyclohexadienyl radical. In the addition to positions ortho- or para- to a substituent, the substituent also contributes to the stabilisation of the transition state. In contrast to this, if the addition takes place at a meta-position there is no such contribution by the substituent. An example is the ortho- or para-substitution in nitrobenzene by the phenyl radical, represented by (XVIII).
In summary, the presence of a substituent in the phenyl radicals conferred upon them a measure of electrophilic or nucleophilic character. This depends upon the polar properties of the substituent, so that the relative rate at which the radical attacks the different nuclear positions in which the substrate (partial rate factors) are modified.

1.9.2. Polyhalogeno-biaryls: The homolytic substitution reactions of polyhalogeno-phenyl radicals to give biaryls, in non-aqueous systems, has been of considerable interest particularly in recent years. Most of the work in this field has been done on polyfluoro-compounds. The subject has been reviewed recently. Comparatively less work has been carried out for polychloro-compounds. There is no indication of any substantial work on polybromo-compounds.

1.9.3. The pentafluorobiaryls: Fluorine is a highly electronegative element and consequently the chemistry of highly fluorinated aromatic compounds is expected to be different from that of benzene and its derivatives.

Arylation of polyfluoroaromatic compounds, among halogens, has been the subject of much study, either because of a more electronegative substituent or because of a strong carbon-fluorine bond in these systems which makes their chemistry more interesting.

Thermal decomposition of pentafluorobenzoyl peroxide in benzene gives mainly pentafluorobiphenyl together with pentafluorobenzoic acid and small amounts of phenylpentafluorobenzoate (Scheme 8).
The decomposition of pentafluorobenzoyl peroxide has also been carried out in chlorobenzene and bromobenzene\textsuperscript{70b}. The main products being pentafluorobenzoic acid and phenyl pentafluorobenzoates. The latter product is thought to arise by the replacement of chlorine and bromine by pentafluorobenzoyloxy radicals, which are stabilised by the formation of charge transfer complexes with halogenobenzenes (Scheme 9).

\[
\begin{align*}
\text{C}_6\text{F}_5\text{CO.O}^- + \text{Ph} &\rightleftharpoons \text{PhC}_6\text{F}_5 + \text{C}_6\text{F}_5\text{CO.O}^- \text{X} \\
\text{C}_6\text{F}_5\text{CO.C}_6\text{F}_5 &\rightarrow \text{PhC}_6\text{F}_5 + \text{C}_6\text{F}_5\text{CO}_2\text{H} \\
\end{align*}
\]
The pentafluorobenzoyl hypohalite (XIX) may ultimately give penta-
fluorobenzoic acid.

Thus it appears from the above results that carbon-halogen bond
breaking occurs in preference to carbon-hydrogen bond and that the
reaction is so rapid that the aroyloxy radical reacts before decarboxylation.

In the studies of the reactivity of pentafluorophenyl radical
(from pentafluoroaniline) with different substrates such as chloro-
bromo- and nitro- benzene, the yields of the respective biaryls were
found lower than those obtained with benzene, but the proportions of the
isomeric products were significant. These results are given in Table 9 which
includes the corresponding data for the phenylation of these compounds,
for comparison.

Table 9

Distribution of isomers formed in phenylation and
pentafluorophenylation (80°) 71

<table>
<thead>
<tr>
<th>Radical</th>
<th>Substrate</th>
<th>Isomers (%)</th>
<th>Ratio (o + p)/m-</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅⁺</td>
<td>C₆H₅Cl</td>
<td>56.9</td>
<td>25.6</td>
</tr>
<tr>
<td>C₆H₅⁺</td>
<td>C₆H₅Br</td>
<td>55.7</td>
<td>28.8</td>
</tr>
<tr>
<td>C₆F₅⁺</td>
<td>C₆H₅NO₂</td>
<td>62.5</td>
<td>9.8</td>
</tr>
<tr>
<td>C₆F₅⁺</td>
<td>C₆H₅Cl</td>
<td>64.7</td>
<td>20.6</td>
</tr>
<tr>
<td>C₆F₅⁺</td>
<td>C₆H₅Br</td>
<td>61.6</td>
<td>26.3</td>
</tr>
<tr>
<td>C₆F₅⁺</td>
<td>C₆H₅NO₂</td>
<td>20.8</td>
<td>53.4</td>
</tr>
</tbody>
</table>

These results support the view that pentafluorophenyl radicals shows
substantial electrophilic character, owing to the electron attraction of
the fluorine atoms. Thus with chloro- and bromo- benzene, both of which
give the ortho- and para- substitution products with electrophilic reagents, the extent of ortho-para-substitution is greater with pentafluorophenyl than with phenyl radicals, as is indicated in the last column of Table 9. On the other hand, this ratio is very much lower for pentafluorophenylation than for phenylation when the substrate contains the strongly meta- directing nitro-group.

Decomposition of benzoyl peroxide in hexafluorobenzene is also found to give 2,3,4,5,6-pentafluorobiphenyl.

The mechanism proposed is given below:

\[
\begin{align*}
\text{Initiation} & : & \text{Bz}_2\text{O}_2 & \rightarrow 2\text{BzO}^* \\
\text{Ph}^* + \text{C}_6\text{F}_6 & \rightarrow \sigma_F^- \\
2\sigma_F^- & \rightarrow \sigma_F^- - \sigma_F^- \\
\text{Termination} & : & \text{BzO}^* + \text{C}_6\text{F}_6 & \rightarrow \sigma_F'^- \\
2\sigma_F'^- & \rightarrow \sigma_F'^- - \sigma_F'^- \\
\text{Termination} & : & \sigma_F'^- & \rightarrow \sigma_H^* \\
\text{Rearrangement} & : & \sigma_H^* + \text{BzO}^* (\text{Bz}_2\text{O}_2) & \rightarrow 2'\text{F}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{F}_5 + \text{BzOH} (+ \text{BzO}^*) \\
\sigma_F'^- + \text{BzO}^* (\text{Bz}_2\text{O}_2) & \rightarrow \sigma_F^- - \text{OBz} (+ \text{BzO}^*) \\
\sigma_F'^- + \text{BzOH} & \rightarrow \text{Ph} \cdot \text{C}_6\text{F}_5 + \text{HF} + \text{BzO}^* \\
\sigma_F^- - \text{OBzOH} + \text{HF} & \rightarrow \text{Ph} \cdot \text{C}_6\text{F}_7 + \text{BzOH}
\end{align*}
\]

The defluorination of \(\sigma\)-complex (\(\sigma_F^-\)) is shown to occur by benzoic acid. The benzoic acid may be formed by the rearrangement of \(\sigma_F^-\) to \(\sigma_H^-\) which leads to 2,2',3,4,5,6-hexafluorobiphenyl.
The significance of benzoic acid in biaryl formation, in these systems, has been realized recently\(^\text{74}\). In presence of added p-fluorobenzoic acid the yield of 2,3,4,5,6-pentafluorobiphenyl is increased at the expense of both 2,2'3,4,5,6-hexafluorobiphenyl and of the radical combination products.

The kinetics of the decomposition of benzoyl peroxide was originally studied by Nozaki and Bartlett\(^\text{75}\). The decomposition is induced in part by the radicals present in a solution of decomposing benzoyl peroxide. The result is a reaction of higher order accompanying unimolecular decomposition. This observed rate constant is represented as,

\[
-d[P]/dt = k_1[P] + k_3/2 [P]^{3/2}
\]

The order with respect to peroxide concentration of the induced decomposition has a value of three halves if termination reaction between two like radicals are involved and one if the termination is between two unlike radicals.

Williams and co-workers\(^\text{76}\) have shown that, in the decomposition of benzoyl peroxide in benzene, the σ-complex is responsible for the induced decomposition of the peroxide. The following mechanistic route has been proposed to account for these observations:

\[
P = (\text{PhCO}_2)_2
\]

\[
(\text{PhCO}_2)_2 \rightarrow 2\text{PhCO}_2^*.
\]

\[
\text{PhCO}_2^* \rightarrow \text{Ph}^* + \text{CO}_2
\]

\[
\text{Ph}^* + \text{PhH} \rightarrow \sigma^*
\]

\[
\text{PhCO}_2 + \text{PhH} \rightarrow \sigma^*
\]

\[
\sigma^* + P \rightarrow \text{Ph}_2 + \text{PhCO}_2\text{H} + \text{PhCO}_2^*
\]

\[
\sigma^{**} + P \rightarrow \text{PhCO}_2\text{PH} + \text{PhCO}_2\text{H}
\]

\[
\sigma^* + \text{PhCO}_2^* \rightarrow \text{Ph}_2 + \text{PhCO}_2\text{H}
\]
The subject of homolytic aromatic substitution on pentafluorobiaryls has been reviewed recently.\textsuperscript{68}

1.9.4. \textbf{The pentachlorobiaryls:} Analogous reactions to the participation of pentafluorophenyl radicals in the arylation in non-aqueous media have been utilised recently by Bolton, Mitchell and Williams for the generation of pentachlorophenyl radicals.\textsuperscript{60}

Pentachloroaniline and pentachlorohydrazine have been used as source of pentachlorophenyl radicals. High yields of 2,3,4,5,6-pentachlorobiphenyl arising from the pentachlorophenylation of benzene have been found. Decomposition of pentachlorophenyl radicals precursors in toluene and chlorobenzene also produced the respective biaryls.

The mechanism of these reactions are consistent with those already established for the reaction of pentafluorophenyl radicals with aromatic substrates.

1.9.5. \textbf{Free radical halogenation:} Many hydrogen-containing compounds participate in chain reactions with molecular halogens (principally bromine and chlorine) or their derivatives such as N-bromosuccinimide, N-chlorosuccinimide, t-butylhypohalites and polyhalogenated methanes.

The present section describes a survey of the free radical halogenation reactions of aromatic compounds, emphasising the incidence of substitution reactions.
Radical halogenation can be carried out by thermolysis or photolysis. The photochemical method is a more attractive way as the reactions are easy to be performed.

Photochemical reactions of chlorine and bromine are of great importance and have been used for many addition and substitution reactions of organic compounds. The subject is well documented\textsuperscript{22a,b}.

Absorption of light by irradiation of a molecule could cause a chemical change since light behaves as a particle, according to Planck's quantum mechanical theory. A unit of energy or quantum is related to the wave length of radiation $\lambda$ by eq:

$$E = \frac{hc}{\lambda},$$

where $h$ is Planck's constant and $c$ the velocity of light.

Ultraviolet of wavelength $3000 \AA$ or below can be effective in producing chemical changes in halogen compounds.

Following irradiation with electromagnetic waves a molecule may undergo transitions. Atoms or molecules will absorb light only if the two energy states within the atom or molecule are separated by an amount equal to the energy of the light wave. Excitation of a molecule to a higher energy level involves promotion of an electron from a bonding ($\sigma$ or $\pi$) or a non bonding ($\pi$) orbital to an antibonding orbital ($\sigma^*$ or $\pi^*$). Four types of transitions are possible,

$$\sigma \rightarrow \sigma^*, \quad \pi \rightarrow \pi^* \quad \pi \rightarrow \pi^* \quad \text{and} \quad \pi \rightarrow \pi^*$$

of these, the last two are said to occur in the u.v. region and are responsible for a vast majority of photochemical reaction.

1.9.6. Free radical chlorination reactions: Photochemical reaction of chlorine and benzene at room temperature is well known. The product is addition of chlorine to give five different isomers of benzene hexachloride\textsuperscript{77},
The stereochemistry of the main isomers has been determined. The major isomer is the \( \alpha \)-benzene hexachloride with the following conformation,

\[
\begin{align*}
\text{Chlorine position} & \\
1,2 & = \text{axial} \\
3,4,5,6 & = \text{equatorial}
\end{align*}
\]

The mechanism is postulated to be a free radical addition. No nuclear substitution has been found.

Free radical halogenation of alkylbenzenes mostly give side-chain rather than nuclear products. However, when there is no \( \alpha \)-C-H group for this type of halogenation it is perhaps surprising to find that nuclear substitution accompanies the side-chain halogenation. Different workers have reported the radical chlorination of \( \text{t-butylbenzene} \). Following the earlier work of Kharasch and co-workers, Boocock and Hickinbottom reported that the liquid phase chlorination of \( \text{t-butylbenzene} \) gives predominantly \( \beta\beta\)-dimethylphenylethyl chloride (XX) - a side-chain product, and some 3-chloro-\( \text{t-butylbenzene} \). On the other hand, Backhurst and Ingold found a \( \alpha\alpha \)-dimethylphenylethyl chloride (XXI) - a side-chain rearranged substitution product as the main constituent in the gas phase halogenation of \( \text{t-butylbenzene} \) under illumination. The products of free radical chlorination of \( \text{t-butylbenzene} \) together with their relative amount (%) is shown in Scheme 10.
The results of liquid phase chlorination of t-butylbenzene shows a predominance of substitution in the side-chain over nuclear substitution by the chlorine atom. No other nuclear substitution product, apart from 3-chloro-t-butylbenzene, is reported to be formed in this reaction.

The intermediate in reactions shown in Scheme 10 was proposed to be the neophyl or 2-methyl-2-phenylpropyl radical, which has a greater tendency to undergo rearrangement. This probably proceeds via the intermediate bridged radical (XXIIa).

The following scheme was proposed by Kharasch and co-workers to account for an isomerisation of the neophyl radical (XXIIa) in ethereal solution. These radicals were generated by a Grignard reaction with neophyl chloride.
The process of rearrangement is outlined in Scheme 11.

Scheme 11
Extensive work on the gas phase halogenation of benzene derivatives involving nuclear substitution has been done and the subject is well reviewed by Kooyman.  

Vapour phase chlorination of biphenyl, in the temperature range 350 - 450°C, gives predominantly meta-chlorobiphenyl. This result is quite different from that obtained from the liquid phase electrophilic chlorination of biphenyl. The two results are compared in Table 10.

### Table 10

Chlorination of biphenyl

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Process</th>
<th>Ortho-</th>
<th>Meta-</th>
<th>Para-</th>
</tr>
</thead>
<tbody>
<tr>
<td>84</td>
<td>Vapour phase chlorination of biphenyl at 350 - 450°C</td>
<td>35-38</td>
<td>47-52</td>
<td>14-16</td>
</tr>
<tr>
<td>85</td>
<td>Liquid phase chlorination (electrophilic). Chlorine in acetic acid at 25°C</td>
<td>53</td>
<td>0</td>
<td>47</td>
</tr>
</tbody>
</table>

Liquid phase chlorination of biphenyl in carbon tetrachloride solution, initiated by sunlight leads to two isomers of hexachlorocyclohexyl-benzene, (XXIIIa) and (XXIIIb).
This is evidently a free radical process.

Vapour phase chlorination of benzotrifluoride and halogenobenzenes has also been investigated by the same group of workers. In all these cases the amount of meta-substitution is higher than ortho- and para-substitution. The results are summarised in Table 11.

Table 11
Isomer distribution in chlorination of benzene derivative at 375°C 83.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Monosubstitution products (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ortho-</td>
</tr>
<tr>
<td>Fluorobenzene</td>
<td>9</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>11</td>
</tr>
<tr>
<td>Bromobenzene*</td>
<td>-</td>
</tr>
<tr>
<td>Benzotrifluoride</td>
<td>13</td>
</tr>
</tbody>
</table>

* Br-Cl exchange was observed giving mainly dichlorobenzene.

Kooyman proposed a tentative mechanism of nuclear halogenation of benzene derivatives in gas phase. The primary step is a rapidly reversible formation of a complex between the reactants, the aromatic ring acquiring a positive charge. This complex then rearranges which is followed by loss of hydrogen halide to give the substitution product. The mechanism is outlined in eq. (38) and (39).

\[
\text{ArH} + X_\text{2} \rightarrow \text{ArH}^+X^-_\text{2} \quad \ldots \ldots \quad (38)
\]

\[
\text{ArH}^+X^-_\text{2} \rightarrow \text{Rearr.} \rightarrow \sigma\text{-complex} \rightarrow \text{ArX} + \text{HX} \quad \ldots \ldots \quad (39)
\]

For instance, the 2-halogenation of pyridine proceed according to this mechanism, eq. (40).
Hydrogen halide is lost in a nucleophilic attack at the position of high positive charge (acidity) in the intermediate.

Kooymen further argued that the observed H/D isotope effect shows that the breaking of C-H bond is involved in the rate-determining stage. The similarity of the H/D isotope effect in chlorination and bromination shows that the nuclear carbon-hydrogen bond is not broken by atomic halogen in a slow stage, in contrast with the hydrogen abstraction by atomic bromine which is known to involve a much larger H/D isotope effect\(^87\). Isomer patterns governed by acidity rather than electron-availability at the site of attack should be expected in a "nucleophilic" process; eq. (39).

Benson and co-workers\(^88\) later proposed a free radical mechanism for such systems, on the basis of their detailed kinetic studies. They argued that the stability of the appropriate intermediate radical is more appropriate. This is outlined in Scheme 12.
$X + ArX \rightleftharpoons (A)$

$(A) + X_2 \rightarrow (B)$

$(B) + X \rightarrow (C)$

$(C) \rightarrow \text{products}$

Scheme 12
1.9.7. Free radical bromination reactions: Benzene is known to undergo a photochemical bromination reaction to give an addition product, "benzene hexabromide", together with a small amount of bromobenzene at the room temperature. The formation of bromobenzene could either be through some electrophilic or a free radical process. However, the early kinetic photochemical studies of the bromination of benzene showed both substitution and addition to proceed at rates which depended upon the concentration of bromine, benzene and of light. This was interpreted in terms of a mechanism which relied upon the intermediacy of bromine atoms.

\[
\begin{align*}
\text{Br}_2 & \xrightarrow{h\nu} 2\text{Br} \\
\text{C}_6\text{H}_6 + \text{Br}^- & \xrightarrow{k_1} \text{C}_6\text{H}_5^- + \text{HBr} \\
\text{C}_6\text{H}_5^- + \text{Br}_2 & \xrightarrow{k_2} \text{C}_6\text{H}_5\text{Br} + \text{Br}^- \\
\text{C}_6\text{H}_5^- + \text{HBr} & \xrightarrow{k_3} \text{C}_6\text{H}_6 + \text{Br}^- \\
\text{C}_6\text{H}_6 + 2\text{Br}^- & \xrightarrow{k_4} \text{C}_6\text{H}_6\text{Br}_2 \\
\text{C}_6\text{H}_6\text{Br}_2 + 2\text{Br}^- & \xrightarrow{k_4(a)} \text{C}_6\text{H}_6\text{Br}_6 \\
\text{Br}^- + \text{Br}^- & \xrightarrow{k_5} \text{Br}_2
\end{align*}
\]

The kinetics are complicated by the hydrogen bromide produced, as \(k_3\) the only equation using hydrogen bromide, reverses \(k_1\) and so must slow down the reaction. Beside this the abstraction of hydrogen from benzene to give phenyl radical is energetically unfavourable. No evidence of free phenyl radicals (e.g. formation of biphenyl by dimerisation) was reported.

The liquid-phase photobromination of naphthalene is also similar in nature to that of benzene. Mayor and Hardy observed a high yield of 1,2,3,4-tetrahydro-1,2,3,4-tetrabromonaphthalene (80%) and a small amount of 1-bromonaphthalene (15%) in the photobromination of naphthalene in carbon tetrachloride solution at 25°C. The following mechanism (Scheme13)
has been suggested to account for the formation of addition accompanied by the substitution product in this reaction.

Scheme 13
The postulated unstable radical (XXIVa) which reacts with bromine to give an addition product is also able to react with bromine to form a substitution product. Results are established which shows that (XXIVb) loses hydrogen bromide and bromine, on heating, to give 1-bromonaphthalene and 1,4-dibromonaphthalene.

Photobromination of aralkyl hydrocarbons has received considerable attention especially from the point of view of quantitative studies. They show long chain length. In radical conditions, side-chain substitution is more favourable than nuclear substitution. However, when there is no reactive benzylic hydrogen present, nuclear substitution competes with the side-chain. Free radical bromination of t-butylbenzene gives side-chain and nuclear substituted products. Results of different workers is summarised in Table 12.

The predominance of nuclear over side chain substitution depends upon the reaction conditions in these systems.

No explanation has been given for this variation but it seems likely that these differences may arise from a decreased selectivity of bromine atom (if this is the only active participant) with the increase in temperature. At low temperature, bromine enters the apparently preferred position i.e. para- to the t-butyl group. At 167°C (b.p. of t-butylbenzene) or above the so-called "selective" bromine atom undergoes side-chain substitution thus replacing a primary hydrogen to give (XXV),

\[
\begin{align*}
\text{Me} \\
\text{Me-C-CH}_2\text{Br} \\
\end{align*}
\]

(XXV)
<table>
<thead>
<tr>
<th>Conditions</th>
<th>Side chain substitution</th>
<th>Nuclear substitution (Monobromo-t-butilbenzene)</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp.</td>
<td>Catalyst</td>
<td>2-isomer</td>
<td>3-isomer</td>
</tr>
<tr>
<td>90°C</td>
<td>Benzoil</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>167°C</td>
<td>Peroxide</td>
<td>Light</td>
<td>Mainly</td>
</tr>
<tr>
<td>226°C</td>
<td>Light (gas phase)</td>
<td>Mainly</td>
<td>---</td>
</tr>
</tbody>
</table>

(a) \( \beta \beta \)-Dimethylphenylethyl bromide
(b) \( \alpha \alpha \)-Dimethylphenylethyl bromide
(c) Accompanied by small amount of 2-methyl-1-phenylopropane.
and also photochemically more stable meta-bromo-t-butylbenzene (compared
to para-bromo-t-butylbenzene). At temperature 226° (gas phase) only the
side-chain substitution product (XXV) is formed, whereas no nuclear
product is observed under these conditions.

In liquid phase free radical halogenation of t-butylbenzene, on
the whole, the predominance of nuclear over side-chain substitution or
vice versa also depends upon the halogen atom used. It is known from other
evidences, that the t-butyl group is halogenated slowly, which is a
reasonable assumption that there is a competing nuclear attack. However,
in the liquid phase bromination the main reaction is a nuclear attack,
whereas in liquid phase chlorination it is the side-chain in which
substitution takes place mostly. Support for this is provided by free
radical bromination which is known to be much slower at a saturated
system than chlorination, and consequently the main reaction is nuclear
bromination.

Photobromination of toluene is a very fast process which gives
predominantly side-chain substitution product (98%). This is suggested to
be a chain process and tends to decrease with the increasing concentration
of bromine. At high concentration of bromine it is thought that the chain
propogating species may be a complexed bromine atom \text{Br}^-_. This is of
lower energy than bromine atom and consequently less effective for
hydrogen abstraction.

