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THE EFFECT OF CATALYSTS IN ~~COMPETITIVE~~ HOMOLYTIC ARYLATION

by

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TO MY PARENTS

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ABSTRACT

The effects of additives such as ferric benzoate and cupric benzoate on the thermal decomposition of benzoyl peroxide in benzene, fluorobenzene, chlorobenzene, bromobenzene, _p_-dichlorobenzene, 1,3,5-trichlorobenzene, methyl benzoate, benzophenone and benzonitrile have been investigated. In the reactions of benzene, chlorobenzene and bromobenzene, the effects of _m_-dinitrobenzene, nitrosobenzene, pentafluoronitrosobenzene, _o_- and _p_-chloranil and cupric _p_-substituted (methyl-, chloro- and nitro-) benzoates were also examined. The additives catalysed the reactions so as to results in high yields of biaryl and benzoic acid to the exclusion of all other products and also exhibited different effects on the isomeric distribution of these substrates. Explanations have been suggested to account for these observations.

The effects of cupric benzoate and ferric benzoate on the competitive reactions of fluorobenzene, chlorobenzene, bromobenzene _p_dichlorobenzene, 1,3,5-trichlorobenzene, methyl benzoate, benzophenone and benzonitrile with benzene as a standard solvent have been studied. Relative rates and partial rate factors are significantly altered in the presence of these metal benzoates.

Competitive reactions of chlorobenzene and bromobenzene with _p_-dichlorobenzene as a standard solvent in the presence and absence of cupric- or ferric benzoate, also of chlorobenzene with 1,3,5-trichlorobenzene as a standard solvent in the presence and absence of ferric benzoate have been studied. The relative rates obtained from these reactions in the absence of additives converted into the relative rates with respect to benzene as a standard solvent disagreed

with those determined directly from the competitive reactions between these substrates and benzene in the absence of additives. However good agreement is obtained in the presence of additives.

The assumption regarding the additivity of directing group on activation for phenylation reactions were tested in the presence and absence of additives, by comparing the relative rates obtained from the competitive reactions of p-dichlorobenzene and 1,3,5-trichlorobenzene with benzene as a standard solvent to those values calculated by substitution of measured partial rate factors for chlorobenzene in the presence and absence of additives. A good agreement is obtained with regard to the additivity of effects of the substitution in the presence of additives, although the agreement is much poorer for the uncatalysed reactions.

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III. DISCUSSIONS

I. INTRODUCTION

1. Homolytic Aromatic Substitution

The thermal decomposition of benzoyl peroxide in the dry state was first studied by Brodie (1864)[1], who found that a mole of carbon dioxide was produced per mole benzoyl peroxide decomposed. Lippman (1886)[2] found biphenyl as well as carbon dioxide as the reaction products of the thermal decomposition of benzoyl peroxide in sand. When the same reaction products were also found when the reaction was carried out in benzene, it was concluded wrongly that the solvent does not take part in the reaction. This statement was corrected by Gelissen and Hermans (1925)[3] who began their investigations into the decomposition of the peroxide in various aromatic solvents, and showed that the reaction proceeded according to their so called "RH" scheme:-

$$1) \qquad (ArCO.O)_2 + RH \begin{array}{l} \nearrow ArH + ArCO.OR + CO_2 \quad (a) \\ \searrow ArR + ArCO.OH + CO_2 \quad (b) \end{array}$$

The above scheme indicates that biaryls are formed by reaction (1.b) only when RH is aromatic, and that they are always of the unsymmetrical type ArR, where one group (Ar) is provided by peroxide and other by the solvent.

The actual mechanism at this stage was not defined, but it was latter interpreted as a homolytic process.[4-7]

Grieve and Hey (1934)[8] suggested that the reactive species involved in the phenylation of aromatic substrates, both by the Gomberg reaction and by the decomposition of nitrosoacetanilide, was the free phenyl radcal. Hey and Waters (1937)[9] elaborated the above proposition and their review is one of most significant publications in the history of free-radical chemistry.