Recently, studies of liquid phase photobromination of halogeno-
benzenes have been published. Reactions were performed at room temperature
under the influence of u.v. light, using molecular bromine and N-bromo-
succinimide, separately, as source of bromine atoms. Results are summarised
in Table 13.
<table>
<thead>
<tr>
<th>Substrate</th>
<th>Bromine + hν</th>
<th>NBrS* + hν</th>
<th>Vapour phase bromination 425° (83)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorobenzene</td>
<td>20 - 25</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>15 - 20</td>
<td>63</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>55 - 65</td>
<td>27</td>
<td>24</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>10 - 20</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>60 - 80</td>
<td>94</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>10 - 20</td>
<td>4</td>
<td>24</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>15 - 25</td>
<td>7</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>30 - 50</td>
<td>72</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>35 - 55</td>
<td>21</td>
<td>21</td>
</tr>
</tbody>
</table>

* N-Bromosuccinimide
An important feature of these results is the predominance of meta-isomer in attack of chlorobenzene. N-Bromosuccinimide seems to be more effective in producing the meta-isomer principally. This type of isomer distribution is in agreement with the analogous gas phase reactions reported by Kooyman and co-workers. The selectivity apparently depends on the acidity of the different protons in an ionic species obtained by one electron transfer between the ring and the halogen.

1.9.8. Interchange of halogen atoms in aromatic compounds: Aromatic halogen is not readily replaced by another halogen in ionic reactions. However, in free radical conditions halogen exchange has been found to take place. Miller and Walling first reported detailed study of this phenomena. Photochlorination of bromobenzene at 90° gives high yield of chlorobenzene eq.(41). The process is accelerated by benzoyl peroxide and inhibited by nitrobenzene. Competitive chlorination of toluene and bromobenzene showed that toluene is only 4 to 5.6 times as reactive than bromobenzene. This indicates that such halogen exchanges are rapid processes. A mechanism involving the formation and collapse of the σ-complex has been suggested; this is outlined in Scheme 14.

\[
\begin{align*}
\text{Cl}_2 + 2 \text{Br} & \rightarrow \text{Cl} \quad \text{Different stages} \rightarrow 2 \text{ClBr} + \text{Br}_2 \quad \ldots \ldots (41)
\end{align*}
\]
This is supported by the later investigators. In any event, the transition state of the displacement step would not appear to involve appreciable bond breaking. Such type of displacement could be a concerted one-step process, a two-step process involving a relatively stable σ-complex or some intermediate between the two extremes. Support for the addition-elimination type of mechanism comes from the isolation of minor quantities of addition products i.e. mixed polychlorobromocyclohexanes. Support for the π-complex mechanism is provided by the fact that such exchange process is retarded in the presence of electron-withdrawing substituents. A similar halogen exchange process has been reported in the gas phase studies by Kooyman.

Evidence has been found that chlorine from chlorobenzene is also displaced by bromine atoms during the liquid phase photobromination. This happens in a more or less analogous way to that established by Miller and Walling for exchange processes. Substitution of chlorine by bromine also initiates consecutive chlorination reaction. The chlorine atom released in the medium can itself substitute a hydrogen or a bromine in another molecule of halogenobenzene.

Summary

The following points have been investigated and discussed in this chapter.

(1) The formation and stability of transient free radicals. It has been found that there are many factors which affect the stability of these free radicals; these include polar, steric and solvent effects.

(2) Polar properties of free radicals. Some of the polar properties of free radicals were illustrated on the basis of which they are classified as more polar or less polar.
(3) **Electrophilic aromatic substitution reaction involving halogenation.** A difference in behaviour of a halogen electrophile and a halogen atom towards their attack on aromatic ring has been noticed.

(4) **Homolytic aromatic substitution involving phenyl and poly-halogenophenyl radicals.** Some of the reactions and properties of pentafluorophenyl radicals have been studied. Pentafluorophenylation of several aromatic compounds shows electrophilic behaviour on the part of the pentafluorophenyl radical. Pentachlorophenyl radicals are also described by analogy to pentafluorophenyl radicals.

(5) **Free radical halogenation of aromatic compounds.** The incidence of substitution, in such cases, is emphasised. The formation of addition and substitution products is found to depend upon the temperature and also the concentration of halogen. Gas phase halogenation gives mainly substitution products. Reactions are different from heterolytic halogenation not only in the sense that addition products accompany the substitution products but also that in most of the cases meta-substitution predominates over ortho-para-substitution. Possible mechanisms have been explored to account for this trend.

(6) **Halogen exchange process.** Unlike ionic reactions, the halogen exchange process takes place quite easily in the free radical halogenation reactions of aromatic compounds.
2. Experimental

2.1. Analytical methods

The following methods were used for the analysis of compounds throughout the work.

(a) Infrared spectroscopy: A Perkin-Elmer 457 grating infrared spectrometer was used for recording the spectra.

(b) Nuclear magnetic resonance spectroscopy: All $^1$H and $^{19}$F n.m.r. spectra were recorded on a Perkin-Elmer R12B instrument, at 60 MHz and 56.4 MHz respectively.

(c) Mass spectrometry: Mass spectra were taken on a VG-Micromass 12B instrument, at 70 eV and 2-4 kV accelerating potential.

(d) Elemental analysis: Elemental analysis (C, H, N) was carried out on a Perkin-Elmer 240 elemental analyser.

(e) Thin layer chromatography: Alumina and kiesel gel TLC plates having a thickness of 0.25 mm were used. Plates were examined under ultraviolet light or were stained by iodine.

(f) Gas liquid chromatography: This was carried out on a Pye 104 instrument, using a flame ionisation detector and nitrogen as carrier gas. Identification of the reaction products was achieved by comparing the retention times with those of authentic samples under exactly similar conditions. Peak heights were taken as the mean of at least four samples and quantitative results obtained by the methods of internal standardisation using triangulation to calculate peak areas. Peak areas were calculated as the average of at least five runs.

All the isomer distribution ratios (%) were also calculated by this method.
A list of the different glass columns employed for the separation of reaction products on gas liquid chromatography, is given below in Table 14.

**Table 14**

<table>
<thead>
<tr>
<th>Code No.</th>
<th>Details</th>
<th>Compounds separated</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP-15C</td>
<td>15% Apiezon L, supported on 100-120 mesh celite, 9 ft x 1/8 inch O.D. column.</td>
<td>Bromo-t-butylbenzenes</td>
</tr>
<tr>
<td>OV-1</td>
<td>1% Methyl silicon gum, supported on 100-120 mesh, 5 ft x 1/8 inch O.D. column.</td>
<td>Polybromobenzenes, Bromobiphenyls.</td>
</tr>
<tr>
<td>PEGA</td>
<td>2% Polyethylene glycol adipate, supported on 100-120 mesh, acid washed, 5 ft x 1/8 inch O.D. column.</td>
<td>Bromochlorobenzenes Bromofluorobenzenes Bromobenzotrifluoride</td>
</tr>
<tr>
<td>FFAP</td>
<td>1% FFAP (modified carbowax) supported on chromosorb Q, 9 ft x 1/8 inch O.D. column.</td>
<td>Mono and di-bromobiphenyls.</td>
</tr>
<tr>
<td>SE-30P</td>
<td>1% Silar, supported on chromosorb Q, 9 ft x 1/8 inch O.D. column.</td>
<td>Mono and di-bromobiphenyls</td>
</tr>
</tbody>
</table>

2.2. **Purification of solvents**

The following organic solvents were dried with magnesium sulphate and distilled on a column (70 cm x 2 cm) packed with glass helices. Middle fractions were collected in all cases. Gas chromatographic analysis showed no impurities.

- (a) Benzene b.p. 79.5 - 80.5° / 760 mm
- (b) Toluene b.p. 109 - 110° / 760 mm
- (c) t-Butylbenzene b.p. 168° / 760 mm 80° / 22 mm
- (d) Chlorobenzene b.p. 132° / 760 mm
- (e) Fluorobenzene b.p. 84.5 - 85.5° / 760 mm
- (f) Bromobenzene b.p. 156 - 17° / 760 mm
- (g) Carbon tetrachloride b.p. 76.7° / 760 mm
(h) Cyclohexene b.p. 83° / 760 mm

(i) Benzotrifluoride b.p. 98 - 99° / 725 mm

(j) Hexafluorobenzene b.p. 81 - 82° / 760 mm

(k) Pentyl nitrite b.p. 104° / 51° / 132 mm

These boiling points were confirmed by the literature 100.

Section A. Homolytic Arylation Involving Polybromoaromatic Amines

2.3. Synthesis of compounds

2.3.1. Pentabromoaniline

(a) 2,6-Dibromo-4-nitroaniline.

p-Nitroaniline (35 g, 0.25 mole) was dissolved in a mixture of water (1 l) and concentrated sulphuric acid (250 g) with vigorous stirring. Bromine (80 g, 0.5 mole) was then added dropwise, when a flocculent yellow precipitate separated. Stirring was continued till all the bromine had been added.

The yellow solid thus produced was filtered off, washed with water and dried. Recrystallisation, from ethanol, gave 2,6-dibromo-4-nitroaniline (68 g, 92%); m.p. 205-206° (Lit. 206 - 207°).

(b) 3,5-Dibromonitrobenzene

Powdered sodium nitrite (52 g, 0.75 mole) was added in small portions to concentrated sulphuric acid (100 ml) with gentle stirring; the temperature was kept below 0°. A solution of 2,6-dibromo-4-nitroaniline (68 g, 0.23 mole) in concentrated sulphuric acid (100 ml) was added dropwise with stirring, the temperature being held below 5°. Stirring was continued for four to six hours. The solution was then poured, with vigorous stirring, into a mixture of 50% hypophosphorous acid (330 g, 2.5 moles) and ice (1 kg); considerable foaming occurred. The mixture was left overnight. The brown solid was filtered off, washed with water and dried at 50°. Extraction with ethanol gave, on cooling, 3,5-dibromonitrobenzene.
(38.5 g, 60%). Distillation at 3 mm gave a yellow-green solid b.p. 112°, but did not improve the melting point, 104-105° (Lit. 105°).

(c) 3,5-Dibromoaniline.

3,5-Dibromobenzene (29 g, 0.1 mole) was vigorously stirred in water (1 litre). Iron powder (34 g) was then added followed by concentrated sulphuric acid (7 ml). Addition of sodium hydroxide (11 g, 0.27 mole) followed by steam distillation of the product gave 3,5-dibromoaniline (20 g, 80%); m.p. 53 - 54° (Lit. 55 - 56°).

(d) Pentabromoaniline

To a stirred, ice cooled solution of 3,5-dibromoaniline (16.9 g, 0.067 mole) in glacial acetic acid (25 ml) was added dropwise, a mixture of bromine (40 g, 0.25 mole) and glacial acetic acid (25 ml). After a few hours of stirring, the mixture was poured into water (100 ml), and stirred well. The product was filtered, washed thoroughly with water and dried. Recrystallisation, from toluene, gave pentabromoaniline (28 g, 86%); m.p. 261-262° (Lit. 262°). The infrared spectrum showed the characteristic -NH₂ absorption in the region 3500 - 3000 cm⁻¹.

2.3.2. 2,3,4,5,6-Pentabromobiphenyl:

The following methods have been adapted for the preparation of this compound.

(a) Reaction between pentabromoiodobenzene and iodobenzene in the presence of activated copper bronze.

(b) An attempted Grignard reaction involving the formation of pentabromophenylmagnesium-bromide.

(a) This method involves two different stages.

(i) Preparation of pentabromoiodobenzene from pentabromoaniline.

(ii) Reaction of pentabromoiodobenzene with iodobenzene in the presence of activated copper bronze.
(i) Pentabromiodobenzene

The method used for the preparation of this compound is based upon those of Willgerodt and Wilcke\(^{102a}\), and of Hodgson and Mahadevan\(^{102b}\).

Pentabromoaniline (9.75 g, 0.02 mole) was dissolved in concentrated sulphuric acid (100 ml). The mixture was cooled to 0° by means of an ice salt mixture. To this was added sodium nitrite (10.5 g, 0.15 mole) slowly, with stirring, keeping the temperature below 5°C. After the addition of sodium nitrite the mixture was allowed to attain room temperature and then poured into crushed ice (1 kg). To this was added a solution containing potassium iodide (16.6 g, 0.01 mole) and the suspension was stirred. A thick brown precipitate appeared together with a large volume of gas. The suspension was continuously stirred while coming to room temperature and allowed to stand for one hour after which it was filtered. After washing with a solution of sodium metabisulphite, to remove the elemental iodine, the solid material was taken up in chloroform (80 ml) and to this was added concentrated sulphuric acid (d = 1.8, 30 ml) in order to remove unreacted amine. The two layers separated and the chloroform layer was washed with water and dried with magnesium sulphate. Evaporation of the solvent and recrystallisation of the crude material, from chloroform, gave pentabromiodobenzene (5.7 g, 48%); m.p. 312 - 313° (lit. 315 - 316°)\(^{103}\). Calculated for \(\text{C}_6\text{Br}_5\text{I}\): C, 12.1%; found: C, 11.9%. M (mass spectrometry), 594; calculated for \(\text{C}_6\text{Br}_5\text{I}\): 594.

(ii) This method was based on F.H. Case's synthesis of polybromobiphenyls\(^{104}\).

A 10 x 1.5" long glass tube containing redistilled iodobenzene (55.5 g, 0.27 mole) was heated, with stirring, on a metal bath above 180°.
A mixture of pentabromoiodobenzene (5.98 g, 0.01 mole) and activated copper bronze *(5 g) was added in portions for 35 minutes. Heating was continued for an additional half hour. The brown solution was cooled to room temperature slowly and was extracted with benzene to a total volume of 150 ml. The mixture was concentrated to 30 ml by distilling under vacuum. The brown mass was eluted twice through an alumina column, using a mixture (1:4) of chloroform and petroleum ether (60-80°) as eluent. Evaporation of the solvent gave a white solid.

Thin layer chromatography of this white solid on silica gel plates, using petroleum ether (60-80°) as eluent, provided evidence for the presence of 2,3,4,5,6-pentabromobiphenyl together with a trace of an impurity which could not be separated even after recrystallisation from ethanol.

2,3,4,5,6-Pentabromobiphenyl thus obtained (1.3 g, 25%) had melting point 135-136°. Calculated for $\text{C}_{12}\text{H}_{5}\text{Br}_5$: C, 26.22; H, 0.91; found: C, 25.20; H, 0.9%. M (mass spectrometry), 544, calculated for $\text{C}_{12}\text{H}_{5}\text{Br}_5$ 544 [Bromine isotope ratio 1:5:10:10:5:1].

(b) This attempted reaction involves two steps.

(i) Generation of pentabromophenylmagnesium bromide from hexabromobenzene and phenylmagnesium bromide in dry tetrahydrofuran at 0°.

(ii) Reaction of pentabromophenylmagnesium bromide with iodobenzene in the presence of cuprous chloride.

---

*Copper bronze was activated as in Vogel "Qualitative Organic Analysis" Longman, 1957, 192.*
A solution of phenylmagnesium bromide was prepared in the usual manner from bromobenzene (3.4 g, 0.02 mole) and magnesium turnings (0.5 g) in sodium-dry tetrahydrofuran (50 ml).

Approximately 5 ml of this solution was added dropwise, to a vigorously stirred slurry of hexabromobenzene (5.5 g, 0.01 mole) in sodium-dry tetrahydrofuran, at 0°. After the addition of phenylmagnesium bromide, the stirring was further continued for four hours maintaining the temperature strictly at 0°. The slurry of hexabromobenzene did not become clear, showing that possibly none or very little pentabromophenylmagnesium bromide had been formed, in contrast to Smith, Tamborski and Moore's observation.

This reaction did not work even after several improvements.

2.3.3. 2,4,6-Tribromobiphenyl

This compound was prepared in two different stages;

(a) Preparation of 2,4,6-tribromoiiodobenzene from tribromoaniline.

(b) Reaction of 2,4,6-tribromoiiodobenzene with iodo benzene.

(a) 2,4,6-Tribromoaniline (10 g, 0.03 mole) was diazotised and the diazonium ion was decomposed by iodide, using the same method as for pentabromoiodobenzene (page 83). Recrystallisation from ethanol, gave needles of 2,4,6-tribromoiodobenzene (7.9 g, 60%); m.p. 104° (Lit. 105°). Calculated for C_{6}H_{2}Br_{3}I: C, 16.4; H, 0.45; found C, 16.3; H, 0.4%. M (mass spectrometry), 438 calculated for 12C_{6}H_{2}^{79}Br_{3}I, 438 [Bromine isotope ratio 1:3:3:1].

(b) A mixture of 2,4,6-tribromoiodobenzene (5 g, 0.011 mole) and activated copper bronze (4 g) was slowly added to refluxing iodo benzene (50 ml) in a 10 x 1.5" long glass tube. After one hour of stirring above 180°, the mixture was cooled. Extraction with benzene and washing on an
alumina column with petroleum ether (60-80°C) gave a white solid. Gas chromatography of this residue revealed the presence of mostly unreacted 2,4,6-tribromiodobenzene and ca. 10% 2,4,6-tribromobiphenyl (by comparison with the products of reaction No. 2.4.2). This could not be separated.

2.4. Arylation reactions of polybromoaromatic amines

2.4.1. The decomposition of pentabromoaniline and pentyl nitrite in benzene:

Pentabromoaniline (4.8 g, 0.01 mole) was dissolved in redistilled dry benzene (100 ml). To this solution, redistilled pentyl nitrite (10-15 m mole) was added dropwise, at room temperature. The solution became cloudy.

After the evolution of gas ceased (10-15 min) the mixture was heated, first gently and then under reflux in an oil bath for 2½ hours. When the reaction mixture had cooled to room temperature, the excess of benzene was removed by distillation under vacuum and the residue was analysed by gas chromatography for low boiling products. Pentyl alcohol was found to be present.

The above residue was then dissolved in chloroform (100 ml) and extracted with water and sodium hydroxide (2 N, 2 x 15 ml) respectively. The two layers separated. Acidification of the aqueous extract with nitric acid (2 M) followed by addition of a few drops of silver nitrate (0.1 M) gave a yellow precipitate indicating the presence of bromide ions.

The unreacted amine was removed from the reaction product by treating the chloroform layer with sulphuric acid (d = 1.85; 3 x 15 ml). This was followed by washing with water (2 x 20 ml) and drying over calcium chloride, and evaporating the solvent under vacuum.
The residue was steam distilled to remove the low boiling components such as pentyl alcohol, pentyl nitrite, aldehydes etc.

Thin layer chromatography of the crude material, on silica gel plates and with petroleum ether (60-80°) as eluent, provided evidence for the presence of pentabromobenzene, 2,3,4,5,6-pentabromobiphenyl (by a comparison with their authentic samples) and an unidentified compound, using ultraviolet light as the detector.

Mass spectrometry of the same material showed the presence of hexabromobenzene which could not be detected on thin layer chromatography plates.

The mixture was partially crystallised from ethanol, to give a pale yellow solid. This on further recrystallisation, from benzene, gave hexabromobenzene (1.1 g, 35%); m.p. 313-314° (Lit. 316°)\(^\text{100}\).

After the removal of hexabromobenzene by recrystallisation, the residue left behind was washed on an alumina column with hexane as eluent. Evaporation of the solvent gave a white solid which was found to be a mixture of pentabromobenzene and pentabromobiphenyl (TLC).

This mixture was then chromatographed on a long, narrow silica gel column, with petroleum ether (60-80°) as eluent, and fractions were collected. The first batch, when evaporated to dryness gave pentabromobenzene (0.8 g, 29%); m.p. 159° (Lit. 160-161°)\(^\text{100}\). A mixed melting point, with an authentic sample of pentabromobenzene, did not show any depression. Calculated for \(\text{C}_6\text{Br}_5\text{H}\); C, 15.22; H, 0.21; found C, 15.39; H, 0.18%. M (mass spectrometry), 468, calculated for \(^{12}\text{C}_6\text{Br}_5\text{H}\), 468.

The second batch of the fraction, on evaporation, gave a white solid which on recrystallisation, from ethanol, gave 2,3,4,5,6-pentabromobiphenyl (0.5 g, 16%); m.p. 137-138°. Calculated for \(\text{C}_{12}\text{HBr}_5\); C, 26.22; H, 0.9; found: C, 26.4; H, 0.9%. M (mass spectrometry), 544, calculated for \(^{12}\text{C}_{12}\text{Br}_5\text{H}\); 544.
Mass spectrum of 2,3,4,5,6-pentabromobiphenyl

$^{12}C_{12}H_{5}^{79}Br_{5}$

M.W. 544
2.4.2. The decomposition of 2,4,6-tribromoaniline in benzene using pentyl nitrite:

2,4,6-Tribromoaniline (3.3 g, 0.01 mole) was dissolved in dry and redistilled benzene (100 ml). Pentyl nitrite (10-15 m mole) was added dropwise with occasional shaking.

After the evolution of gas ceased (10-12 min), the mixture was heated first gently and then under reflux in an oil bath for 2½ hours.

When the solution had cooled to room temperature, the excess of benzene was removed by distillation under vacuum. The products were analysed by gas liquid chromatography, on an OV-1 column at 160°, which revealed the presence of pentyl alcohol, 2,4,6-tribromobenzene, 2,4,6-tribromobiphenyl and 2,4,6-tribromoaniline (unreacted) by a comparison of the retention times with those of authentic samples. The results are given in Table 15.

Although, the authentic sample of 2,4,6-tribromobiphenyl prepared (page 86) was impure, it had one peak in the g.l.c. which had the same retention time as that ascribed to 2,4,6-tribromobiphenyl in the above reaction product.

Mass spectrometry of the crude product confirmed the presence of 2,4,6-tribromobiphenyl. The molecular ion ($M^+$) showed prominent peaks at m/e 388, 390, 392 and 394, and the presence of three bromine atoms (isotope ratio 1:3:3:1); bromine fragmentation was the major mode of breakdown.

2.4.3. The decomposition of 2-bromoaniline in benzene using pentyl nitrite:

Pure 2-bromoaniline (1.73 g, 0.01 mole) was dissolved in redistilled, dry benzene (100 ml). To this solution was added dropwise pentyl nitrite (10-15 m.mole) and the mixture was shaken periodically. The mixture became cloudy and the evolution of gas was apparent.
When the addition of pentyl nitrite was complete, the solution was heated, at first gently and then under reflux for $2\frac{1}{2}$ hours.

After cooling the mixture to room temperature, the excess of benzene was distilled off under vacuum and the products were analysed by gas chromatography, using Apiezon column at 160°. The results are summarised in Table 15.

Isolation of the 2-bromobiphenyl was effected by eluting the reaction product from an alumina column with petroleum ether (60-80°), and after repeated fractional distillation under reduced pressure 2-bromobiphenyl (0.78 g, 47%), b.p. 162/10 mm (Lit. 42/18 mm) was obtained. Gas chromatography revealed no impurity in the sample. M (mass spectrometry), 232, calculated for $^{12}C_{12}\text{Br}_9$, 232.

The infrared spectrum showed bands in the region 730 cm$^{-1}$, 750 cm$^{-1}$ and 775 cm$^{-1}$ which are characteristic of 2-substituted benzenes.

<table>
<thead>
<tr>
<th>Ar.NH$_2$</th>
<th>Products (%) from decomposition of polybromoamines in benzene, using pentyl nitrite, at 80°.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar.</td>
<td>Moles consumed</td>
</tr>
<tr>
<td>Pentabromo-($X = 1$)</td>
<td>$6 \times 10^{-3}^{(a)}$</td>
</tr>
<tr>
<td>2,4,6-Tribromo-($X = 3$)</td>
<td>$5.4 \times 10^{-3}$</td>
</tr>
<tr>
<td>2-Bromo-($X = 5$)</td>
<td>$7.6 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

(a) Estimated by acid-extraction method.
(b) Estimated by g.l.c. assuming the response to be the same as that for the respective amine.
(c) Also formed hexabromobenzene (30-35%) as side-product.
Section B. Photochemical Bromination Reactions

2.5.1. Preliminary methods:

(a) Description of photochemical apparatus.

All photochemical bromination reactions were carried out in a Hanovia 1L photochemical reactor with a 100-watt medium pressure mercury arc tube emitting predominantly ultraviolet light at 254 μm, 265 μm, 297 μm, 313 μm and 366 μm.

(b) Estimation of bromine

The amount of molecular bromine left, after a photochemical reaction, in the reaction mixture was determined by the addition of potassium iodide

\[
\text{Br}_2 + 2\text{KI} \rightarrow \text{I}_2 + 2\text{KBr}
\]

followed by the titration of the liberated iodine with standard sodium thiosulphate solution using starch as indicator.

\[
\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6
\]

Standard solutions of sodium thiosulphate (N/10, N/20) were prepared by dissolving the appropriate amounts of the substance in distilled water, and making the volume up to one litre and were then standardised with a solution of potassium iodate.

(c) Estimation of hydrogen bromide

A potentiometric titration method was used to determine the amount of hydrogen bromide formed in photochemical reactions.

The usual procedure adapted was to flush out the reaction mixture, at the end of the reaction, with nitrogen so that the hydrogen bromide should be collected in water (100 ml) in a beaker connected at the outlet of the photocell. The remaining hydrogen bromide in the organic reaction mixture was extracted with water (3 x 75 ml). All the aqueous layers were combined and made up to 500 ml. This was followed by a titration
with silver nitrate (0.05 M) solution. The rapid change in the potential of the indicator electrode responsive for the concentration of bromide ions was recorded potentiometrically.

All results are placed in Tables 18 and 19.

2.6. Preparation of compounds

2.6.1. Benzene hexabromide:

Bromine (32 g, 0.2 mole) was dissolved in redistilled dry benzene (500 ml). The mixture was irradiated with u.v. light for 30 hours at room temperature with a slow stream of nitrogen.

Benzene was removed by distillation under reduced pressure. The white solid so obtained gave, on recrystallisation from toluene, benzene hexabromide (29 g, 86%); m.p. 216-218° (Lit. 212°). Calculated for C_{6}H_{6}Br_{6}: C, 12.9; H, 1.0; found: C, 12.9; H, 1.0%.

2.6.2. Hexabromochlorohexane:

To a one litre flask containing chlorobenzene (500 ml) was added bromine (32 g, 0.2 mole). The mixture was mixed thoroughly and a fine capillary was fitted at the neck of the flask as an outlet of gas.

The whole mixture was placed in sunlight for three weeks. When most of the colour of bromine had disappeared, the chlorobenzene was evaporated under reduced pressure. Recrystallisation from ethanol gave hexabromocyclohexane (23 g, 60%); m.p. 125° (Lit. 126°). Calculated for C_{6}H_{6}Br_{6}Cl: C, 12.2; H, 0.8; found C, 12.2; H, 0.8%.

2.6.3. Naphthalene tetrabromide:

1,2,3,4-Tetabromo-1,2,3,4-tetrahydronaphthalene was prepared by the gradual addition of bromine (32 g, 0.2 mole), over a period of
of 2 - 3 hours, to carbon tetrachloride (500 ml) containing naphthalene (13 g, 0.1 mole), under illumination in the photochemical reactor. After 16 hours the carbon tetrachloride layer was washed with sodium metabisulphate solution (10%) and dried. Complete evaporation of the solvent, under vacuum gave a solid residue. Three recrystallisations, from chloroform, gave the tetrabromide of naphthalene (5 g, 23% on the basis of 48% conversion of bromine). Calculated for \( C_{10}H_8Br_4 \): C, 26.78; H, 1.78; found C, 26.8; H, 1.7%.

N.M.R. (Me\(_4\)Si, CDCl\(_3\), 90 MHz) at room temperature, \( \delta \) 4.9 - 5.2 (2H D), \( \delta \) 5.6 - 5.73 (2HD).

\( \delta \) 7.34 - 7.5 (4H aromatic, symmetrical multiplet).

Integral ratio 2:2:4. (2:2 aliphatic, 4 aromatic).

This is discussed in detail on page 184.

2.6.4. 2-Bromo-t-butylbenzene

(a) 4-Nitro-t-butylbenzene

Concentrated nitric acid (80 ml, 1.3 moles, sp.gr. 1.42) was added gradually to vigorously stirred t-butylbenzene (134 g, 1 mole), at room temperature. After 7 - 8 hours of stirring, the mixture was washed with water (3 x 50 ml) and dried with calcium chloride.

The yellow oil was distilled under reduced pressure. The first fraction contained the bulk of t-butylbenzene; the second fraction was 4-nitro-t-butylbenzene (61 g, 34%) boiling at 125°/12 mm (Lit. 125-30°/10 mm).

(b) 2-Bromo-4-nitro-t-butylbenzene

A mixture of 4-nitro-t-butylbenzene (25 g, 0.13 mole), bromine (20 g, 0.13 mole) and finally divided iron powder (1 g) was heated in an oil bath at 90°. Evolution of hydrogen bromide was moderately brisk.
and after half an hour, a further portion of bromine (16.0 g, 0.1 mole) was added slowly and the whole mixture was heated for 8 hours maintaining the temperature at 90°.

When cold, the product formed a semi-solid mass. On distilling in a current of superheated steam, a yellowish oily solid collected in the receiver. This semi-solid substance was extracted with benzene (3 x 50 ml) and dried.

After evaporating the benzene under vacuum and recrystallisation from ethanol, needles of 2-bromo-4-nitro-t-butylbenzene (23 g, 68%); m.p. 94° (Lit. 94.5°) were obtained.

(c) 2-Bromo-4-amino-t-butylbenzene

Concentrated hydrochloric acid (2 ml) was added to a solution of the foregoing bromo-compound (20 g, 0.07 mole) in alcohol (60 ml) and the mixture heated under reflux to the boiling point, finally divided iron (6 g) then being added in four equal portions.

After four hours reduction was complete and the alcoholic solution was filtered from iron, and water added to the filtrate, which was extracted with ether. The amine hydrochloride, precipitated on addition of hydrochloric acid to the ethereal extract, was filtered, washed with ether and dissolved in hot dilute hydrochloric acid. The amine was then precipitated by addition of sodium hydroxide (2 M) and extracted with ether. Distillation gave 2-bromo-4-amino-t-butylbenzene (10 g, 64%), a pale yellow liquid b.p. 156-160°/11 mm (Lit. 153-155°/11 mm).

(d) 2-Bromo-t-butylbenzene

2-Bromo-4-amino-t-butylbenzene (10 g, 0.043 mole) was dissolved in alcohol (30 ml) and concentrated sulphuric acid (50 ml) and cooled at 0°, with slow stirring. The sulphate crystallised out. Pentyl nitrite (0.05 mole) was then added dropwise. Stirring was continued for an additional 30 minutes at 0°.
The reaction mixture was allowed to attain room temperature slowly and was finally heated on a water bath.

The red oily liquid so obtained was extracted with chloroform (2 x 25 ml) and washed with water, 10% sodium hydroxide and again water. After drying with magnesium sulphate, the excess of chloroform was evaporated by distillation under atmospheric pressure. The crude product was distilled, over a short fractionating column, under reduced pressure. 2-Bromo-t-butylbenzene was collected at 96–98°/10 mm (Lit. 98/12 mm) as a colourless oil in 64% yield (5.9 g). N.M.R. (Me₄Si, CDCl₃, 60 MHz) at room temperature, δ 1.3 - 1.5 (8H t-butyl group, integral ratio 6.3). δ 6.8 - 7.7 (4H aromatic, complex multiplet). M (mass spectrometry) 212, calculated for \( ^{12} \text{C}_{10} \text{H}_{13} \text{Br} : 212. \)

2.6.5. 3-Bromo-t-butylbenzene:

This preparation is based on the method of C.S. Marvel et al. and B.W. Larner et al.

(a) 4-Nitro-t-butylbenzene
t-Butylbenzene (134 g, one mole) was nitrated using concentrated nitric acid (80 ml, 1.3 moles, sp.gr 1.42). Yield of 4-nitro-t-butylbenzene was 59 g, 33%.

(b) 4-Amino-t-butylbenzene

Concentrated hydrochloric acid (120 ml) was added slowly to 4-nitro-t-butylbenzene (59 g, 0.3 mole) and granulated tin (60 g, 0.5 atoms) at room temperature. The mixture was heated gently at first and after the initial reaction subsided, under reflux for two hours. Then it was cooled and left overnight.

A saturated solution of sodium hydroxide (120 g in 100 ml) was added gradually to make the solution strongly alkaline. Crude amino-compound
was distilled in a current of superheated steam, extracted with ether and dried over calcium chloride. After removing ether by evaporation, the product was distilled under reduced pressure to give 4-amino-t-butylbenzene (36 g, 81%); b.p. 84-90°/10 mm (Lit. 228°/762°).

(c) 4-t-Butylacetanilide

A mixture of acetic anhydride and acetic acid (0.25 mole, each) was added to the foregoing amino-compound (38.5 g, 0.25 mole) containing zinc dust (20 g) to prevent oxidation. After heating for 30 minutes the hot mixture was poured in 500 ml of water, resulting in the precipitation of 4-t-butylacetanilide. This was filtered off, washed with water and dried. Recrystallisation from ethanol, gave pure 4-t-butylacetanilide (33 g, 70%); m.p. 166° (Lit. 169°).

(d) 2-Bromo-4-t-butylacetanilide

Bromine (24 g, 0.15 mole) was added slowly to 4-t-butylacetanilide (19 g, 0.1 mole), acetic acid (75 ml) and iron filings (0.1 g) at 35 - 40°. After six hours of stirring, the mixture was added to ice water, and the 2-bromo-4-t-butylacetanilide was recrystallised from alcohol in colourless plates (21 g, 78%); m.p. 156° (Lit. 156 - 157°).

(e) 2-Bromo-4-t-butylianiline hydrochloride

The above anilide (20 g, 0.074 mole) was hydrolysed by boiling with hydrochloric acid (20 ml) and alcohol (30 ml) for three hours. On concentration, 2-bromo-4-t-butylianiline hydrochloride (15.5 g, 80%) was obtained in colourless plates; m.p. 192° (Lit. 193 - 4°).

(f) 3-Bromo-t-butylbenzene

The foregoing hydrochloride (15 g, 0.055 mole) in acetic acid (150 ml), water (100 ml) and concentrated hydrochloric acid (35 ml) at 0°, was treated with sodium nitrite (7.6 g, 0.1 mole) in water (50 ml) and then
added to hypophosphorous acid (180 ml). After three days, the separated oily layer of 3-bromo-t-butylbenzene was removed with chloroform and the organic layer was washed with water, 10% sodium hydroxide and then water. After evaporation of the chloroform, the product was distilled to give pure 3-bromo-t-butylbenzene (8.5 g, 74%); b.p. 88-94°/20 mm. (Lit. 222°/740 mm).

N.M.R. (Me₄Si; CDCl₃; 60 MHz) at room temperature: δ 1.25 (9H t-butyl group); δ 6.91 - 7.63 (4H multiplet aromatic with coupling constant 1.8 Hz). M (mass spectrometry), 212, calculated for 12C₁₀H₁₃Br: 212.

2.6.6. 4-Bromo-t-butylbenzene

A mixture of iron powder (3 g) and t-butylbenzene (134 g, 1 mole) was cooled to 0 - 5° with stirring while bromine (200 g, 1.25 mole) was added dropwise over two hours. After leaving the mixture overnight, the excess of bromine was removed with a solution of sodium metabisulphite (10%). This was followed by two washings with sodium bicarbonate solution (10 %) and two with water. After drying over calcium chloride, the product was distilled under reduced pressure to give 4-bromo-t-butylbenzene (150 g, 70%): b.p. 80-82°/2 mm (Lit. 80-81°/2 mm).

N.M.R. (Me₄Si; CDCl₃; 60 MHz) at room temperature: δ 1.18 (9H t-butyl group) δ 7.0-7.42 (4H symmetrical pattern, aromatic, with coupling constant 8Hz). M (mass spectrometry), 212, calculated for 12C₁₀H₁₃Br: 212.

2.6.7. 1,3-Di-t-Butylbenzene

(a) 3,5-Di-t-butyltoluene

Aluminium chloride (3 g) was added in the course of 3 - 4 hours to a mixture of toluene (60 g, 0.65 mole) and t-butylchloride (92.5 g, 1 mole).
After standing for 24 hours the reaction mixture was poured into a mixture of ice and dilute hydrochloric acid. The oily layer was washed successively with water and sodium carbonate (10%) solution and dried over magnesium sulphate. On distilling under reduced pressure, using a short column, a fraction boiling at 95 - 130°/18 mm was collected. This on cooling gave 3,5-di-t-butyltoluene (120 g, 59%); m.p. 30-31°. (Lit. 31-2°).

(b) 3,5-di-t-butylbenzoic acid

A mixture containing 3,5-di-t-butyltoluene (35 g, 0.17 mole), pyridine (120 g, 1.5 mole), water (60 ml) and potassium hydroxide (15 g) was poured in a 500 ml three neck flask equipped with a reflux condenser, thermometer and a dropping funnel. The system was heated to 95° and potassium permanganate (67 g) was added in small portions to the vigorously stirred mixture. Stirring was continued for 2 hours after addition at 95°. The manganese dioxide formed was filtered off and washed with potassium hydroxide (2 M) solution.

In order to recover the unreacted hydrocarbon, the filtrate was extracted with ether. From the ethereal layer 3,5-di-t-butyltoluene (10 g) was recovered by distillation.

The aqueous layer was concentrated on a steam bath to about 150 ml and the crude acid precipitated by acidifying with sulphuric acid (4 M). This product was filtered off, washed with cold water, dried and recrystallised, from a mixture of acetic acid and water, to give pure 3,5-di-t-butylbenzoic acid (14.8 g, 53% based on 70% conversion of hydrocarbon); m.p. 169-170° (Lit. 171-172°).

(c) 1,3-di-t-butylbenzene (This method is not given in ref.111a,b)

The foregoing acid (10 g, 0.04 mole) was dissolved in quinoline (30 g, 0.23 mole) to which cupric carbonate (1 g) was added. The mixture was heated under reflux till the evolution of carbon dioxide had ceased.
After cooling, the mixture was poured in water (100 ml). The dark oily layer was extracted with petroleum ether (60-80°) (3 x 40 ml) and washed with dilute hydrochloric acid and then water. After drying with magnesium sulphate the product was distilled under reduced pressure to give 1,3-di-t-butylbenzene (3.2 g, 43%) which boiled at 80-95°/20 mm.

N.M.R. (Me₄Si; CDCl₃; 60 MHz) at room temperature; δ 7.13 - 7.35 (aromatic protons 3H & 1H B); δ 1.22 (18H & di-t-butyl group).

Infrared spectra was identical with the one that is reported in the literature.

2.6.8. 3-Bromocyclohexene:

In a 250 ml round-bottom flask was placed a mixture of cyclohexene (8.2 g, 0.1 mole), N-bromosuccinimide (14 g, 0.079 mole), benzoyl peroxide (0.1 g) and dry carbon tetrachloride. The flask was flushed with nitrogen and then refluxed for forty minutes with stirring. The succinimide was removed by filtration and washed with carbon tetrachloride. After evaporating excess of solvent and olefin, the residue was distilled under reduced pressure to give 3-bromocyclohexene (6.3 g, 50%) b.p. 68-70°/18 mm (Lit. 68°/15 mm).

2.6.9. 1,2-Dibromocyclohexane:

A mixture containing cyclohexene (31 g, 0.37 mole) carbon tetrachloride (100 ml) and absolute alcohol (10 ml) was cooled in an ice salt mixture. When the temperature had reached to -5°, a solution of bromine (70 g, 0.43 mole) in carbon tetrachloride (100 ml) was added dropwise with stirring. The temperature was maintained between -5 to -1°.

When all the bromine had been added (2 - 3 hours), the contents of the flask were directly transferred to a Claisen flask and the excess of carbon tetrachloride and cyclohexene were distilled off. This was followed by distillation under reduced pressure. The first small fraction contained
some low boiling products. The second fraction was pure 1,2-dibromo-
cyclohexane (70 g, 79%) boiling at 110-112/18 mm. (Lit. 108-12°/25 mm).

To preserve the 1,2-dibromocyclohexane from atmospheric decomposition,
it was shaken for five minutes with one-third of its volume of alcoholic
potassium hydroxide (20%). The mixture was diluted with its own volume
of water and the organic layer was washed free of alkali, dried and
distilled. There was ca. 10% loss on purification.

2.6.10. 1-Bromocyclohexene

1,2-Dibromocyclohexane (50 g, 0.2 mole) was added dropwise to
boiling quinoline (58 g, 0.4 mole) in such a way that the rate of refluxing
was not disturbed. After the addition, the mixture was steam distilled
and the product was extracted with ether.

Evaporation of the ether, followed by distillation under reduced
pressure gave 1-bromocyclohexene (13.5 g, 42%) B.P. 58-62°/15 mm.
(Lit. 58°/15 mm)

2.6.11. 4,4'-Dibromobiphenyl

Finely powdered biphenyl (15.4 g, 0.1 mole) was placed in an
evaporating dish. The dish was set on a porcelain rack in a 30 cm
desiccator with a 10 cm evaporating dish under the rack containing bromine
(39 g, 0.24 mole). The desiccator was closed. A very small opening was
provided for the escape of hydrogen bromide. The biphenyl was left in
contact with the bromine vapours overnight.

The crude 4,4'-dibromobiphenyl obtained (23 g, 75%) was recrystallised
with benzene; m.p. 160-161° (Lit. 162-163°).

Calculated for C_{12}H_{8}Br_{2}: C, 46.1; H, 2.5; found C, 46.1; H, 2.5%.
M (mass spectrometry) 310, calculated for $^{12}_{12}C_{12}H_{8}Br_{2}$: 310.
2.7.1. **Photochemical bromination of benzene:**

(a) **At room temperature**

Bromine (16.0 g, 0.1 mole) was dissolved in dried and redistilled benzene (500 ml) and placed in the photochemical reactor. The apparatus was covered with aluminium foil to avoid the loss of u.v. radiations.

The solution was irradiated for sixteen hours in two eight hour periods. A slow stream of nitrogen was passed to maintain an inert atmosphere. A water trap was fitted at the gas outlet of the apparatus to collect the hydrogen bromide evolved during the reaction.

At the end of the reaction, bromine consumption and the amount of hydrogen bromide collected were determined by the methods mentioned on page 91 and 92. The results are given in Table 18.

After removing the residual bromine by a solution of sodium metabisulphite (10%), the benzene layer was dried with magnesium sulphate. Excess of solvent was removed by fractional distillation at atmospheric pressure using a column (30 cm x 2 cm) filled with glass helices.

Gas chromatography of the mixture on an Apiezon column revealed small amounts of bromobenzene and \( p \)-dibromobenzene. The results are given in Table 16.

Complete evaporation of the benzene under vacuum gave a solid residue which on recrystallisation from toluene gave benzene hexabromide (80-85%, based on 90% bromine conversion); m.p. 216-218° (Lit. 212°). Calculated for \( \text{C}_6\text{H}_6\text{Br}_6 \): C, 12.9; H, 1.0; found: C, 12.9; H, 1.0%.

(b) **At 50-55°**

Bromine (16.0 g, 0.1 mole) was dissolved in dried, redistilled benzene (500 ml) in the photochemical reactor covered with aluminium foil. The reactor was placed in an oil bath preheated to 50°C.
The mixture was irradiated under a very slow stream of nitrogen. The hydrogen bromide evolved was collected in water (75 ml).

After sixteen hours of illumination, the solution was worked up for free bromine and for hydrogen bromide formed as on page 91 and 92. The results are given in Table 18.

The benzene solution was washed with a solution of sodium metabisulphite (10%) and water, and dried over magnesium sulphate before removing the excess of benzene by fractional distillation at atmospheric pressure.

Gas chromatography of the mixture showed the presence of bromobenzene, isomeric dibromobenzenes, 1,3,5-tribromobenzene and some high boiling residue. The results are given in Table 16.

An infrared spectrum of the concentrated sample showed bands in the region of 770-735, 725-680 and 860-800 cm\(^{-1}\) corresponding to ortho-, meta- and para-disubstituted benzene\(^{101}\). An additional band of medium intensity in the region 750-810 was also found for meta-di-substituted benzene.

Two different methods were used for the analysis of addition products in this reaction product, as the g.l.c. technique was not suitable for these compounds:

(a) Evaporation of the benzene under vacuum gave a tarry residue which, on washing with cold petroleum ether (60-80°), gave a pale yellow solid from which after twice recrystallisation from toluene, benzene hexabromide (7 g, 40%); m.p. 216-218° (Lit. 212-213°)\(^{100}\) was obtained.

(b) The second method involves the steam distillation of the residue, obtained on evaporation of benzene. The solid left after the steam distillation was washed with ethanol. This on twice recrystallisation from toluene gave benzene hexabromide (5 g, 32%); m.p. 216-218° (Lit. 212-213°)\(^{100}\).

Calculated for C\(_8\)H\(_6\)Br\(_6\): C, 12.9; H, 1.0; found C, 12.9; H, 1.0%.
### Table 16

Products (moles) from photochemical bromination of benzene

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Temperature</th>
<th>$\text{C}_6\text{H}_6\cdot\text{Br}_6$</th>
<th>$\text{C}_6\text{H}_5\cdot\text{Br}$</th>
<th>$\text{C}_6\text{H}_4\cdot\text{Br}_2$</th>
<th>1,3,5-$\text{C}_6\text{H}_2\cdot\text{Br}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7.1a (1)</td>
<td>Room temperature</td>
<td>$23 \times 10^{-3}$</td>
<td>$5 \times 10^{-3}$</td>
<td>-</td>
<td>ca. $1 \times 10^{-4}$</td>
</tr>
<tr>
<td>2.7.1b (2)</td>
<td>50 - 55°</td>
<td>$13 \times 10^{-3}$</td>
<td>$15 \times 10^{-3}$</td>
<td>$1.8 \times 10^{-3}$</td>
<td>$8 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

**Isomer distribution ratio (%) of dibromobenzene**

<table>
<thead>
<tr>
<th>o-</th>
<th>m + p</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>81</td>
</tr>
</tbody>
</table>

(1) 0.09 mole of bromine consumed

(2) 0.09 mole of bromine consumed
2.7.2. Photochemical decomposition of benzenehexabromide at 50°:

(a) In toluene

Benzene hexabromide (5.0 g, 9 m.mole) was dissolved in dried and redistilled toluene (500 ml). This was transferred to the photochemical reactor covered with an aluminium foil and placed in an oil bath preheated to 50–55°.

The mixture was illuminated for sixteen hours with a slow stream of nitrogen passing through.

At the end of the reaction, the hydrogen bromide collected was estimated as described on pages 91 and 92. The results are given in Table 19.

After washing with sodium metabisulphite (10%) solution, the mixture was dried with calcium chloride. The excess of toluene was removed by fractional distillation.

Gas liquid chromatography (15% OV-1, 120°) revealed the presence of the following components; benzyl bromide, bibenzyl, bromobenzene, isomeric dibromobenzenes, small amounts of 1,3,5-tribromobenzene, and an unidentified product. The results are given in Table 17.

The unreacted benzene hexabromide was recovered by complete evaporation of the toluene on a rotary evaporator. The residue was washed with petroleum ether (60–80°) (15 ml). The insoluble hexabromide was filtered off.

(b) In benzene

The work-up was similar to the previous section.

Gas liquid chromatography of the mixture on an OV-1 column at 120° showed the presence of bromobenzene, isomeric dibromobenzenes, 1,3,5-tribromobenzene, and some high boiling residue. The relative proportions of these compounds is reported in Table 17.
(c) In carbon tetrachloride

The procedure was similar to that described in the previous sections.

Gas chromatography on an OV-1 column at 120° revealed the presence of bromobenzene, isomeric dibromobenzenes; very small amounts of 1,3,5-tribromobenzene, hexachloroethane and some unidentified products. The results are summarised in Table 17.

(d) In cyclohexene

The decomposition was very slow, as was evident from the colour of the solution after 16 hours of irradiation.

Gas chromatographic analysis showed the following compounds; 1,2-dibromocyclohexane, 3-bromocyclohexene, and small amounts of bromobenzene, dibromobenzenes and some unidentified products. No evidence was found for the presence of 1-bromocyclohexene. The results are given in Table 17.

2.7.3. Thermal decomposition of benzene hexabromide at 50-80°

(a) In benzene

Benzene hexabromide was heated to 50-80° in toluene and benzene separately, in the absence of u.v. light.

The hexabromide (5.5 g, 0.01 mole) was dissolved in dried and distilled solvent (500 ml) and the mixture was placed in an oil bath preheated first at 50° and finally to 80°. After 16 hours between 50-80° without u.v. light no change in colour was observed which suggested that the adduct had not undergone decomposition.

Gas chromatographic analysis confirmed the above result as no product of thermal decomposition neither in the solvent nor on the g.l.c. column was present.
(b) In presence of benzoyl peroxide

Benzene hexabromide (5.5 g, 0.01 mole) was dissolved in redistilled dried benzene (500 ml). Benzoyl peroxide (0.1 g) was added and the mixture was heated in an oil bath at 80°.

After 16 hours of reflux the mixture was pale yellow which indicated the decomposition of adduct.

Gas chromatography showed minor amounts of bromobenzene (ca. 9 x 10^-4 mole) and p-dibromobenzene (ca. 1 x 10^-4 mole).

(c) In presence of 4-chlorobenzoyl peroxide

The procedure was similar to the previous one.

Gas chromatographic analysis showed the presence of bromobenzene (ca. < 4 x 10^-4), dibromobenzenes (ca. < 1 x 10^-4 mole) and 1,4-chloro-bromobenzene.

2.7.4. Photolysis of 1,4-dibromobenzene in toluene;

1,4-Dibromobenzene was photolysed in toluene using 1,2,3-trichlorobenzene as an internal standard.

(a) At room temperature

1,4-Dibromobenzene (2.36 g, 0.01 mole) and 1,2,3-trichlorobenzene (1.8 g, 0.01 mole) were dissolved in dried and distilled toluene (500 ml). The mixture was irradiated for sixteen hours at room temperature.

Gas chromatography showed only 2% decomposition of the 1,4-dibromobenzene to give only traces of benzyl bromide and bromobenzene.

(b) At 50°

1,4-Dibromobenzene and 1,2,3-trichlorobenzene (0.01 mole each) were irradiated at 50° in toluene for sixteen hours.

Gas chromatographic analysis of the mixture showed only 6-8% decomposition of 1,4-dibromobenzene to give some benzyl bromide.
Table 17
Products from photochemical decomposition of benzene hexabromide in different solvents, at 50-55°, for 16 hours.

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Solvent</th>
<th>Moles of hexabromide used</th>
<th>Moles of hexabromide consumed</th>
<th>( \text{C}_6\text{H}_5\text{Br} )</th>
<th>( \text{C}_6\text{H}_4\text{Br}_2 )</th>
<th>1,3,5-Tri-(b) bromobenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7.2</td>
<td>Toluene (a)</td>
<td>9 x 10^{-3}</td>
<td>5.3 x 10^{-3}</td>
<td>1.3 x 10^{-3}</td>
<td>8 x 10^{-4}(b)</td>
<td>9 x 10^{-5}(b)</td>
</tr>
<tr>
<td>(a)</td>
<td>Benzene</td>
<td>10 x 10^{-3}</td>
<td>7.8 x 10^{-3}</td>
<td>9 x 10^{-3}</td>
<td>4.8 x 10^{-3}(c)</td>
<td>1.1 x 10^{-3}(c)</td>
</tr>
<tr>
<td>(b)</td>
<td>Carbon tetrachloride</td>
<td>6 x 10^{-3}</td>
<td>2.1 x 10^{-3}</td>
<td>1.2 x 10^{-3}</td>
<td>4 x 10^{-4}(d)</td>
<td>--</td>
</tr>
<tr>
<td>(c)</td>
<td>Cyclohexene (f)</td>
<td>10 x 10^{-3}</td>
<td>1.8 x 10^{-3}</td>
<td>ca. 1.8 x 10^{-4}</td>
<td>-- (g)</td>
<td>-- (g)</td>
</tr>
<tr>
<td>(d)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Also formed benzyl bromide (8 x 10^{-3} mole), bibenzyl (3 x 10^{-4}).
(b) \( \sigma^-/\pi^- + \pi^- \) ratio 20:80
(c) \( \sigma^-/\pi^- + \pi^- \) ratio 19:81
(d) \( \sigma^-/\pi^- + \pi^- \) ratio not determined (g.l.c. peak overlapping).
(e) Also formed bromotrichloromethane (> 2 x 10^{-4} mole)
(f) Also formed 1,2-dibromocyclohexane, and 3-bromocyclohexene (ratio approx 2:1)
(g) \( \sigma^-/\pi^- + \pi^- \) ratio not determined (low yields)
(h) Isomer not determined with certainty.
Table 18
Estimation of free bromine and hydrogen bromide in the photobromination reactions of benzene derivatives, using bromine (0.1 mole)

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Substrate brominated</th>
<th>Solvent (500 ml)</th>
<th>Temperature</th>
<th>Moles of bromine consumed (±4×10⁻³)</th>
<th>Moles of hydrogen bromide estimated</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7.1a</td>
<td>Benzene</td>
<td>Benzene</td>
<td>R.T.</td>
<td>90 × 10⁻³</td>
<td>8 × 10⁻³</td>
</tr>
<tr>
<td>2.7.1b</td>
<td>Benzene</td>
<td>Benzene</td>
<td>50-55⁰</td>
<td>90 × 10⁻³</td>
<td>34 × 10⁻³</td>
</tr>
<tr>
<td>2.7.8</td>
<td>Biphenyl (1 mole)</td>
<td>Benzene</td>
<td>50-55⁰</td>
<td>98 × 10⁻³</td>
<td>60 × 10⁻³</td>
</tr>
<tr>
<td>2.7.9a</td>
<td>Biphenyl (0.5 mole)</td>
<td>Benzene</td>
<td>50-55⁰</td>
<td>94 × 10⁻³</td>
<td>45 × 10⁻³</td>
</tr>
<tr>
<td>2.7.9b</td>
<td>Biphenyl (0.1 mole)</td>
<td>Benzene</td>
<td>50-55⁰</td>
<td>70 × 10⁻³</td>
<td>35 × 10⁻³</td>
</tr>
<tr>
<td>2.7.5</td>
<td>Biphenyl (0.5 mole)</td>
<td>Carbon tetrachloride</td>
<td>50-55⁰</td>
<td>60 × 10⁻³</td>
<td>31 × 10⁻³</td>
</tr>
<tr>
<td>2.7.6a</td>
<td>Biphenyl (0.1 mole)</td>
<td>Carbon tetrachloride</td>
<td>50-55⁰</td>
<td>24 × 10⁻³</td>
<td>16 × 10⁻³</td>
</tr>
<tr>
<td>2.7.6b</td>
<td>Biphenyl (1.0 mole)</td>
<td>Carbon tetrachloride</td>
<td>50-55⁰</td>
<td>70 × 10⁻³</td>
<td>40 × 10⁻³</td>
</tr>
<tr>
<td>2.7.10</td>
<td>Biphenyl (0.75 mole)</td>
<td>Bromobenzene</td>
<td>50-55⁰</td>
<td>60 × 10⁻³</td>
<td>42 × 10⁻³</td>
</tr>
<tr>
<td>2.7.11</td>
<td>Naphthalene (0.1 mole)</td>
<td>Carbon tetrachloride</td>
<td>50-55⁰</td>
<td>80 × 10⁻³</td>
<td>40 × 10⁻³</td>
</tr>
<tr>
<td>2.7.13a</td>
<td>Fluorobenzene</td>
<td>Fluorobenzene</td>
<td>R.T.</td>
<td>40 × 10⁻³</td>
<td>35 × 10⁻³</td>
</tr>
<tr>
<td>2.7.13b</td>
<td>Chlorobenzene</td>
<td>Chlorobenzene</td>
<td>R.T.</td>
<td>51 × 10⁻³</td>
<td>41 × 10⁻³</td>
</tr>
<tr>
<td>2.7.16</td>
<td>Benzotri-fluoride (0.57 mole)</td>
<td>Carbon tetrachloride</td>
<td>R.T.</td>
<td>24 × 10⁻³</td>
<td>15.6 × 10⁻³</td>
</tr>
<tr>
<td>2.7.17</td>
<td>t-Butyl-benzene</td>
<td>t-Butyl-benzene</td>
<td>R.T.</td>
<td>60 × 10⁻³</td>
<td>48 × 10⁻³</td>
</tr>
</tbody>
</table>
Table 19

Estimation of hydrogen bromide and free bromine in the photochemical decomposition of benzene hexabromide (BHB)/hexabromochlorocyclohexane (HBCC), in different solvents at ca. 50°

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Reactants</th>
<th>Moles of hydrogen bromide</th>
<th>Moles of free bromine</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7.2a</td>
<td>BHB in toluene</td>
<td>$12 \times 10^{-3}$</td>
<td>---</td>
</tr>
<tr>
<td>2.7.2b</td>
<td>BHB in benzene</td>
<td>$20 \times 10^{-3}$</td>
<td>---</td>
</tr>
<tr>
<td>2.7.2c</td>
<td>BHB in carbon tetrachloride</td>
<td>$3 \times 10^{-3}$</td>
<td>$2 \times 10^{-3}$</td>
</tr>
<tr>
<td>2.7.2d</td>
<td>BHB in cyclohexene</td>
<td>ca. $8 \times 10^{-5}$</td>
<td>---</td>
</tr>
<tr>
<td>2.7.14a</td>
<td>HBCC in toluene</td>
<td>$18 \times 10^{-3}$</td>
<td>---</td>
</tr>
<tr>
<td>2.7.14b</td>
<td>HBCC in benzene</td>
<td>ca. $12 \times 10^{-3}$</td>
<td>---</td>
</tr>
</tbody>
</table>
2.7.5. Photobromination of biphenyl in carbon tetrachloride:

A mixture of bromine (16 g, 0.1 mole) and biphenyl (77 g, 0.5 mole) was dissolved in redistilled, dry carbon tetrachloride (500 ml). After twenty hours of irradiation at ca. 50° the reaction was stopped. The free bromine and hydrogen bromide were estimated. The results are given in Table 18.

Gas chromatography of the reaction product on 1% FFAP column, showed the presence of isomeric monobromobiphenyls together with minor quantity of 4,4'-dibromobiphenyl. The results are given in Table 20.

2.7.6. The effect of change in concentration of biphenyl on isomer distribution of monobromobiphenyls:

(a) Photobromination of biphenyl (0.1 mole) in carbon tetrachloride

A mixture containing biphenyl (15.4 g, 0.1 mole) and bromine (16 g, 0.1 mole) in carbon tetrachloride (500 ml) was irradiated under the same conditions as for the previous reaction.

Analytical results of the product are given in Table 20.

(b) Photobromination of biphenyl (1 mole) in carbon tetrachloride

Biphenyl (154 g, 1 mole) was brominated under exactly the same conditions as for reaction 2.7.5. The results are given in Table 20.

2.7.7. Investigation for the presence of any addition product in reaction 2.7.5:

To detect the presence of an addition products, [e.g. \( \text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_5\cdot\text{Br}_4 \) or \( \text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_5\cdot\text{Br}_6 \)], in the product mixture of reaction 2.7.5 the following reactions were performed.

The crude product, present in carbon tetrachloride, was washed with sodium metabisulphite (10%), sodium carbonate (20%; 3 x 75 ml) and with water (2 x 75 ml) to remove the free bromine and hydrogen bromide present. After drying, the carbon tetrachloride was evaporated under reduced pressure. The residue obtained was washed with cold petroleum
Table 20

Photochemical bromination of biphenyl in carbon tetrachloride at ca. 50° for twenty hours

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Moles of biphenyl used</th>
<th>Products (moles)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Monobiphenyl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ortho-</td>
</tr>
<tr>
<td>2.7.5</td>
<td>0.5</td>
<td>6.9 x 10^{-3}</td>
</tr>
<tr>
<td>2.7.6 (a)</td>
<td>0.1</td>
<td>3.48 x 10^{-3}</td>
</tr>
<tr>
<td>(b)</td>
<td>1.0</td>
<td>9.2 x 10^{-3}</td>
</tr>
</tbody>
</table>

0.1 Mole of bromine in 500 ml of carbon tetrachloride was used in all cases.

Conversion of bromine was 63, 24 and 70% using 0.5, 0.1 and 1.0 mole of biphenyl, respectively.

4,4'-Dibromobiphenyl isomer not determined with certainty.
ether (60-80°) by suction to remove any trichlorobromomethane present. The residue was divided into three portions.

The first portion was boiled in toluene (100 ml) for three hours. Gas chromatography showed no benzyl bromide which could form on thermal decomposition of any adduct \([C_6H_5\cdot C_6H_5Br\cdot C_6H_5\cdot C_6H_5Br]_n\) present in the mixture. The same toluene solution was again refluxed, with added benzoyl peroxide (0.24 g, 1 m.mole), for four hours. Gas chromatography revealed the presence of benzyl bromide (0.4 g, 2.3 m.mole). (A blank reaction using para-bromobiphenyl in toluene (100 ml) with benzoyl peroxide (0.24 g, 1 m.mole) after two hours of reflux revealed the absence of benzyl bromide, hence, no decomposition).

The second portion was dissolved in dimethylformamide (50 ml) and warmed with alcoholic silver nitrate solution for ten minutes. Precipitates of silver bromide were formed which were soluble in ammonia solution and insoluble in nitric acid.

To the third portion (6 g) was added methanol (50 ml) containing potassium hydroxide (10 g). After three hours of reflux, the mixture was poured into water (100 ml) and extracted with chloroform. The two layers separated.

The chloroform layer was dried and concentrated. Gas chromatography revealed the presence of a very small quantity of a substance which has the same retention time as that of 4,4'-dibromobiphenyl. Isomeric dibromobiphenyls could not be distinguished under the conditions used. No 2,4,6-tribromobiphenyl was found.

2.7.8. The competitive reaction:

The photochemical bromination of biphenyl (1 mole) in benzene (5.5 mole)

A solution of biphenyl (154 g, 1 mole) in redistilled, dry benzene (500 ml, 5.5 mole) was placed in the photochemical reactor. To this
bromine (16.0 g, 0.1 mole) was added and the contents were mixed up thoroughly.

The mixture was irradiated, in an oil bath at 50-55°, for twenty hours.

The amount of hydrogen bromide formed and the free bromine were estimated by the usual methods. The results are given in Table 18. The benzene solution was washed with sodium metabisulphite solution (10%) and water and finally dried over anhydrous magnesium sulphate.

Gas chromatography of the mixture on a 1% FFAP column, revealed the presence of the following compounds; bromobenzene, isomeric dibromobenzenes, monobromobiphenyls and small amounts of dibromobiphenyls. The results are given in Table 21.

2.7.9. The effect of change in concentration of biphenyl on the isomer distribution ratio of monobromobiphenyls:

(a) The photobromination of biphenyl (0.5 mole) in benzene

A mixture of biphenyl (77 g, 0.5 mole) bromine (16.0 g, 0.1 mole) and redistilled, dry benzene (500 ml) was irradiated under the same conditions as in the previous section. The results of free bromine and hydrogen bromide analysis are given in Table 18.

Gas chromatographic analysis of the products formed are given in Table 21.

(b) A reaction analogous to the above one, was performed using biphenyl (15.4 g, 0.1 mole) in benzene (500 ml). The results are given in Table 21.
Table 21

Products (moles) from photobromination of biphenyl and benzene at ca. 50° for twenty hours

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Amount of biphenyl used</th>
<th>Bromobenzene</th>
<th>Dibromobenzene</th>
<th>Monobromobiphenyl⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>ortho-</td>
<td>meta-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>meta-+para-</td>
<td>ortho-</td>
</tr>
<tr>
<td>2.7.8(1)</td>
<td>1 mole</td>
<td>14 x 10⁻³</td>
<td>1.2 x 10⁻³</td>
<td>5.6 x 10⁻³</td>
</tr>
<tr>
<td>2.7.9a(2)</td>
<td>0.5 mole</td>
<td>16 x 10⁻³</td>
<td>1.6 x 10⁻³</td>
<td>6.7 x 10⁻³</td>
</tr>
<tr>
<td>2.7.9b(3)</td>
<td>0.1 mole</td>
<td>16 x 10⁻³</td>
<td>1.51 x 10⁻³</td>
<td>6.98 x 10⁻³</td>
</tr>
</tbody>
</table>

(1) 98 m.mole of bromine consumed
(2) 94 m.mole of bromine consumed
(3) 90 m.mole of bromine consumed
(4) Also formed 4,4'-dibromobiphenyl > 2 x 10⁻³ mole
2.7.10. The competitive reaction:

The photochemical bromination reaction of biphenyl (0.75 mole) and bromobenzene (4.12 mole)

Bromobenzene, dried with anhydrous magnesium sulphate, was carefully distilled twice, on a fractionating column (70 cm x 2 cm). Middle fraction was collected. Gas chromatography showed no impurity.

A mixture of biphenyl (115.5 g, 0.75 mole), bromobenzene (436 ml, 4.12 mole), and bromine (16 g, 0.1 mole) was irradiated, at 50-55°, for eighteen hours.

The results of free bromine present and the hydrogen bromide formed are given in Table 18.

Gas chromatography of the reaction product revealed the presence of isomeric dibromobenzenes and monobromobiphenyls. Results of their quantitative estimations are given in Table 22.

### Table 22

Products (moles) from photobromination of biphenyl and bromobenzene, at 50-55° *

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Dibromobenzene</th>
<th>Monobromobiphenyl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ortho-</td>
<td>meta- + para-</td>
</tr>
<tr>
<td>2.7.10</td>
<td>$1 \times 10^{-3}$</td>
<td>$2.8 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

*Conversion of bromine was 60 m.mole
2.7.11. **Photochemical bromination of naphthalene:**

Bromine (16 g, 0.1 mole) was dissolved in dried and redistilled carbon tetrachloride (500 ml) to which pure naphthalene (13 g, 0.1 mole) was added. The mixture was irradiated at 50-55°C.

Bromine consumption was fast. The reaction was stopped after eight hours. The amount of hydrogen bromide formed and the free bromine left were measured. The results are given in Table 18.

After removing the residual bromine by extraction with a solution of sodium metabisulphite (10%), the carbon tetrachloride layer was dried with magnesium sulphate.

Gas chromatography of the mixture on an OV-1 column showed the presence of α-bromonaphthalene (35% on the basis of 80% conversion of bromine) as the only product formed. No other isomer could be separated when different g.l.c. columns were used.

2.7.12. **Attempted photochemical decomposition of 1,2,3,4-naphthalene tetrabromide:**

1,2,3,4-Naphthalene tetrabromide (4.48 g, 0.01 mole) was dissolved in dry and redistilled toluene (500 ml) and the mixture was irradiated at room temperature for sixteen hours. G.l.c. analysis showed the presence of 1-bromo- and 1,4-dibromonaphthalene but it was difficult to distinguish whether these products arise as a result of photochemical decomposition of naphthalene tetrabromide or thermal decomposition of this tetrabromide on the g.l.c. column. Pure naphthalene tetrabromide is not heat resistant and has been found to decompose on the g.l.c. column, even at fairly low temperature (60°C), to give mono- and di-bromonaphthalenes.
2.7.13. Photochemical bromination of halogenobenzenes:

(a) Fluorobenzene

A solution of dried and redistilled fluorobenzene (500 ml) and bromine (16.0 g, 0.1 mole) was placed in the photochemical reactor covered with aluminium foil to minimise the loss of radiation. The apparatus was flushed with nitrogen.

The mixture was irradiated for sixteen hours, at room temperature, with a continuous slow stream of nitrogen.

The work-up procedure has been described in the previous sections.

Gas chromatographic analysis on a 2% PEGA column at 75° revealed the presence of isomeric bromofluorobenzenes by a comparison of the retention times with commercially supplied (Aldrich Chemicals Ltd) authentic specimens. The authentic materials were found to be pure by g.l.c. examination.

Results are given in Table 23.

After complete evaporation of the fluorobenzene at atmospheric pressure, the residue left was found to be a mixture of bromofluorobenzene isomers. No addition product could be seen.

The \(^{19}\text{F N.M.R. spectrum (56.4 MHz)}\) of a solution of this residue in fluorotrichloromethane showed signals at 114.9, 110.0 and 107.1 ppm (broad singlets) corresponding to para-, meta- and ortho-flurobromobenzene, respectively.

(b) Chlorobenzene

Bromine (16.0 g, 0.1 mole) was dissolved in purified chlorobenzene (500 ml). The mixture was irradiated in the photochemical reactor for sixteen hours, at room temperature. A slow stream of nitrogen was passed throughout the reaction.

Analysis by gas chromatography on a 2% PEGA column at 70° showed the presence of isomeric bromochlorobenzenes and small amounts of bromobenzene. Results are given in Table 23.
Table 23

Products (moles) from photobromination of halogenobenzenes, at room temperature

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Reactants</th>
<th>BrC₆H₄X⁽ᵃ⁾</th>
<th>C₆H₅Br</th>
<th>C₆H₅Brₓ</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7.13</td>
<td></td>
<td>ortho-</td>
<td>meta-</td>
<td>para-</td>
</tr>
<tr>
<td>(a)</td>
<td>Fluorobenzene + bromine⁽ᵇ⁾</td>
<td>12.3 x 10⁻³</td>
<td>2.46 x 10⁻³</td>
<td>26 x 10⁻³</td>
</tr>
<tr>
<td>(b)</td>
<td>Chlorobenzene + bromine⁽ᶜ⁾</td>
<td>6.4 x 10⁻³</td>
<td>27 x 10⁻³</td>
<td>8.6 x 10⁻³</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Isomer distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>(b)</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

(a) X ; F or Cl

(b) 40 m.mole bromine conversion

(c) 51 m.mole bromine conversion
On removing the excess of chlorobenzene under reduced pressure and treating the concentrated mixture with a little petroleum ether (60-80°) (15 ml), a solid residue was obtained. The mixture was left at 0-5° for a few days for crystallisation of the solid to be complete. Finally the solid was filtered and dried. Recrystallisation, from ethanol, gave hexabromochlorocyclohexane m.p. 125° (Lit. 126°). Calculated for C_{6}H_{5}Br_{6}Cl: C, 12.1; H, 0.84, found: C, 12.1; H, 0.84%.

2.7.14. Photochemical decomposition of hexabromochlorocyclohexane at 50°:

(a) In toluene

Recrystallised hexabromochlorocyclohexane (5.0 g, 0.0084 mole) was dissolved in redistilled, dried toluene (500 ml). The mixture was irradiated in the photochemical reactor for sixteen hours. A continuous stream of nitrogen was passed throughout the course of photolysis.

After the required decomposition time, the solution was analysed for free bromine and hydrogen bromide content. The results are in Table 19.

Gas liquid chromatography on a 2% PEGA column at 70° showed the presence of the following compounds: benzyl bromide, bibenzyl, ortho-, meta- and para- bromochlorobenzene and some high boiling residue. The results are given in Table 24.

Evaporation of the toluene from the above product mixture, under reduced pressure, gave a residue (thick liquid) from which no solid unreacted hexabromochlorocyclohexane was recovered.

(b) In benzene

Hexabromochlorocyclohexane (5 g, 0.0084 mole) was photolysed in benzene (500 ml) at 50° for sixteen hours.

Gas chromatography on a 2% PEGA column revealed the presence of the following compounds: bromobenzene, isomeric dibromobenzenes, ortho-, meta- and para-bromochlorobenzene, chlorobenzene and some unidentified products. The results are summarised in Table 24.
Table 24

Products from photochemical bromination of hexabromochlorocyclohexane, at 50-55° in different solvents.

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Solvent</th>
<th>Moles of HBCC used</th>
<th>Moles of HBCC consumed</th>
<th>Br-C₆H₄Cl₆⁺Cl⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7.14</td>
<td></td>
<td></td>
<td></td>
<td>ortho-</td>
</tr>
<tr>
<td>(a)</td>
<td>Toluene *</td>
<td>8.4 x 10⁻³</td>
<td>ca. 8.4 x 10⁻³</td>
<td>4 x 10⁻⁴</td>
</tr>
<tr>
<td>(b)</td>
<td>Benzene †</td>
<td>8.4 x 10⁻³</td>
<td>6.2 x 10⁻³</td>
<td>3.2 x 10⁻⁴</td>
</tr>
</tbody>
</table>

HBCC = Hexabromochlorocyclohexane

<table>
<thead>
<tr>
<th>Isomer distribution ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
</tr>
<tr>
<td>(b)</td>
</tr>
</tbody>
</table>

* Also formed: benzyl bromide (17 x 10⁻³ mole), bibenzyl (2 x 10⁻³ mole) and chlorobenzene (ca.1 x 10⁻³ mole)
† Also formed: bromobenzene (3.8 x 10⁻³ mole), o-, m- and p-dibromobenzene (2 x 10⁻³ mole) and chlorobenzene (4 x 10⁻³ mole)
2.7.15. Attempted photochemical bromination of hexafluorobenzene:

A mixture of dried and redistilled hexafluorobenzene (500 ml) and bromine (16.0 g, 0.1 mole) was irradiated in the photochemical reactor at 50-55°. The reaction was very slow. After thirty hours of irradiation only 6-8% of bromine was consumed.

Gas chromatography indicated some unidentified products which had quite different retention times than that of bromopentafluorobenzene or any isomer of dibromotetrafluorobenzene.

$^{19}$F N.M.R. in CDF$_3$ (60 MHz) was complicated. However, mass spectra of the product revealed the presence of an addition product - hexabromo-hexafluorobenzene. The molecular ion ($M^+$) of the above compound had prominent peaks at m/e 660, 662, 664, 666, 668, 670, 672 and showed the presence of six bromine atoms (isotope ratio 1:5:10:20:10:5:1). Bromine fragmentation was the major mode of breakdown.

2.7.16. Photochemical bromination of benzotrifluoride:

Benzotrifluoride (83 g, 0.57 mole) and bromine (16.0 g, 0.1 mole) were dissolved in dried and distilled carbon tetrachloride (500 ml). This solution was transferred to the photochemical reactor which was covered with aluminium foil to avoid the loss of light. The mixture was irradiated for sixteen hours with a slow stream of nitrogen passing through the reactor.

At the end of the reaction, the solution was analysed for free bromine and hydrogen bromide. The results are in Table 18.

Gas liquid chromatography on a 2% PEGA column at 65° revealed the presence of meta-bromobenzotrifluoride as the major product and very small amounts of ortho- and para- bromobenzotrifluoride, by a comparison of the retention times with their authentic samples. No other product could be detected in this reaction. The results are summarised in Table 25.
Table 25

Products from photobromination of benzotrifluoride
in carbon tetrachloride\(^{(a)}\)

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Monobromobenzotrifluoride (moles)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ortho-</td>
</tr>
<tr>
<td>2.7.16</td>
<td>ca. 6.2 \times 10^{-4}</td>
</tr>
</tbody>
</table>

\(^{(a)}\) 24 m.mole of bromine/500 ml of carbon tetrachloride

2.7.17. **Photochemical bromination of t-butylbenzene:**

Bromine (16 g, 0.1 mole) were dissolved in redistilled dry t-butylbenzene (500 ml) and the mixture was irradiated under usual conditions, at room temperature, for twenty hours.

At the end of the reaction, the solution was analysed from bromine conversion and hydrogen bromide contents. Results are in Table 18.

Gas chromatography on an Apiezon column, revealed the presence of the following compounds: meta- and para-bromo-t-butylbenzene, isomeric di-t-butylbenzenes and small amount of bromobenzene; each was identified by a comparison of their retention times with authentic samples.

The reaction product was separated from t-butylbenzene by careful fractional distillation. The concentrated sample was analysed by proton n.m.r. using the following conditions: MeSi\(_4\), CDCl\(_3\), 60 MHz at room temperature. Result showed singlet at \(\delta 1.4, 1.25\) and 1.18 corresponding to ortho-, meta- and para-bromo-t-butylbenzene, respectively. The peak at \(\delta 1.4\) revealed the presence of 4-5\% ortho-bromo-t-butylbenzene (this compound could not be seen on g.l.c.).

No evidence was found for the presence of methylene proton in the region \(\delta 4-5\) showing the absence of any side-chain substitution product in this reaction.
From the above reaction product components were isolated by preparative gas liquid chromatography. A 9.1 m x 8 mm glass column, packed with 15% Apiezon, supported on 60—70 mesh (acid washed) diatomite, was fitted to the Pye 104 analytical gas chromatography instrument. A splitter (25:1) was connected at the detector end. The column temperature was 180° with carrier gas (N\textsubscript{2}) pressure 25, air 8 and hydrogen 3.5 p.s.i.

2 ml of concentrated sample were injected each time. The products separated sufficiently well and were trapped in a glass U-tube cooled by an acetone-solid carbon dioxide mixture and fitted at the other end of the column.

The following chief fragments were isolated by the above technique; para- and meta-bromo-t-butylbenzene and meta-di-t-butylbenzene. Mass spectra and proton n.m.r. spectra of these samples were consistent with their structure. Results of their qualitative estimation are given in Table 26.

**Table 26**

Products (moles) from photochemical bromination of t-butylbenzene\(^{(a)}\)

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Monobromo-t-butylbenzene</th>
<th>Di-t-butylbenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ortho- + para-(^{(b)})</td>
<td>meta-</td>
</tr>
<tr>
<td>2.7.17</td>
<td>16 x 10^{-3}</td>
<td>35 x 10^{-3}</td>
</tr>
</tbody>
</table>

**Isomer distribution (%) of mono-bromo-t-butylbenzene**

<table>
<thead>
<tr>
<th>o- + p-</th>
<th>m-</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>72</td>
</tr>
</tbody>
</table>

\(^{(a)}\) 60 m.mole of bromine consumed in 500 ml of t-butylbenzene.

\(^{(b)}\) These isomers could not be separated on g.l.c. N.M.R. spectrum, however, showed the presence of ca. 5% ortho-isomer.
2.7.18. **Attempted photolysis of para-bromo-t-butylbenzene:**

The possibility of any photochemical rearrangement of para-bromo-t-butylbenzene to its meta-isomer was checked by this experiment.

Para-bromo-t-butylbenzene (4.4 g, 0.02 mole) was dissolved in redistilled, dry carbon tetrachloride (500 ml). The mixture was irradiated, for sixteen hours, at room temperature.

Gas chromatography of the reaction mixture showed the absence of any meta-bromo-t-butylbenzene. Approximately 30-40% of para-bromo-t-butylbenzene was destroyed. The only product of decomposition was m-di-t-butylbenzene and molecular bromine.

2.7.19. **Photolysis of an equimolar mixture of meta- and para-t-butylbenzene for sixteen hours:**

A mixture of the two isomers (4.4 g, 0.02 mole each) was dissolved in redistilled, dry carbon tetrachloride (500 ml).

The mixture was irradiated, at room temperature, for sixteen hours. Gas chromatography of the mixture showed an equilibrium ratio of 70:30 of the meta- and the para-bromo-t-butylbenzene respectively. It also revealed that both of the reagents were partly destroyed by ultraviolet light.

No difference in the equilibrium ratio was found when this reaction was repeated in the presence of hydrogen bromide (generated by the addition of concentrated sulphuric acid to sodium bromide).
3. Discussion

This chapter is divided into two sections. In the first section some reactions of homolytic aromatic arylation involving polybromophenyl radicals are discussed. The second section consists of results of some of the liquid phase photobrominations of benzene derivatives.

3.1.1. Homolytic aromatic arylation:

The mechanism of the homolytic arylation of aromatic compounds has been extensively studied. The conclusion that the aryl radical \( R^* \) reacts with the aromatic substrate by an addition rather than an abstraction mechanism is confirmed by the repeated observations that the main binuclear products are of the type \( R.Ar \), compounds \( RR \) being formed only in very low yields and compounds \( ArAr \) not at all.

\[
R^* + \begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\end{array} \rightarrow \begin{array}{c}
\text{H} \\
\text{R} \\
\text{X} \\
\text{H} \\
\end{array} \rightarrow \begin{array}{c}
\text{H} \\
\text{R} \\
\text{X} \\
\text{H} \\
\end{array} \\
\text{R} \\
\text{H} \\
\text{R} \\
\text{X} \\
\end{array}
\]

This shows, therefore, that the formation of an arylcyclohexadienyl intermediate is a necessary postulate in the arylation processes. The absence of a significant isotope effect, found in the unreacted solvent isolated in reactions of benzoyl peroxide with deuterated aromatic substrates has established that the removal of the hydrogen atom is
not kinetically significant in the homolytic arylation reactions, which must therefore proceed through the formation of a $\sigma$-complex (a substituted cyclohexadienyl radical); this on oxidation gives biaryls$^{94}$.

3.1.2. **Homolytic aromatic reactions involving pentahalogenophenyl radicals:**

Arylation involving pentafluorophenyl radicals has been extensively studied not only in benzene but also in some simple derivatives, to give good yields of appropriate biaryls (XXVI) arising from the attack of

\[
\begin{align*}
\text{XXXI} & \\
X &= \text{H, F, Cl, Br, NO}_2 \text{ etc.}
\end{align*}
\]

the radical on the solvent.

The pentafluorophenyl radicals may be generated thermally from various sources, e.g. pentafluoro-benzoyl peroxide, phenylhydrazine or aniline, depending upon the reaction conditions.

Aromatic amines yield diazonium species which in the Gomberg reaction, are a source of aryl radicals and give biaryls:

\[
\text{ArNH}_2 \rightarrow \text{ArN}_2^+ \rightarrow \text{ArN=NOH} \rightarrow \text{Ar'H} \rightarrow \text{ArAr'}
\]

Shu Huang$^{58a}$ and Cadogan$^{58b}$ have shown that, in non-aqueous conditions, the same result occurs when pentyl nitrite in the aromatic substrate is used as the diazotosing medium. The intermediacy of phenyl radical as the active participant in these reactions was reported by Cadogan$^{118}$. This was also confirmed by other workers from the ability of phenyl radicals to abstract iodine from aryl iodides$^{119}$. An excellent correlation
of yield of aryl iodide from both aprotic diazotisation and aroyl peroxide decomposition has been demonstrated\(^{120}\). This supports not only the presence of phenyl radicals in the amine-pentyl nitrite system but confirms that these are the major arylating agents. Aryl cations do not display this abstracting ability, e.g. decomposition of benzenediazonium tetrafluoroborate under these conditions does not give any iodine abstraction product\(^{120}\).

By the application of the above diazotisation process to pentafluoroaniline-pentyl nitrite in benzene, Williams and co-workers\(^{59}\) have found good yield of 2,3,4,5,6-pentafluorobiphenyl. The mechanism for attack by pentafluorophenyl radicals is well established\(^{68}\). It is consistent with the result that the initially formed diazo-ether (XXVIIa) decomposes homolytically to give pentafluorophenyl radicals which undergo addition to the benzene ring to form an intermediate σ-complex (XXVIIb) dehydrogenation of this by the pentyloxy-radicals give pentafluorobiphenyl (XXVIIc).

Phenols, azo-compounds and amyl alcohol were formed as side-products. The whole mechanism is outlined in Scheme 15.

\[
\begin{align*}
C_6F_5\cdot NH_2 + O=NOPe & \rightarrow C_6F_5\cdot N=NOPe + H_2O \\
(XXVIIa) & \\
(XXVIIa) & \rightarrow C_6F_5\cdot + N_2 + PeO^- \\
C_6F_5\cdot + ArH & \rightarrow C_6F_5\cdot C_6H_5 + Pe.OH \\
(XXVIIb) & \\
(XXVIIb) + PeO^- & \rightarrow C_6F_5\cdot C_6H_5 + Pe.OH \\
(XXVIIc) & 
\end{align*}
\]

Scheme 15
Recently, reactions of pentachlorophenyl radicals, analogous to pentafluorophenyl radicals have been reported.\(^\text{60}\)

Arylation reactions of aromatic systems involving pentabromo-phenylation by homolytic routes have not been hitherto reported.

3.1.3. The polybromophenyl radicals:

The present work consists of the generation of polybromophenyl radicals, by thermal decomposition of the appropriate amines in benzene in the presence of pentyl nitrite. Application of this reaction, as indicated in the preceding section, to pentafluoro- and pentachloro-anilines has provided an effective source of the pentafluoro- and pentachloro-phenyl radicals, respectively. Substitution products from the arylation of aromatic compounds have been preferred in these systems, since high yields of pentafluoro- and pentachloro-biaryls have been observed.

Firstly, studies were made of the reactions of pentabromophenyl radicals in benzene. These were generated by the thermal decomposition of pentabromoaniline by pentyl nitrite in benzene at 80°. The reaction product after conventional purification methods gave a binuclear product, 2,3,4,5,6-pentabromobiphenyl, together with pentabromo- and hexabromo-benzene. Pentyl alcohol was also identified as one of the reaction products.

The participation of pentabromophenyl radicals is deduced from the formation of pentabromobiphenyl and pentabromobenzene.

Quantitative results of this reaction are given in Table 14 together with the corresponding figures for the reactions of pentafluoro- and pentachloro-phenyl radicals for comparison.

These results show a considerably lower yield of pentabromobiphenyl compared to its pentachloro- and pentafluoro- counterparts. This suggests
Table 14

Products (%) from arylation of benzene by penta-, fluoro, chloro- and bromo-phenyl radicals

<table>
<thead>
<tr>
<th>Source of C₆ₓ₅</th>
<th>C₆ₓ₅.Cₓ₆</th>
<th>C₆ₓ₅.Cₓ₆</th>
<th>Cₓ₆₆</th>
<th>Cₓ₆₆</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆ₓ₅·NH₂</td>
<td>58</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>59</td>
</tr>
<tr>
<td>C₆ₓ₅·NH₂</td>
<td>67</td>
<td>6</td>
<td>2</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>C₆ₓ₅·NH₂</td>
<td>15-20</td>
<td>29</td>
<td>30-35</td>
<td>this work</td>
<td></td>
</tr>
</tbody>
</table>

X = F, Cl or Br.

A lesser reactivity of the pentabromophenyl radical towards substitution; it participates more in abstraction than in substitution reactions. Thus the yield of pentabromobiphenyl is lower in the attack of the pentabromophenyl radical upon benzene, since the radicals generated do not readily attack the solvent to give biaryl but undergo side-reaction to give other products.

A possible mechanism for the thermal decomposition of pentabromoaniline - pentyl nitrite in benzene is set out in scheme 16. This is analogous to the mechanism, established by Williams and co-workers for similar reactions of pentafluoro- and pentachloro-anilines,

\[
C₆Br₅·NH₂ + PeONO \rightarrow C₆Br₅·N:NOPe + H₂O
\]

\[
(XXVIIIa)
\]

\[
(XXVIIIa) \rightarrow C₆Br₅· + N₂ + PeO·
\]

\[
C₆Br₅· + C₆H₆ \rightarrow C₆Br₅·H
\]

\[
(XXVIIIb)
\]

\[
(XXVIIIb) + PeO· \rightarrow C₆Br₅·C₆H₅ + PeOH
\]

Scheme 16
The formation of the diazo-ether (XXVIIa) and water is deduced from the cloudiness which appeared immediately upon the addition of pentyl nitrite to the solution. A gas, probably nitrogen, was also evolved for 10-15 minutes at room temperature, this was perhaps due to the initial generation of pentabromophenyl radicals. Evidence for the abstraction of hydrogen from (XXVIIIb) perhaps by pentyloxy-radicals, to give pentabromobiphenyl is obtained from the presence of pentyl alcohol in the reaction product.

The formation of the σ-complex (XXVIIIb) is the most likely route to pentabromobiphenyl since it is difficult to conceive of any other mechanism which does not involve this type of complex. Direct displacement of hydrogen from a benzene nucleus is not a favourable process on energetic grounds since it would be endothermic.

Support for the involvement of an arylcyclohexadienyl intermediate of the type (XXVIIIb) in homolytic arylation reactions is provided by some previous work. De Tar and Long\textsuperscript{121} isolated (XXIXb) and (XXIXc) in addition to biphenyl from the decomposition of benzoyl peroxide in benzene in dilute solution. These products arise from the dimerization and disproportionation
of phenylcyclohexadienyl intermediate (XXIXa).

The formation of (XXVIIIb) as an intermediate is thus explained on this basis.

The last sequence in Scheme 16 involves a bimolecular reaction between two radical species and may therefore be fast. The formation (XXVIIIb) is likely to be the rate-limiting step on energetic considerations. Evidence for this is also obtained by the absence of a significant primary isotope effect from the free radical arylation of benzene-d as well as benzene-benzene-d₆ mixtures, at 78°C with certain peroxides. In view of the formation of side-products, it may well be that this reaction is more complex than is indicated in Scheme 16. Quantitative results in this reaction are uncertain since about 15% of the amine converted could not be accounted for. Gas chromatography could not be used owing to the high boiling points of the products.

No improvement in the yield of pentabromobiphenyl was found when freshly prepared pentyl nitrite was used. This shows that the presence of traces of oxides of nitrogen, aldehydes etc., did not affect the reaction.

From Table 14 it is evident that with the change in halogen from F to Cl and then to Br the yield of the biaryl, arising from the attack of the appropriately substituted phenyl radical on benzene, changes. One possible reason for this is a steric effect which is instrumental in modifying the reactivities of these radicals.

The presence of bromine atoms at the position ortho- to the radical centre has been found to affect the relative rates and yields, compared to benzene, of phenylation reactions. Similar effects were also noticed in phenylation reactions of suitably chloro-substituted phenyl radicals.
Table 15 shows that the incidence of hydrogen abstraction to produce hydrocarbon $\text{C}_6\text{H}_y\text{Cl}_{6-y}$ increases with the number of chlorine atoms, particularly at the site ortho- to the radical centre.

Table 15

<table>
<thead>
<tr>
<th>Radical</th>
<th>$\text{C}_6\text{H}<em>y\text{Cl}</em>{6-y}$</th>
<th>Biaryls</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2,4\text{-Cl}_2\text{-C}_6\text{H}_3^-$</td>
<td>2</td>
<td>98</td>
</tr>
<tr>
<td>$2,6\text{-Cl}_2\text{-C}_6\text{H}_3^-$</td>
<td>38</td>
<td>62</td>
</tr>
<tr>
<td>$2,4,6\text{-Cl}_3\text{-C}_6\text{H}_2^-$</td>
<td>76</td>
<td>24</td>
</tr>
</tbody>
</table>

Therefore, as expected, the presence of five bromine atoms in the pentabromophenyl radical have been found to reduce its reactivity considerably in the pentabromoaniline-benzene-pentyl nitrite reaction. This is evident from the lower yield of the binuclear product - 2,3,4,5,6-pentabromobiphenyl.

Additional support for this was obtained in the present work, by examining the yields of biaryls arising from the attack of 2-bromo- and 2,4,6-tribromo-phenyl radicals on benzene. These radicals were generated from the reaction of their respective amines with pentyl nitrite in benzene at 80$^\circ$.

The relative amounts of biaryls and abstraction products formed, in the polybromophenylation of benzene, are summarised in Table 16.
Table 16
Relative yields (%) of products derived from the reaction of polybromophenyl radicals in benzene

<table>
<thead>
<tr>
<th>Radicals</th>
<th>C\textsubscript{6}H\textsubscript{6} Br\textsubscript{6-y}</th>
<th>Biaryls</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Br-C\textsubscript{6}H\textsubscript{4}</td>
<td>20</td>
<td>58</td>
</tr>
<tr>
<td>2,4,6-Br\textsubscript{3}-C\textsubscript{6}H\textsubscript{2}</td>
<td>29</td>
<td>40-48</td>
</tr>
<tr>
<td>C\textsubscript{6}Br\textsubscript{5} *</td>
<td>29</td>
<td>15-20</td>
</tr>
</tbody>
</table>

* Also formed C\textsubscript{6}Br\textsubscript{6} (34%)

The yield of the biaryls is lowest for the most fully substituted phenyl radicals and highest for the least substituted phenyl radicals.

The presence of two bromine atoms, ortho- to the radical centre, in the tribromophenyl radical apparently offers some resistance, also seen in the pentabromophenyl radicals, to the formation of the \( \sigma \)-complex (XXX) leading to nuclear substitution, thus the tribromobenzene – an abstraction product of the tribromophenyl radical is also formed. However, the yield of tribromobiphenyl is higher than that of pentabromobiphenyl.
This may be because hexabromobenzene accompany as an additional side-product with the latter.

It can be seen from Table 16 that the yield of bromo-biaryls is highest with the less substituted 2-bromophenyl radicals. This apparently offers less resistance, compared to the other two, and gives more nuclear substitution than abstraction products.

3.1.4. The origin of pentabromo- and hexabromo-benzene in the pentabromoaniline-benzene-pentyl nitrite reaction:

The presence of substituent in an aryl radical is expected to influence the reactivity of the radical also by altering the distribution of electron density and thus imposing upon it some measure of electrophilic character, according to whether the substituent is electron-withdrawing or electron-repelling, and by exerting steric effects.

As is evident from Table 14 the yield of pentabromobenzene – a product arising from an abstraction reaction of the pentabromophenyl radical – is higher than that in the corresponding reaction giving pentachlorobenzene. On account of the more bulky structure and less electrophilic power, compared with its pentafluoro- and pentachloro-counterpart the pentabromophenyl radical participates in the facile hydrogen abstraction rather than in nuclear substitution process.

The formation of pentabromobenzene could be explained only by the presence of some hydrogen-donating species. There could be three such possibilities eq. (42), (43) and (44).
The pentyl fragment of the diazo-ether (XXVIIIa) serves as a hydrogen-donor since the hydrogen is very close to the carbon bonded to nitrogen. The resonance stabilisation of the pentyl fragment may, since the unpaired electron is on a secondary carbon atom, help the process.

The abstraction of hydrogen from the α-complex by pentabromophenyl radical, eq.(43), may occur very reluctantly, since the relative yields of pentabromobiphenyl and pentabromobenzene do not reflect such a process. The molar ratio of these two compounds should have been 1:1 had only this process taken place. In contrast to this the molar ratio was 3:7 which makes this process, at best, a minor contributor.

Both water and pentyl alcohol being reactive towards free-radicals, may act as hydrogen-donating species towards pentabromophenyl radicals, eq.(44). But, compared with the participation of the pentyl fragment of (XXVIIIa) these two species (water and pentyl alcohol) probably make less contribution because in the former case the abstractable hydrogen is in the vicinity of the carbon atom under attack. Moreover, the less reactive nature of the pentabromophenyl radical makes attack of water or pentyl alcohol less likely than abstracting hydrogen from the pentyl fragment, eq.(42).
The origin of hexabromobenzene in the same reaction may be explained differently. The products of the reaction with pentabromoaniline-benzene-pentyl nitrite were found by the conventional tests to include bromide ions. This suggests that some ionic reaction takes place by which the bromide ions were displaced from pentabromoaniline. The most likely species for this purpose is water which is formed in the first step of the reaction between the amine and the pentyl nitrite.

\[
\text{C}_6\text{Br}_5\text{NH}_2 + \text{PeONO} \rightarrow \text{C}_6\text{Br}_5\text{N}=\text{NOPe} + \text{H}_2\text{O}
\]

The presence of water was also confirmed by the fact that the solution turned cloudy immediately on addition of pentyl nitrite. Tatlow and co-workers have also found that pentafluoroaniline cannot be diazotised successfully in predominantly aqueous media. The diazonium ion which first results undergoes nucleophilic attack to give hydroxytetrafluorophenyl diazonium ion by the displacement of fluoride ions.

Therefore, it is assumed that the formation of water in the pentabromoaniline-pentyl nitrite reaction brings about similar nucleophilic displacement to give bromide ions:

\[
\begin{align*}
\text{C}_6\text{Br}_5\text{N}_2^+ + \text{H}_2\text{O} & \rightarrow \text{C}_6\text{Br}_4\text{OHN}_2^+ + \text{Br}^- \\
\text{C}_6\text{Br}_5\text{N}_2^+ + \text{Br}^- & \rightarrow \text{C}_6\text{Br}_6 + \text{N}_2
\end{align*}
\]

It should also be noted that, in both cases, the nucleophilic attack to form bromide ion need not necessarily involve a diazonium ionic species. The azo-linkage itself (\(-\text{N}:\text{N}\)-), like the nitroso group (\(-\text{N}:\text{O}\)) is an effective activating substituent for heterolytic nucleophilic displacement of halogens at sites ortho- and para- to it in a benzene ring; although not as effective as the diazonium group (\(-\text{N}_2^+\)) in this respect, it is still
necessary to allow that activation from the azo-group in ArN=NOR may be sufficient to cause the nucleophilic displacement in a pentabromophenyl reagent.

3.1.5. Penta-bromo-, chloro- and fluoro-phenyl radicals- a comparison:

The results in Table 14 shows that the yields of the biaryls has decreased considerably when fluorine or chlorine are replaced by bromine as substituent in the phenyl radicals. This also reflects a measure of the reactivity of the pentabromophenyl radical relative to its fluoro- and chloro- counterparts. These observations are not unexpected. The low yield of the biaryl with pentabromophenyl radicals is possibly a result of the steric and polar effects of the five bromine atoms present.

The participation of the steric effects, mostly due to the two bromine atoms ortho- to the radical centre, is also observed in the reaction using 2,4,6-,tribromophenyl radicals. The approach of the tri- or penta- bromophenyl radical to the benzene nucleus, is thus hindered to some extent, hence the hydrogen abstraction products, namely tribromobenzene or pentabromobenzene, are formed. Such effects were also noted with polychlorophenyl radicals.

The alteration of the reactivity of the pentabromophenyl radical due to the polar effect is also one of the possible reasons for a low yield of pentabromobiaryl. Bromine, being less electron-withdrawing than fluorine or chlorine, makes the pentabromophenyl radical less electrophilic in its attack on the benzene nucleus. Moreover, the formation of hexabromobenzene as one side-product in the reaction using pentabromophenyl radicals also decreases the extent of aromatic substitution. The latter process is helped by the presence of two bromine atoms ortho-
to the bromine (a) which activates this bromine towards nucleophilic

\[
\begin{align*}
\text{Br} & \quad \text{Br} & \\
\text{Br} & \quad \text{Br} & \\
\text{Br} & \quad \text{Br} & \\
\text{Br} & \quad \text{Br} & \\
\end{align*}
\]

attack by water, thus displacing bromide ions which ultimately form hexabromobenzene.

3.1.6. Synthesis of 2,3,4,5,6-pentabromobiphenyl by the Ullmann reaction:

The Ullmann reaction has remained one possible route for the arylation of aromatic compounds. It is generally believed to proceed through an aryl copper intermediate, reaction of which with the iodoaromatic compound, gives biaryl

\[
\begin{align*}
\text{ArI} + 2\text{Cu} & \rightarrow \text{ArCu} + \text{CuI} \\
\text{ArCu} + \text{ArI} & \rightarrow \text{ArAr} + \text{CuI}
\end{align*}
\]

One of the precursors for the synthesis of 2,3,4,5,6-pentabromobiphenyl, by this route, was pentabromoiodobenzene. This was successfully prepared, in the present work, from the diazonium ion as follows:

\[
\begin{align*}
\text{C}_6\text{Br}_5\text{N}_2^+ + \text{I}^- & \rightarrow \text{C}_6\text{Br}_5\cdot\text{I} + \text{N}_2
\end{align*}
\]

Reaction of pentabromoiodobenzene with iodosobenzene in the presence of activated copper bronze gave 2,3,4,5,6-pentabromobiphenyl, although it cannot be purified fully. Its presence was confirmed from mass spectrometry. Therefore this method of synthesis for the above biaryl is not very successful.
3.1.7. Summary of polybromophenylation reactions

The pentabromophenyl radicals were generated by a diazotisation process in benzene with pentyl nitrite, and their reactions were studied. It has been found that the pentabromophenyl radical, undergoes more hydrogen abstraction than aromatic substitution reaction. This effect is different from that found with pentafluoro- and pentachlorophenyl radicals where more substitution and less hydrogen abstraction is found. Thus the pentabromophenyl radical is found to be less reactive compared with its pentafluoro- and pentachloro- counterparts. Apparently this property is due to the different steric and polar nature of bromine compared with fluorine and chlorine atoms. It has also been found that less extensively bromo-substituted phenyl radicals undergo more aromatic substitution and less abstraction compared with more substituted one.

3.2.1. Photochemical bromination reactions

In this section results of some liquid phase photochemical bromination reactions of benzene derivatives are discussed. These reactions were performed at room temperature or at ca. 50°.

Photochemical substitution reactions using molecular bromine as source of bromine atoms, has been an attractive method of bromination. A variety of work has been done on aliphatic substrates, whereas in benzene derivatives it is limited to certain reactions, possibly because of the greater ease with which hydrogen is replaced by bromine in the former case. The subject has been reviewed by Thaler.  

3.2.2. Photobromination of benzene

Benzene and bromine react photochemically at room temperature to produce hexabromocyclohexane and minor quantities of bromobenzene.
The stereochemistry of the major isomers has been determined, although the exact proportion in which they are formed is not given.\textsuperscript{127}

An approximate product ratio shows that the \(\alpha\)-isomer (XXXIIa) predominates over the \(\beta\)-isomer (XXXIIb) and the \(\gamma\)-isomer (XXXIIc).

<table>
<thead>
<tr>
<th>No.</th>
<th>Isomer</th>
<th>Position of bromine atoms</th>
<th>m.p.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(XXXIIa)</td>
<td>aaeeee</td>
<td>212(^\circ)</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>(XXXIIa)</td>
<td>aaeeee</td>
<td>217(^\circ)*</td>
<td>127</td>
<td></td>
</tr>
<tr>
<td>(XXXIIb)</td>
<td>eeeeee</td>
<td>252(^\circ)</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>(XXXIIc)</td>
<td>aaeeee</td>
<td>170(^\circ)</td>
<td>127</td>
<td></td>
</tr>
</tbody>
</table>

* After repeated recrystallisation.
In the present work, bromination of benzene was performed at room temperature and at ca. 50°, separately. At ca. 50° an increase in the amount of substitution at the expense of addition was found. The relative proportion of the products from the two reactions are given in Table 17.

Table 17
Relative proportion (%) of products from photobromination of benzene at different temperatures.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>C\textsubscript{6}H\textsubscript{6}Br\textsubscript{6}</th>
<th>C\textsubscript{6}H\textsubscript{5}Br</th>
<th>C\textsubscript{6}H\textsubscript{4}Br\textsubscript{2}</th>
<th>C\textsubscript{6}H\textsubscript{3}Br\textsubscript{3}</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room temperature</td>
<td>78</td>
<td>5</td>
<td>ca. 3</td>
<td>-</td>
<td>this work</td>
</tr>
<tr>
<td>50 - 55°</td>
<td>45-50</td>
<td>15-17</td>
<td>18.-20</td>
<td>ca. 2-3</td>
<td>this work</td>
</tr>
</tbody>
</table>

* Average values

It can be seen from this table that with a rise in temperature the yield of the addition product, benzene hexabromide, is decreased. This might arise from the decomposition of this adduct at the higher temperature.

The formation of the products mentioned in Table 17 may be discussed in terms of two possible mechanistic routes for these reactions,

(a) a direct substitution reaction,

(b) an addition-elimination reaction.

(a) Substitution involving the formation of phenyl radicals may proceed according to the mechanism suggested by some earlier workers \(89,90\), (c.f. page 70). However, the abstraction of hydrogen from benzene to give phenyl radical is energetically unfavourable since the carbon-hydrogen bond in benzene is strong (\(\sim 102 \text{ kcal mole}^{-1}\)) thus this process is not greatly favoured.
(b) An addition-elimination mechanism involving the participation of cyclohexadienyl type intermediates may be a possible route for the formation of bromo-arenes. The mechanism is outlined in Scheme 17.
The intermediate radical (XXXIIia) could react with bromine in two different ways, (a) by a direct abstraction to give bromobenzene (XXXIIIib) and hydrogen bromide, (b) by further addition of bromine to give the dibromide (XXXIVa) which in turn may either lose hydrogen bromide at ca. 50° to give (XXXIIIib) or undergo subsequent addition to bromine through several stages to give finally hexabromocyclohexane (C₆H₆Br₆).

Such a mechanistic route may be used to account for the relatively higher proportion of addition compared with substitution products at lower temperatures, and for the higher proportion of substitution at the expense of addition products at high temperature (in the present case it is ca. 50°).

The step (XXXIIia) → (XXXIIIib) deserves some considerations on thermochemical grounds, although it will be chemically (not kinetically) indistinguishable from the rest of the reaction. An approximate thermochemical calculation can be made as reaction (45) and (46).

\[
\text{HBr} + \text{Br}^- + \text{Br}^+ \rightarrow \text{C-H} + \text{H-Br} + \text{Br}^* \quad \Delta H = +23 \text{ kcal mole}^{-1}
\]

\[
\sim 100 - 36 = 64 \quad (\text{C-H})
\]

\[
\text{HBr} + \text{Br}^* \text{ or } \text{Br}_2^* \rightarrow \text{C-H} + \text{H-Br} + \text{Br}^* \quad \Delta H = -23 \text{ kcal mole}^{-1}
\]

\[
\sim 100 - 36 = 64 \quad (\text{C-H})
\]

\[
\sim \Delta H = -23 \text{ kcal mole}^{-1}
\]
For direct abstraction, a C\textsubscript{6}H\textsubscript{5}-H bond must be broken, needing $\sim 100 \text{ kcal mole}^{-1}$. In reaction (45) and (46) however the C-H bond involved should be much weaker because, when it is broken, the aromatic character of the ring is restored. The dissociation energy of this bond can be estimated as that of a normal aliphatic C-H bond ($\sim 100 \text{ kcal mol}^{-1}$) less the resonance or aromatisation energy of the benzene ring ($\sim 36 \text{ kcal mole}^{-1}$)\textsuperscript{128} so that in this case it is $\sim 64 \text{ kcal mole}^{-1}$. Therefore, on the basis of this calculation, reaction (45) is endothermic by $\sim 23 \text{ kcal mole}^{-1}$, and hence, this will be less favoured over reaction (46) where the abstraction of hydrogen is performed by Br\textsuperscript{*} (or Br\textsuperscript{2*}) so that the formation of bromobenzene by this step is exothermic by $\sim 23 \text{ kcal mole}^{-1}$, and thermodynamically likely. The energy difference calculated for reaction (45) may be supplied photochemically, thus bromine molecules which have absorbed energy equivalent to at least 23 kcal mole\textsuperscript{-1} (Br\textsuperscript{*}2) may, by releasing this energy in the reaction, convert an endothermic process to a chemically probable one.

It can be seen, further, from Scheme 17, that the dibromide (XXXIVa) formed is very reactive towards further addition with bromine to give the tetrabromide (XXXIVb). It is quite possible, that (XXXIVa) may lose hydrogen bromide to give bromobenzene but this process may be less favoured over further addition, however, it can also be feasible if (XXXIVa) reverts to (XXXIIIa) by the fission of C-Br bond due to the ultraviolet light.

The step (XXXIVa) $\rightarrow$ (XXXIVb) which involves the formation of a tetrabromide from a dibromide seems to be a convenient route on account of the higher thermodynamic stability of tetrabromides compared with dibromides. (Such tetrahalo-adducts of benzene were actually isolated from a photobromination reaction of benzene using iodine as catalyst).\textsuperscript{129c}
The formation of isomeric dibromobenzenes, as shown in Scheme 17, may involve (a) further attack on bromobenzene to give unstable adducts (XXXVa) or (XXXVb) which lose hydrogen bromide to give dibromobenzenes and (b) formation of (XXXIVb) and then the loss of hydrogen bromide to give dibromobenzene.

Attack on bromobenzene by bromine atoms to give (XXXVa) or (XXXVb) may not be a preferred mode of reaction since bromobenzene is deactivated towards further attack of an electrophilic radical like Br•. Thus the participation of step (XXXVa) \(\rightarrow\) (XXXVIa) or (XXXVb) \(\rightarrow\) (XXXVIb) may be considered, at best, a minor contribution to the isomeric dibromobenzenes.

The formation of dibromobenzenes via the loss of hydrogen bromide from the tetrabromo-adduct (XXXIVb) seems to be a reasonable mechanism; such precursors of dibromobenzenes are also precursors of benzene hexabromide, the major addition product.

The loss of hydrogen bromide to give substitution products at higher temperature is not an unexpected observation. Besides, this process bears certain analogies to the photochemical bromination of naphthalene, and hence, may be preferred over addition reaction. Di- and tetra-bromides of naphthalene lose hydrogen bromide on heating and give mono- and di-bromonaphthalenes respectively.\(^9\) Therefore, on this basis, the formation of dibromobenzenes, through the loss of hydrogen bromide, may be expected to take place preferentially at higher temperature (ca. 50° in the present case). This may explain why only a very small amount of dibromobenzene (ca. 1 x 10⁻⁴ mol) was formed in the photobromination of benzene at room temperature.

The formation of tribromobenzene(s) may involve attack on any of the three isomeric dibromobenzenes to form addition products (XXXVIc).
These lose hydrogen bromide to give isomeric tribromobenzenes. Since dibromobenzenes are further deactivated towards attack by bromine the yield of tribromobenzenes formed by direct substitution is very low.

Further support for an addition-elimination mechanism is obtained from the photochemical decomposition reaction discussed in the next section.

3.2.3. Photochemical decomposition of benzene hexabromide (BHB)

Support for the involvement of the addition-elimination mechanism, proposed in Scheme 17 for the photobromination of benzene at ca. 50°, is obtained from the light-induced decomposition of BHB.

Pure benzene hexabromide, dissolved in toluene, was decomposed photochemically at ca. 50°. The reaction product was analysed for bromo-substituted benzenes formed via the elimination of hydrogen bromide from BHB.

The reaction product was found to contain, besides benzyl bromide and some polybrominated compounds, bromobenzene, the isomeric dibromobenzenes and minor quantities of tribromobenzene(s). The isomer distribution ratio of dibromobenzenes was found to be very nearly the same as that observed in the photobromination of benzene.

In an analogous reaction, BHB was also decomposed in benzene. The isomer distribution ratio of dibromobenzenes from the three different reactions is shown in Table 18.

Table 18

<table>
<thead>
<tr>
<th>Process</th>
<th>Dibromobenzene (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ortho-</td>
</tr>
<tr>
<td>Photobromination of benzene at 50-55°</td>
<td>19</td>
</tr>
<tr>
<td>Decomposition of BHB in toluene</td>
<td>20</td>
</tr>
<tr>
<td>Decomposition of BHB in benzene</td>
<td>19</td>
</tr>
</tbody>
</table>
In toluene the products of photochemical decomposition of BHB must have arisen from the elimination of hydrogen bromide and molecular bromine in different stages. Although the yields of bromo-, dibromo- and tribromo- benzenes were much lower than in benzene, possibly due to decomposition of the products by ultraviolet light, the isomer distribution ratio of dibromobenzenes is significant.

The stereochemistry of α-benzene hexabromide may be deduced from considering the reaction of alcoholic potassium hydroxide with benzene hexahalides (C₆H₆X₆). Base-catalysed dehydrobromination of α-benzene hexabromide give predominantly 1,2,4-tribromobenzene. Orloff and Kolka suggested, on the basis of a detailed survey of the mechanism of alkaline dehydrochlorination of different isomers of benzene hexachloride, that the possible mode of elimination follows the reactivity sequence:

\[ \text{trans-1,2} > \text{trans-1,4} > \text{cis-1,2} > \text{cis-1,4} \]

α-Benzene hexahalide has the halogen positions a a e e e e and therefore has a pair of trans-1,2- oriented hydrogen and halogen atoms to cause the formation predominantly of 1,2,4-trihalogenobenzene on alkaline dehydrohalogenation eq.(47)

\[ \text{X(α)} \quad \text{X} \quad \text{X} \quad \text{KOH} \rightarrow \quad \text{X} \quad \text{X} \quad \text{X} \quad +3\text{HX} \quad \ldots \ldots \quad (47) \]

α-Benzene hexabromide, used in the present work of photochemical decomposition in organic solvents, also has the conformation a a e e e e (position of bromines). The possibility of an analogous (heterolytic)
mode of photo-dehydrobromination is therefore ruled out since an entirely different product distribution was found in the present system, i.e. more dibromobenzenes and less tribromobenzenes.

Thus for the reasons mentioned above a mechanism different from the alkaline dehydrobromination of benzene hexabromide seems more close to represent the formation of bromo-arenes. Scheme 18 interprets the photo-induced decomposition of BHB.

Scheme 18 Probable pathways of the decomposition of benzene hexabromide
Support for the elimination of two axial bromine atoms from (XXXVIIa) leading to the tetrabromo-adduct (XXXVIIb) is provided by the fact that axial halogen atoms are known to be in a less stable conformation than the equatorial halogen atoms. Therefore, on absorption of ultraviolet radiation by the molecule the two axial bromine atoms split off homolytically thus producing (XXXVIIb) in which all bromine and hydrogen substituents are in a cis-relationship, since all four bromine atoms are trans- to each other (e e e e). Thus only the elimination of hydrogen and bromine cis- to each other seems possible. 1,2-Elimination leads to (XXXIX) which ultimately gives m- or p-dibromobenzene.

1,4-Elimination from (XXXVIIb), which would be slow, gives (XXXVIII). The intermediates (XXXIX) and (XXXVIII) are of similar thermodynamic stability. Further dehydrobromination from (XXXVIII) leads to o- or p-dibromobenzene. Tribromobenzenes are possibly formed as a result of consecutive bromination and dehydrobromination of dibromobenzenes, but the yield is too low to allow interpretation of this process.

3.2.4. Photobromination of biphenyl

Free radical halogenation of biphenyl has been studied by Kooyman and co-workers, although less extensively. However, electrophilic halogenation has been investigated in a more quantitative way in recent years. This occurs more rapidly in biphenyl than in benzene and mainly at the para-position with a smaller proportion of ortho-attack and very little, if any, of the meta-isomer is formed. The electron-withdrawing effect (-I) of the phenyl substituent is considered to have a deactivating influence on the meta-position.

The present work involves a study of the liquid phase photobromination of biphenyl with molecular bromine in different solvents.
3.2.5. In carbon-tetrachloride

The photobromination of biphenyl at ca. 50° was performed in carbon tetrachloride since this solvent is reasonably inert under the reaction conditions. Monobromobiphenyls were essentially found to be the main reaction product. Minor quantities (3-4%) of a substance whose retention (g.l.c.) was the same as that ascribed to 4,4'-dibromobiphenyl, were also found to be present.

An important feature of this reaction is that substitution predominates over addition (60-65% based on 24% conversion of bromine after twenty hours of illumination).

Isomer distribution ratios of monobromobiphenyls are given in Table 19. For comparison similar ratios for electrophilic bromination of biphenyl is also given.

Table 19

<table>
<thead>
<tr>
<th>Process</th>
<th>Monobromobiphenyl (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ortho-</td>
</tr>
<tr>
<td>Photochemical bromination of biphenyl in carbon tetrachloride, at 50-55° (this)</td>
<td>24</td>
</tr>
<tr>
<td>Bromination of biphenyl in 50% aqueous acetic acid</td>
<td></td>
</tr>
<tr>
<td>Acid catalysed bromination of biphenyl by hypobromous acid in presence of 50% aqueous dioxane</td>
<td>56.8</td>
</tr>
</tbody>
</table>

The isomer distribution obtained by photochemical bromination is markedly different from that found in electrophilic bromination. A different effective species must be operating in the photochemical process as a
significant amount of substitution takes place at the meta-position which is usually deactivated in heterolytic reactions.

Support for a mechanism other than a purely heterolytic process is also obtained from the results of certain gas-phase reactions of biphenyl reported by Kooyman and co-workers which give up to 40% 3-chlorobiphenyl. Liquid-phase chlorination of biphenyl, in carbon tetrachloride solution, initiated by sun-light gives an addition product hexachlorocyclohexyl benzene \( (C_6H_5.C_6H_5.C_6Cl_4) \). The formation of a tetrachloro-addition product \( (C_6H_5.C_6H_5Cl_4) \) is also reported elsewhere.

The exact mechanism by which isomeric monobromobiphenyls were formed, from photochemical bromination of biphenyl in carbon tetrachloride, could not be decided, but evidence has been found which points to the incidence of an addition-elimination mechanism (see below).

The formation of addition products in the photobromination reaction of biphenyl is not unexpected, for the following reasons.

(a) Up to 30-34% of the consumed bromine could not be accounted for.

(b) Liquid-phase chlorination of biphenyl (sun-light) at low temperature give only addition product.

(c) Liquid-phase chlorination and bromination (light) of benzene also give addition products.

The presence of an addition product arising from the photobromination of biphenyl in carbon tetrachloride is inferred from a benzoyl peroxide induced thermal decomposition of the reaction product in toluene. The presence of benzyl bromide was taken as an indication of the homolytic decomposition of some sort of addition product (it must be mentioned here that halogen addition products of benzene for instance, benzene hexabromide, have been found to decompose thermally only in presence of traces of benzoyl peroxide).
Besides this, the formation of silver bromide precipitated by the action of alcoholic silver nitrate on the reaction product also strengthens the idea of the presence of an addition product (under exactly similar conditions, benzene hexabromide gave precipitate of silver bromide by warming with alcoholic silver nitrate although bromobiphenyls did not).

After finding an indication for the presence of some sort of addition, an attempt was made to investigate the structure of this product. For this purpose, the reaction product of the photobromination of biphenyl, was treated with alkali and the product was analysed for 2,4-dibromo- and 2,4,6-tribromo-biphenyl arising from (XLII) and (XL), respectively. (Alcoholic dehydrohalogenation of benzene hexahalides and tetrahalides have been reported to give trihalogenobenzenes and dihalogenobenzenes, respectively).\textsuperscript{129a,b}

$$\begin{align*}
\text{(XL)} & \quad \text{alk. KOH} \quad \text{(XLI)} \\
\text{(XLII)} & \quad \text{alk. KOH} \quad \text{(XLIII)}
\end{align*}$$
Neither the tribromobiphenyl nor more than a small amount of dibromobiphenyls was detected in the gas chromatography. The dibromobiphenyl could have been present before the reaction, since about 3-4% of 4,4'-dibromobiphenyl was formed by the photobromination of biphenyl. Moreover, owing to its long retention time (g.l.c.) this could not be distinguished from (XLIII) with certainty.

The phenyl group is a bulky group so that a hexabromocyclohexylbenzene (LX) is probably formed only reluctantly, and decomposes more readily than does hexabromocyclohexane \( \text{C}_6\text{H}_6\text{Br}_6 \) photochemically at \( \text{ca.} \ 50^\circ \). Therefore the formation of 2,4,6-tribromobiphenyl is not likely. Scheme 19a shows the probable pathways to the substitution and the addition products from the photobromination of biphenyl.

Great reactivity is to be expected in the first step, i.e. the formation of the intermediate (XLIV) or its ortho-analogue, since aryl group will stabilise these more strongly than the intermediate where bromine is attached to the meta-position. The driving force for the elimination of hydrogen from (XLIV) may be increased not only due to the electron-withdrawing effect of the phenyl group but also because of the aromatic stability gained by the formation of (XLV). It is not clearly established here that the only route to say, 4-bromobiphenyl is (XLIV) \( \rightarrow \) (XLV) (see page 144). Isomeric monobromobiphenyls may also have arisen through the intermediate formation of dihydro-dibromobiphenyl e.g. (XLVI) by the loss of hydrogen bromide. The possibility of the formation of some type of addition product e.g. (XLVII) cannot be ruled out on account of the reasons mentioned on page 151, although its stereochemistry could not be determined here.
Scheme 19a Probable pathways to the substitution and the addition products from photobromination of biphenyl
Small quantities of (XLIX) probably arise from the bromination of say, (XLV) in which a bromine radical is likely to enter the unsubstituted ring as this would be apparently less deactivated than the other ring containing a bromine substituent. However, due to some experimental difficulties (g.l.c.) the two dibromo-isomers (XLVIII) and (XLIX) were not clearly distinguished.

3.2.6. Competitive reactions:

(a) Photobromination of a mixture of biphenyl (one mole) and benzene (5.5 mole)

The directive effects of a substituent, attached to the benzene ring, are expressed by the partial rate factors, $F_o$, $F_m$ and $F_p$, representing the rates of attack at a single position ortho-, meta- and para- to the substituent, respectively, relative to the rate of attack at a single position in benzene.

In the present work, an attempt was made to determine the relative rate and the partial rate factor for photobromination of biphenyl by a competition reaction in benzene solution. The following results have been observed.

(a) The overall yield of the bromo-arenes were less than the total consumption of molecular bromine. Of the total bromine consumed 30% could not be accounted for. This suggests that the bromine atoms find alternative destinies other than bromo-arenes.

(b) The relative rates and partial rate factors are as under:

<table>
<thead>
<tr>
<th>Relative rate</th>
<th>Partial rate factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{Ph,Ph}{Ph.H}$</td>
<td>$F_o$ $F_m$ $F_p$</td>
</tr>
<tr>
<td>8.17</td>
<td>3.88 2.38 17.31</td>
</tr>
</tbody>
</table>
The limitations of these figures, and the validity of the partial rate factors derived under these conditions, are considered later (p.160); it is unlikely that they may allow a simple interpretation.

(b) Bromination of a mixture of biphenyl (0.75 mole) and bromobenzene (4.12 mole)

The relative rates and the partial rate factors from bromination of biphenyl and bromobenzene, were converted into the relative rate with respect to benzene as standard, by making the following conversions:

\[ \frac{\text{PhX}}{\text{PhH}} K = \frac{\text{PhX}}{\text{PhY}} K \cdot \frac{\text{PhX}}{\text{PhH}} K \]

where PhX and PhY represents the substituted benzenes.

Of the total substitution product accounted for in this reaction, 91% monobromobiphenyl and 9% dibromobenzenes were formed despite a molar ratio 0.75 : 4.12 of biphenyl and bromobenzene, respectively.

The derived relative rates and the partial rate factors for bromobenzene are as under:

<table>
<thead>
<tr>
<th>Relative rate</th>
<th>Partial rate factors*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhBr (\text{K})</td>
<td>(F_{o-}) 0.33 (F_{m-}) 0.061 (F_{p-}) 0.157</td>
</tr>
</tbody>
</table>

* Partial rate factors for the meta-position is calculated by assuming 35% substitution at this position. This is an average of the result of photobromination reported elsewhere.
The result shows a decrease in the rate of bromination of bromobenzene which is apparently deactivated by the bromo-substituent.

It can also be seen from the relative rate of bromination of biphenyl with respect to benzene (section (a)) that as expected biphenyl is more reactive than benzene. The results suggest that the order of reactivity to bromine atoms is in the following sequence,

\[ \text{Biphenyl} > \text{Benzene} > \text{Bromobenzene} \]

This reflects the electrophilic behaviour of the bromine atom in this free-radical process.

(c) Discussion of the partial rate factors

There could be two possible lines of thought which could be used to discuss the experimental observations of section (a) and (b). The first is to discuss the results of the apparent partial rate factors of biphenyl in terms of the relative stabilities of the intermediates (L), (LI) and (LII) and compare the relative rates of reactions of biphenyl. The second is to discuss the validity of these factors because the photobromination reaction of biphenyl and benzene also give some addition products. This makes the results complicated.

The resonance contributing structures of ortho-, meta- and para-attack for phenyl-bromocyclohexadienyl intermediate are shown in Scheme 19b.
Scheme 19b
It can be seen from the canonical structures contributing to (L), (LI) and (LII) that ortho- and para-substitution are more favoured than meta-substitution. Partial rate factors for biphenyl (p. 155) also reveal a greater reactivity at the ortho- and para-positions compared with the meta-position, although the effect is not so pronounced as in ionic reactions.

The isomer distribution ratio is clearly different from that found in ionic bromination of biphenyl. The meta-isomer is also formed to a significant extent. This clearly shows that free-radical reactions are less influenced by the polar effects than their heterolytic counterparts. The overall predominance of the para-isomer is possibly due to steric reasons which favour this position over the ortho-position since both the bromine and the phenyl groups are bulky.

A comparison of the experimentally determined relative rates of reactions of biphenyl in the present work, with those derived in other conditions, as shown in Table 20, reveals that in the photobromination,

<table>
<thead>
<tr>
<th>Process</th>
<th>PhPh $K$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photobromination of biphenyl</td>
<td>8.17</td>
<td>this work</td>
</tr>
<tr>
<td>Bromination of biphenyl in 50% aqueous acetic acid</td>
<td>$3.94 \times 10^3$</td>
<td>133</td>
</tr>
<tr>
<td>Homolytic phenylation of biphenyl with benzoyl peroxide</td>
<td>2.94</td>
<td>134</td>
</tr>
</tbody>
</table>

the biphenyl molecules are under attack by free radical species, i.e. bromine atoms which are electrophilic in nature. Thus the relative rates in Table 20 show that biphenyl is more reactive towards bromine than towards
phenyl radicals which are known to have a neutral or a slightly nucleophilic character\textsuperscript{51a}.

The discussion of the validity of partial rate factors of biphenyl, in the photobromination reaction is a little complicated since the mechanism by which the isomeric monobromobiphenyls are formed is yet to be clearly established. An attempt is, however, made below to clarify the situation.

The relative yields of say, 4-bromobiphenyl and of bromobenzene in a competitive experiment with biphenyl-benzene may be linked in principle with the rate of attack by bromine upon a para-position in biphenyl compared to that upon a single position in benzene. But there are a number of assumptions involved in such an assertion. Apart from the reservation that the molecularity of the substitution process is the same in each case, and that the step linking product formation with this substitution step are the same or proceed to identical extents whether competition occurs or not, (i.e. the presence of the second competing system does not cause a change in the proportion of the first substrate which forms product) there is the particular possibility that there may be a variety of routes for the formation of any one substitution product, and that these may contribute to different extents in the presence of a competing process.

The simplest interpretation of the yields of bromo-arenes formed in these reactions links directly with partial rate factors;

\[ \frac{k_{Ph/p}}{k_{H}} \times \frac{\text{Yield of p-bromobiphenyl}}{\text{Biphenyl}} = \frac{\text{Yield of p-bromobenzene}}{\text{Benzene}} \]

This assumes a mechanism in which (a) attack of bromine upon the arene is rate-determining and (b) diversion from a stable side-product occurs to a negligible extent.
Consider the two reactions in competition with each other as shown in Scheme 20.

\[ C_6H_6 \xrightarrow{Br^-/Br_2} \text{Decomposes slowly by light to give some } C_6H_5Br \text{ and } \text{Br*} \]

\[ 4\text{Br* several stages} \]

\[ \text{Decomposes faster than those of benzene to give bromo-biphenyls}^\dagger \]

\[ \text{This is assumed by analogy to that in benzene} \]
The first step i.e. the attack by Br• on the aromatic ring is a slow step on the basis of the thermodynamics since the aromatic character of the ring is destroyed, and hence it will be endothermic by approximately 30 kcal mole⁻¹. The rest of the steps are usually faster since the species (LIV) and (LIVa) are more reactive and hence react at a much faster rate. By several stages both (LIV) and (LIVa) give addition products which may decompose by light to give substitution products. Support for this is obtained from the fact that the benzene hexabromide (C₆H₆Br₆) is decomposed by ultraviolet light to give bromine (which may react further with the available substrate) and substituted benzene which is not formed by the attack of bromine directly upon benzene. It therefore follows that the inclusion of bromobenzene formed by this route into measurements of the rate of attack of benzene by bromine is invalid.

Apart from this, the formation of bromobiphenyls during these photolytic processes may arise from apparent rearrangements in which the site of attack and the site of ultimate substitution may not necessarily be the same, e.g. step (LIVa) → (LV) or (LVa). This means that the observed orientation of attack upon biphenyl may neither reflect nor simply parallel the relative extents to which bromine attack took place, for the formation of isomeric bromobiphenyls relies not only on this factor but also upon the various modes of decomposition of the dihydro-dibromobiphenyl (LIVa).

It is interesting to compare the amounts of addition and substitution products arising from the photobromination of benzene and biphenyl separately. A comparison is made below;
Photobromination Products (%)

<table>
<thead>
<tr>
<th></th>
<th>Substitution</th>
<th>Addition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>38 - 40</td>
<td>45 - 50</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>60 - 65</td>
<td>30 - 35</td>
</tr>
</tbody>
</table>

The greater amount of substitution in biphenyl suggests that the steps leading to the formation of bromobiphenyls are faster than those in benzene. This in turn suggests two possibilities, (a) step (LIVa) → (LV) is more favoured in biphenyl, compared to the analogous step benzene, due to the presence of aryl group, and (b) the bromine addition products of biphenyl are less stable than their benzene counterparts probably for stereochemical reasons, and so they decompose more readily to give the substitution products.

The measured apparent relative rates, partial rate factors, products and isomer distribution ratios points to the conclusion that the nature of the reaction is likely to be homolytic initiated by the attack of bromine atoms upon biphenyl. The high relative reactivity of biphenyl towards bromine radicals, compared with phenyl radicals which are regarded as neutral or slightly nucleophilic, is consistent with expected electrophilic behaviour of bromine atoms. The partial rate factors determined are not too unexpected in such system, although they are less reliable, for the reasons given above, but being closer to unity than those found for a heterolytic attack, they suggest a homolytic process. An addition-elimination mechanism is operating either exclusively or in competition, with the direct substitution, the difference could not be established very clearly in the present work.
3.2.7. **Effect of change in concentration of biphenyl, in benzene and carbon tetrachloride separately, on isomer ratio of monobromobiphenyls**

A change in selectivity of a halogen atom in different solvents, especially aromatic solvents, is well known\(^{20c}\). This is attributed to the formation of a loose complex between halogen atom and the \(\pi\)-system of the benzene ring. The halogen atom does not then react in its free state and since the complex is more stable than the free atom, the effective reagent is less reactive, and hence more selective than the free atom in a non-complex forming solvent.

Mayo and Hardy\(^{91}\) reported the retardation of the rate of side-chain bromination of toluene by naphthalene. The reaction gives predominantly addition product - 1,2,3,4-tetrahydro-1,2,3,4-tetrabromonaphthalene. They ascribed the retardation of the rate of the substitution reaction to the inhibition of the chain reaction (48) and (49) caused by a lowering of the concentration of chain-carrying bromine atom through reaction (50).

\[
\begin{align*}
\text{CH}_3 + \text{Br}^* & \rightarrow \text{CH}_2 + \text{HBr} \quad \cdots \cdots (48) \\
(LVI) + \text{Br}_2 & \rightarrow \text{CH}_2\text{Br}^* + \text{Br}^* \quad \cdots \cdots (49) \\
\begin{align*}
\text{Br}^* & \leftrightarrow (LVI\text{a}) \\
\downarrow & \quad \uparrow \\
(LVI\text{b}) & \quad (LVII\text{a}) \\
\text{Br} & \rightarrow \end{align*}
\end{align*}
\]
However, it is suggested elsewhere\textsuperscript{21}, that the retardation of the side-chain substitution is because the reaction (48) is performed, not by a free, but by a complexed bromine atom, either (LVIIa) or (LVIIb).

\[(LVIIa) \text{ or } (LVIIb) + \xrightarrow{} \text{HBr} + C_{10}H_{8}\]

In the present work of photochemical bromination, with different concentrations of biphenyl in benzene and in carbon tetrachloride solution separately, a difference in the isomer ratio of monobromobiphenyls was found. This points to a variation in the selectivity of bromine atoms. A comparison of isomer distribution ratios, found in different conditions, is given in Table 21.

<table>
<thead>
<tr>
<th>Solvent (500 ml)</th>
<th>Moles of biphenyl used</th>
<th>ortho-</th>
<th>meta-</th>
<th>para-</th>
<th>(\text{Ratio } (o + p)/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.1</td>
<td>32</td>
<td>9</td>
<td>59</td>
<td>10.1</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.5</td>
<td>32</td>
<td>10</td>
<td>58</td>
<td>9.0</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.0</td>
<td>26</td>
<td>16</td>
<td>58</td>
<td>5.25</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>0.1</td>
<td>24</td>
<td>27</td>
<td>49</td>
<td>2.70</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>0.5</td>
<td>23</td>
<td>28</td>
<td>49</td>
<td>2.57</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>1.0</td>
<td>24</td>
<td>21</td>
<td>55</td>
<td>3.76</td>
</tr>
</tbody>
</table>
It can be seen from Table 21 that the \((o + p)/m^-\) ratio is higher in benzene than in carbon tetrachloride solution. This variation is possibly the result of a certain degree of complexation of bromine atoms caused by benzene. Although benzene is less reactive than biphenyl, as found by a competition reaction (page 155), it is present in large excess (500 ml), so that most of the bromine atoms generated may become complexed in the \(\pi\)-system of benzene rather than that of biphenyl. Thus their reactivity is reduced, their selectivity increased, as a result, a high \((o + p)/m^-\) ratio is found in benzene.

\[
\begin{align*}
C_6H_6 + Br & \rightarrow \text{Br-Ph} \\
\text{Ph} & \rightarrow \text{Ph-Br} \\
\text{(LVIII)}
\end{align*}
\]

When, however, the concentration of biphenyl is changed, from 0.5 to 1 mole (Table 21) in benzene, such complex formation between benzene and bromine atoms is reduced to a certain extent, because of the increased concentration of biphenyl. Thus the selectivity of bromine radicals is reduced as a result, and a lower \((o + p)/m^-\) ratio is found.
Support for the above arguments comes from a comparison of isomer distribution ratio obtained in benzene with those obtained in carbon tetrachloride solution (Table 21). It can be seen that the ratio \((\text{o} + \text{p})/\text{m}^-\) has decreased considerably in carbon tetrachloride solution. This shows clearly a lesser complexing effect than that found in benzene. Thus, the reactivity of bromine atoms, generated in carbon tetrachloride solution, is higher than that in benzene. Consequently, the less preferred meta-position (compared to ortho- and para-) is attacked significantly by the free bromine atom, which shows reduced selectivity under such conditions.

An explanation could be offered in one case where a higher \((\text{o} + \text{p})/\text{m}^-\) ratio of monobromobiphenyl is obtained in carbon tetrachloride solution with a relatively high concentration of biphenyl (1 mole), that the biphenyl is acting as a complexing agent itself so that the orientation is now approaching that of the "benzene" series of results (Table 21).

3.2.8. (a) Photobromination of halogenobenzenes

The reported photochemical bromination of fluorobenzene and of chlorobenzene, at room temperature, although a slow process, gives nuclear substitution products. This is also confirmed in the present work. The isomer distribution pattern is markedly different from that of the ionic process. The isomer ratio of monobromohalogenobenzenes arising from the photobromination of the fluoro- and chloro-benzene is given in Table 22 together with the corresponding figures from the heterolytic bromination, for comparison.
### Table 22
Isomer ratio of bromohalogenobenzenes (%)

<table>
<thead>
<tr>
<th>PhX</th>
<th>$\text{Br}_2 + \text{hv}$</th>
<th>$\text{Br}_2 + \text{Fe}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ortho- meta- para-</td>
<td>ortho meta- para-</td>
<td></td>
</tr>
<tr>
<td>Fluoro-</td>
<td>30 6 64</td>
<td>20-25 15-20 55-65 2 0 98</td>
<td>this work</td>
</tr>
<tr>
<td>Chloro-</td>
<td>16 65 19</td>
<td>10-20 60-80 10-20 12 0 88</td>
<td>this work*</td>
</tr>
</tbody>
</table>

* Also found hexabromochlorocyclohexane

The reaction conditions are conducive to radical reactions, but owing to the unexpectedly high proportion of the meta-isomer in the photobromination of chlorobenzene, a parallelism to the results obtained at high temperatures by Kooyman, has been suggested.

However, the origin of bromo-arenes requires some further discussion. A formal addition-elimination mechanism may be proposed:

\[ X + \text{Br}^* \rightarrow \text{Br} \quad \text{Br}_2^* \text{or } \text{Br}^* \rightarrow X \quad \text{HBr} + \text{Br}^* \]

In this mechanism the intermediate radical loses hydrogen to another species, possibly bromine. This has obvious analogies with the heterolytic mechanism and may be favoured over the process in which bromine atoms bring about the aromatisation of the $\sigma$-complex under conditions where...
very low standing concentrations of these atoms occur. However, the second process in eq (51) is endothermic by ca. 25 kcal mole$^{-1}$, and so would be likely only when one or other of the reagent molecules possessed this degree of excitation energy. As this is less than the energy needed to rupture the bond in the bromine molecule (46 kcal mole$^{-1}$), the incidence of the aromatisation reaction in eq (51) is thermodynamically likely, but only with bromine molecules possessing some degree of extra activation energy. This is represented in eq (51) as Br$_2^*$. 

Another mechanism, involving the formation of an intermediate ion pair (ArH$^+$X$^-_2$) has been suggested by Kooyman$^{83}$ as shown previously in eq. (38) and (39) (page 67).

Benson and co-workers$^{88}$ proposed a free radical mechanism, involving cyclohexadienyl radicals and substituted cyclohexadienes as intermediates. This is outlined previously in Scheme 12 (page 69). The relative extent to which the bromine atom is found attached in bromo-arenes, to the original site of attack, is determined by the relative rates of the two competing decompositions. Kooyman interpreted his results in terms of the polarities of the displaced hydrogen atoms; Benson argued that the stabilities of the various intermediate radical should be more appropriate.

In so far as the two modes of explanation focus attention upon similar aspects of molecular energetics, they may be regarded as equivalent. The possibility of this second interpretation - and it is substantiated by Benson's detailed kinetic analysis - means that the observed orientation of attack upon an arene may neither reflect nor simply parallel the relative extent to which bromine attack took place, for the formation of bromo-arene relies not only on this factor but also upon the various modes of decomposition of the dihydro-dihalogenoarene (LIX).
Reaction between trifluoriodomethane and halogenobenzenes at 198º also proceeds by an addition-elimination process. The formation of addition products (LXa), (LXb) and (LXc) takes place by a radical chain sequence involving the addition of trifluoriodomethane to the ring. Substitution is then completed by the loss of hydrogen iodide from these adducts to give the appropriate halobenzotrifluoride. This is outlined in Scheme 21 for the formation of ortho-isomer only.

Scheme 21

The loss of hydrogen iodide from the addition product at these elevated temperatures producing the substitution product has been suggested to be a rapid process.
The above example strengthens the idea that at high temperatures the loss of hydrogen halides from the addition product i.e. an addition-elimination mechanism is a probable route to the substitution products in these homolytic aromatic substitution reactions. Therefore, the mechanism of photobromination of halogenobenzenes was investigated in the present work.

As mentioned in Table 22 (see footnote) a small amount of addition product (HBCC) was also found in the reaction product of photobromination of chlorobenzene (a similar type of product may have been found in photobromination of fluorobenzene also, but owing to either ready decomposition or a greater solubility it could not be detected). The presence of this product supports the view that the bromohalogenobenzenes may have been formed from the subsequent photochemical decomposition of the initially formed adduct through the elimination of hydrogen bromide. This was studied in the present work.

Pure HBCC was photochemically decomposed in different solvents at ca. 50°. Besides bromine, hydrogen bromide, chlorobenzene and bromobenzene, isomeric bromochlorobenzenes were found as the products. The amount of bromochlorobenzenes was low (possibly due to the consecutive photochemical decomposition) but a close resemblance was found in their isomer ratio, to those obtained from the direct photobromination of chlorobenzene. A comparison is given in Table 23.

**Table 23**

<table>
<thead>
<tr>
<th>Process</th>
<th>Monobromochlorobenzene (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ortho-</td>
</tr>
<tr>
<td>Photobromination of chlorobenzene at ca. 25°</td>
<td>16</td>
</tr>
<tr>
<td>Photochemical decomposition of HBCC* at ca. 50°</td>
<td>(a) in benzene</td>
</tr>
<tr>
<td></td>
<td>(b) in toluene†</td>
</tr>
</tbody>
</table>

* Hexabromochlorocyclohexane  †Also formed benzyl bromide
There can be two ways in which this observation may be discussed. Firstly, the similarity in the isomer ratio of bromochlorobenzenes obtained from the two different reactions suggests a common route for their formation, namely an addition-elimination mechanism. The origin of these substitution products would then be through the subsequent decomposition of the initially formed adduct(s). This is similar to the evidence obtained from the photochemical decomposition of benzene hexabromide in toluene (c.f. page 146) and hence, provides another example supporting an addition-elimination mechanism.

Secondly, some of the chlorobenzene formed from the photochemical decomposition of HBCC via the fission of carbon-bromine bonds, is possibly re-attacked by Br• thus reproducing an addition product of the type (LXI)

\[
\text{C}_6\text{H}_5\text{Cl} \xrightarrow{2\text{Br•}} \text{several stages} \xrightarrow{-\text{HBr}} \text{Cl} \quad \text{or m-isomer}
\]

which acts as a precursor for bromochlorobenzenes. Evidence for this route was obtained from the apparent faster decomposition of HBCC compared with benzene hexabromide. A possible reason for this is a different stereochemical nature of HBCC since the presence of a chlorine atom between the two bulky bromine atoms in this adduct (LXII) could make this photochemically less stable. This is also evident from the fact that very little amount of this product was formed in the

\[
\text{(LXII)}
\]
photobromination of chlorobenzene, in contrast to the photobromination of benzene which gives $\sim 50\%$ of benzene hexabromide.

However, both of the possibilities discussed above focus attention upon a common addition-elimination process.

A mechanism is outlined in Scheme 22, for the m- and the p-isomers only, to account of the formation of the products from the photobromination of halogenobenzenes.

\[ \text{Scheme 22} \]

\[ X = F \text{ or } Cl \]
The mechanism (Scheme 22) is suggested from the data available in the photobromination of halogenobenzenes. For benzene derivatives it would normally be expected that (LXIII) produced by 1,2-addition initiated by a bromine atom could undergo further rapid addition at the conjugated double bonds after which elimination may give dihalo-arenes. It is not certain, however, that this would be the situation for a 1,4-adduct (LXIV) since in such compounds the double bonds are isolated and deactivated by the adjacent substituents. However, as the whole addition process is apparently slowly reversible under these conditions, the products (LXIII) and (LXIV) may eventually be wholly diverted to give the product of elimination (C₆H₄Br.X). 1,4-Elimination of hydrogen bromide from (LXIV) might well compete with 1,2-elimination from (LXIII) thus giving more para-substitution and hence less or possibly no addition product. This might well be the case in fluoro-benzene.

3.2.8. (b) Photochemical exchange of halogens

Photochemical exchange of halogens in aromatic compounds is a well known reaction and has been observed by many previous workers\textsuperscript{136a,b}. Miller and Walling\textsuperscript{97} first made a detailed study of this phenomena from the liquid-phase chlorination of bromobenzene and suggested an addition-elimination mechanism to account for this exchange. This was also supported by the later investigators\textsuperscript{98}. Gouvenour and Soumillion\textsuperscript{96} recently observed that bromine also replaces chlorine in the liquid phase bromination of chlorobenzene.

This interchange of halogens was also found in the present work. Photobromination of chlorobenzene also gives bromobenzene (5%) among the other products. This product is obviously the result of replacement of chlorine from chlorobenzene by bromine.
Direct displacement of chlorine by bromine has a little precedent in these systems on account of the endothermicity of the reaction. An approximate thermodynamic calculation suggests that the reaction (52) would be endothermic by \( \sim 30 \text{ kcal mole}^{-1} \). Hence this possibility is ruled out.

\[
\text{C}_6\text{H}_5\text{Cl} + \text{Br}^\cdot \rightarrow \text{C}_6\text{H}_5^\cdot + \text{BrCl}
\]  

A mechanism, although by no means conclusive, analogous to that proposed by others for chlorination of bromobenzene seems more plausible. Addition appears well established as the usual path for the attachment of halogen atom to aromatic systems. The formation of \( \pi \)-complexes of the type (LXV) is well known and has been widely investigated. Furthermore, the formation of complexes between arenes and halogen atoms is indirectly supported from the selectivity studies of Russell.

3.2.9. (a) Photobromination of t-butylbenzene

Halogenation of t-butylbenzene is known to give both nuclear and side-chain substitution products depending upon the reaction conditions. There appears to be no previous record of the liquid phase photobromination of t-butylbenzene with molecular bromine, although Boocock and Hickinbottom have reported results of bromination of t-butylbenzene with N-bromo-succinimide in the presence of benzoyl peroxide which mainly gives 4-bromo-t-butylbenzene.
t-Butylbenzene has now been brominated with molecular bromine at room temperature with ultraviolet light as the free-radical initiator. The reaction, although slow gives nuclear substitution products (70%) accompanied by some di-t-butylbenzenes. No side-chain substitution product was found. The isomer distribution ratios of monobromo-t-butylbenzenes is given in Table 24 which includes the corresponding figures for the bromination of t-butylbenzene under different conditions for comparison.

It can be seen from Table 24 that the isomer ratios obtained from the photochemical bromination fall in the order \( m^- > p^- > o^- \), while in the electrophilic bromination the order of \( p^- >> m^- > o^- \). The electronic requirements for homolytic and heterolytic reactions are different: in the former the meta-position in t-butylbenzene is usually more reactive than the ortho- and para-position (see below). This has actually been found in the present work where the m-bromo-t-butylbenzene predominates, over the o- and p-isomer in the products from photochemical bromination.

It is interesting to compare the results of the present reaction with some other homolytic reactions of t-butylbenzene. Data for the phenylation of t-butylbenzene show that the isomeric t-butylbiphenyls are formed in a ratio \( \text{ortho-} 10 ; \text{meta-} 63 \text{ and para-} 27\% \). This is a well established free radical reaction which proceeds through the formation of a cyclohexadienyl intermediate complex, dehydrogenation of which gives the phenylated product. This isomer ratio is similar to that of monobromo-t-butylbenzenes obtained in the present work in the sense that in both, the meta-isomer predominates over the ortho- and the para-isomer. Thus substituents are not invariably ortho-para-directing towards homolytic substitution reactions.
Table 24
Isomer distribution (%) of monobromo-t-butylbenzenes found under different conditions.

<table>
<thead>
<tr>
<th>Process</th>
<th>ortho-</th>
<th>meta-</th>
<th>para-</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photobromination of t-butylbenzene, at room temperature, for 20 hours</td>
<td>4(^{(a)})</td>
<td>72</td>
<td>24</td>
<td>this work</td>
</tr>
<tr>
<td>Photochemical equilibrium of an equimolar mixture of m- and p-bromo-t-butylbenzene after 16 hours of illumination(^{(c)})</td>
<td>0</td>
<td>69</td>
<td>31</td>
<td>this work</td>
</tr>
<tr>
<td>Photochemical decomposition of pure p-bromo-t-butylbenzene for 16 hours(^{(c)})</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>this work</td>
</tr>
<tr>
<td>Equilibrium between o-, m- and p-bromo-t-butylbenzene attained after 24 hours (AlCl(_3)), starting from 99.8% of o-isomer.</td>
<td>0</td>
<td>67.8</td>
<td>32.2</td>
<td>138a</td>
</tr>
<tr>
<td>Electrophilic bromination of t-butylbenzene in acetic acid at 25(^{0}).</td>
<td>1.23</td>
<td>1.47</td>
<td>97.3</td>
<td>138b</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Evidence for this isomer was obtained only by n.m.r. spectroscopy.

\(^{(b)}\) Conversion of bromine was 0.06 mole i.e. 60%.

\(^{(c)}\) With partial decomposition of the starting material(s).
The experimental findings from the photobromination of t-butylbenzene support the interpretation in terms of the inductive effect of the t-butyl group. When the bromine atom approaches the ortho- positions of the t-butylbenzene molecule (due to electrostatic attraction) it is diverted by steric repulsion and hence seeks the next site of higher electron density - the meta-position. The meta-position would become increasingly activated and thus the formation of the intermediate (LXVI) takes place,

\[
\text{Bu}^t \begin{array}{c}
\text{Br} \\
\text{H} \\
\text{Br}
\end{array} + \text{Br} \quad \text{slow} \quad \begin{array}{c}
\text{Bu}^t \\
\text{H} \\
\text{Br}
\end{array}
\]

(LXVI)

The reaction may then be completed in two different ways:

\[
\begin{array}{c}
\text{Bu}^t \\
\text{Br} \\
\text{H}
\end{array} + \text{HBr or Br}
\]

(LXVII)

\[
\text{Bu}^t \\
\text{Br} \\
\text{H}
\]

(LXVII)

\[
\begin{array}{c}
\text{Bu}^t \\
\text{H} \\
\text{Br}
\end{array} \quad \text{or} \quad \begin{array}{c}
\text{Bu}^t \\
\text{Br} \\
\text{H}
\end{array}
\]

(LXVIIIa)

The step (LXVI) \(\rightarrow\) (LXVII) is favourable only if the requirements mentioned on page 144 are met. Since the reaction was performed at room temperature so the possibility of occurrence of step (LXVI) \(\rightarrow\) (LXVIIIa)
or (LXVIIIb) is expected to be higher. The adduct(s) may then decompose to give isomeric bromo-t-butylbenzenes. The elimination of hydrogen bromide to give any particular isomer of bromo-t-butylbenzene partly depends upon the steric factor. Steric repression of the t-butylbenzene would favour the elimination of hydrogen bromide from (LXVIIIa) to give the m-bromo-t-butylbenzene which would also be formed in competition with the p-bromo-t-butylbenzene, from (LXVIIIb).

Therefore, it is reasonable to ascribe a substantial portion of the orienting influence of the t-butyl group to its inductive and steric effects.

An alternative scheme, that the product distribution (i.e. the stability order m- > p- > o-) results from thermodynamic stability rather than kinetic control, was ruled out. In a separate reaction involving the ultraviolet irradiation of p-bromo-t-butylbenzene (Table 24) under the same conditions in which the photobromination of t-butylbenzene was performed, no o- or m-bromo-t-butylbenzene was found although the starting material was partially decomposed by the ultraviolet light.

3.2.9. (b) The origin of side-products from photobromination of t-butylbenzene

Bromobenzene (ca. 5%) and the isomeric di-t-butylbenzenes (15-20%) were formed along with the bromo-t-buylbenzenes in this reaction. The isomer distribution observed in the di-t-butylbenzenes was o- : m- : p- : ; 2 : 76 : 22%; there was some doubt about the presence of the o-isomer.

Table 24 shows that the bromo-t-butylbenzenes are themselves unstable under the reaction conditions; thus an equimolar mixture of m- and p-bromo-t-butylbenzene gave a mixture containing 69% m- and 31% p-isomer. Both were consumed during this time to give bromine and
di-t-butylbenzenes, but (Table 24) there was no evidence that the p-isomer rearranged to the m-compound.

The relative amounts of the bromo-t-butylbenzene isomer whether obtained directly from the photobromination of t-butylbenzene or found after photochemically induced decomposition of the bromo-t-butylbenzene products, were substantially the same as that found by Olah and co-workers\textsuperscript{138a} from the equilibration of o-bromo-t-butylbenzene by aluminium chloride. The isomerisation therefore appears to rely upon the presence of a Lewis acid catalyst; hydrogen-bromide is the likely species in the present series of reactions. It is significant that m-di-t-butylbenzene is the major product in all these rearrangements; its formation may be illustrated as shown in Scheme 23.

\begin{equation}
\begin{array}{ccc}
\text{Bu}^t & \text{+ HBr} & \text{Bu}^t \text{Br} \\
\hline
\text{Bu}^t & \text{Br} \quad \text{Bu}^t & \text{H} \\
\hline
\text{Bu}^t & \text{+ Bu}^t \text{Br} & \text{Bu}^t \text{+ Bu}^t \text{Br} \\
\hline
\text{Bu}^t & \text{Br} \quad \text{Bu}^t & \text{Br} \\
\hline
\text{Bu}^t & \text{Bu}^t \text{Br} \quad \text{Bu}^t \text{Br} & \text{Bu}^t \text{+ other isomers} \\
\hline
\text{Bu}^t & \text{Bu}^t \text{Br} \quad \text{Bu}^t \text{Br} & \text{Bu}^t \text{+ Br}_2 \\
\hline
\end{array}
\end{equation}

(similarly for other isomers)

\textbf{Scheme 23} Probable pathways for the rearrangement of bromo-t-butylbenzenes
This process, involved the catalytic action of hydrogen bromide, explains the identification of bromine, bromobenzene, and di-t-butylbenzenes as products of the photochemical decomposition of the bromo-t-butylbenzene isomers, and is consistent with the observations of other workers\textsuperscript{138a}.

Side-chain reaction of t-butylbenzene has been reported in vapour phase processes\textsuperscript{93}, but were not observed here. The lower temperature of the reaction, together with possible complexing in the liquid phase between bromine and t-butylbenzene (see page 166), may be the cause of this difference by increasing the selectivity of the halogen.

3.2.10. **Photobromination of benzotrifluoride:**

The photobromination of benzotrifluoride, at room temperature, is now found to give mostly m-bromobenzotrifluoride. Gas phase bromination has also been reported to lead to a large degree of meta-substitution\textsuperscript{83}.

In heterolytic conditions the \(-\text{CF}_3\) group is known to be meta-directing towards electrophiles. The suggestion that the substituent effect of this group contains a hyperconjugative component (LXIXa) was first made in 1950 by Robert on the basis of dipole moment studies\textsuperscript{139a}. However, arguments against the importance of hyperconjugation as implied by structure (LXIXa) have been brought forward by Holtz\textsuperscript{139b} and also by Sheppard\textsuperscript{140} (from comparison with other substituents). An interaction between the fluorine lone-pair electrons and the \(\pi\)-electrons of the ring was described as involving contributions from structures such as (LXIXb).
In considering the relevance to the present free radical bromination it is assumed that the attacking species, the bromine atom, behaves as an electrophile because of the parallelism in the results of nuclear substitution.

3.2.11. Photochemical decomposition of benzene hexabromide in cyclohexene

An attempt was made to use benzene hexabromide as a source of bromine atoms in cyclohexene. In principle, the products could arise from two sources, (a) from the decomposition of the hexabromide through the elimination of hydrogen bromide, (b) from the bromination of cyclohexene. The latter were thought here to be interesting, since 1,2-dibromocyclohexane, if formed under these conditions may decompose to give 1-bromo-cyclohexene as follows;

\[
\text{(LXX)} \xrightarrow{\text{hv}} \text{Br} \\
\text{Br} \\
\text{H} \\
\text{Br} \\
\text{H} \\
\hline
\text{Br} \\
\text{(LXXI)}
\]

However, no evidence was found for the presence of (LXXI), although the reaction product was found to contain (LXX). This may well be because hydrogen and bromine are not in trans-diaxial configuration at C₁ and C₂, so that the reversal of the addition, by eliminating two bromine atoms, is preferred.

3.2.12. Photobromination of naphthalene

Photobromination of naphthalene in carbon tetrachloride solution at 20° is known to give mostly addition accompanied by 15% of the substitution product. Attempts were made to investigate this under
the analogous conditions at 50°. This gave ca. 35-40% of substitution product. The reaction product was associated with an analytical difficulty in gas liquid chromatography since the addition product 1,2,3,4-tetrahydro-tetrabromonaphthalene decomposed under the analytical conditions to give 1-bromonaphthalene. It could not be ascertained whether this material was formed during or after the reaction. The addition compound could not be separated without some decomposition despite several attempts.

A further attempt was made to determine the stereochemistry of the purified 1,2,3,4-tetrahydro-1,2,3,4-tetrabromonaphthalene with the help of n.m.r. spectroscopy by comparison with that reported for some of the isomeric naphthalene tetrachlorides by de la Mare and co-workers. A comparison of the n.m.r. spectra of naphthalene tetrabromide with its tetrachloride counterpart is shown in Table 25.

From the coupling constants, the naphthalene tetrabromide appeared to be close to the ε-isomer of the tetrachloride which is reported to be in rapid equilibrium with its stereoisomeric form. No change in the spectrum of naphthalene tetrabromide was found at -70° where it was expected to hold to one, stable, conformation. No significant information could be obtained from selective decoupling of the protons. Therefore, it may be possible that naphthalene tetrabromide has a stereochemistry close to that of the isomeric ε-tetrachloride (Table 25). However, this too is ambiguous.

3.2.13. Photobromination of hexafluorobenzene

Homolytic removal of a fluorine atom from hexafluorobenzene, both thermally and photochemically, is well known.

Photobromination of hexafluorobenzene was attempted with molecular bromine, by analogy to benzene. The reaction was found to proceed very slowly.
Table 25
Proton magnetic spectra of some naphthalene tetrahalides

<table>
<thead>
<tr>
<th>Compound</th>
<th>α-TC (a)</th>
<th>γ-TC</th>
<th>ε-TC</th>
<th>TB (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M.P.</td>
<td>182°</td>
<td>134°</td>
<td>85-87°</td>
<td>109°</td>
</tr>
<tr>
<td>Reference</td>
<td>40b</td>
<td>40b</td>
<td>40b</td>
<td>this work</td>
</tr>
<tr>
<td>Spectrum type</td>
<td>A₂X₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>τ (p.p.m)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aromatic</td>
<td>2.48</td>
<td>2.26</td>
<td>2.4</td>
<td>3 - 3.4</td>
</tr>
<tr>
<td></td>
<td>(single)</td>
<td>(single)</td>
<td>(A₂X₂)</td>
<td></td>
</tr>
<tr>
<td>1-H</td>
<td>4.28</td>
<td>4.48</td>
<td>4.53</td>
<td>5.08</td>
</tr>
<tr>
<td>2-H</td>
<td>4.93</td>
<td>5.42</td>
<td>4.96</td>
<td>4.47</td>
</tr>
<tr>
<td>3-H</td>
<td>4.93</td>
<td>5.42</td>
<td>4.96</td>
<td>4.49</td>
</tr>
<tr>
<td>4-H</td>
<td>4.28</td>
<td>4.48</td>
<td>4.53</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Coupling constants (c/sec):

| J₁,₂       | 3.5  | 8.0  | 5.8  | 1.65   |
| J₂,₃       | 11.0 | 8.0  | 3.5  | 4.6    |
| J₃,₄       | 3.5  | 8.0  | 8.8  | 1.65   |

Chlorine positions in solution a'eea'  e'ee'  a'gee'  e'ee' a'ee'

(a) Tetrachloride
(b) Tetrabromide
Only $\approx 10\%$ of bromine was consumed in forty-eight hours to give an addition product - hexabromo-hexafluorocyclohexane as evidenced by the mass spectrometry of the reaction product. Gas chromatography showed minor quantities of unidentified products. No evidence was found for either bromopentafluorobenzene or dibromo-tetrafluorobenzene by gas chromatography and n.m.r. spectroscopy.

3.2.14. Summary

Results of the photobromination of benzene derivatives suggests that both nuclear addition and substitution reaction are operative in the liquid phase system. However, at higher temperature ($50-55^\circ$) nuclear substitution is more favoured. This is found to take place mainly through the initially formed addition product. Thus an addition-elimination mechanism appears the more reasonable scheme to account for the formation of bromo-arenes. Direct substitution by molecular bromine upon the benzene nucleus is discounted on energetic grounds unless photochemical activation provides sufficient energy.

Partial rate factors for biphenyl are consistent with its expected reactivity in a free radical system. Their validity is, however, not certain and their limitations are discussed.

The isomer distribution ratios of bromo-arenes formed from various substrates are very much different from those found in heterolytic reactions. The usual ortho-para-directing effect of electron-withdrawing substituents is not observed. In most cases, the meta-position is apparently more reactive than the ortho- and para-positions.
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