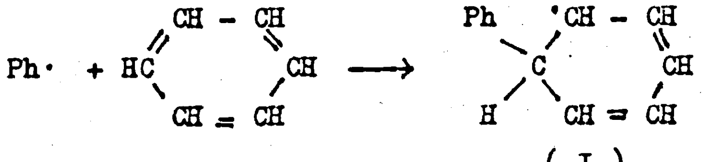
The products of the decomposition of diaroyl peroxides in aromatic solvents were rationalised in terms of free-radical intermediatws in the following scheme : -

$$\begin{array}{llll} (a) & (ArCO{\cdot}O)_2 \longrightarrow & Ar{\cdot} + ArCO{\cdot}O{\cdot} + CO_2 & \\ (b) & Ar{\cdot} + R\text{-}H \longrightarrow & Ar\text{-}R + H{\cdot} & (2) \\ (c) & ArCO{\cdot}O{\cdot} + H{\cdot} \longrightarrow & ArCO{\cdot}OH & \end{array}$$

By extending this scheme the formation of minor products such as esters and polyphenyls could also be rationalised.

$$\begin{array}{ll} (d) & Ar{\cdot} + R\,C_6H_5 \text{ ——— } R\,C_6H_4Ar + H{\cdot} \\ (e) & ArCO{\cdot}O{\cdot} + R\text{-}H \text{ ——— } ArCO{\cdot}OR + H{\cdot} \end{array}$$

It was considered that the available experimental results could be interpreted in terms of attack on the aromatic substrate by electrically neutral phenyl radicals, and later Waters (1941)[10] formulated the initial act in the substitution process as addition to the aromatic ring (I).



(I)

However it was another 15 years before the full range of the chemical behavior of the product of that addition, i.e. phenylcyclohexadienyl radical, was explained.

A. Kinetics and Mechanism of Benzoyl Peroxide

The mechanism of the decomposition of benzoyl peroxide in aromatic solvents has been elucidated by the study of the kinetics of the reaction and by product analysis.

Brown (1940)[11] was the first to study the kinetics of the decomposition of benzoyl peroxide in organic solvents. By measurement of carbon dioxide evolution, he interpreted the decomposition as occurring by parrallel unimolecular and bimolecular reactions according to the rate equation : -

$$(3) \qquad d\underline{C}/d\underline{t} = k_1C + k_2C^2$$

where $\underline{C}$ is the concentration of the peroxide at time $\underline{t}$ and $\underline{k}_1$ and $\underline{k}_2$ are first and second order rate constants respectively.

Brown also showed the activation energy of the first order reaction to be 30 kcal mole^{-1}. This was confirmed by Cuthbertson, McClure and Robertson (1942)[12] and by Altschul and Bartlett (1945)[13].

The detailed investigations of Nozaki and Bartlett (1946)[14] demonstrated that the overall reaction can be represented by two simultaneous reactions, a unimolecular decomposition and a 3/2- order reaction, the previous interpretation of this chain reaction as second order being incorrect.

The activation energy of the unimolecular decomposition in benzene was estimated as 30 kcal mole^{-1}. This reaction is clearly the "primary" dissociation of the peroxide (4), which has also been demonstrated by

$$(4) \qquad C_6H_5CO\cdot O\cdot O\cdot CO\cdot C_6H_5 \longrightarrow 2C_6H_5CO\cdot O\cdot$$

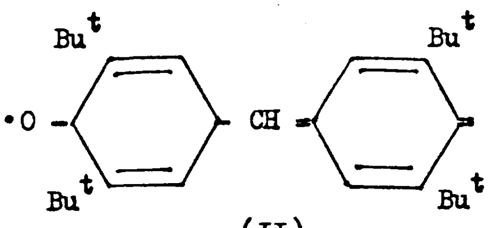
several workers by elimination of the subsequent chain reaction in the presence of free-radical "scavenger", or by carring out the reaction in very dilute concentrations of peroxidw.

Barnett and Vaughan (1947)[15] carried out the decomposition of benzoyl peroxide in twenty-three solvents and found that, at low concentrations the reaction is basically of the first order, although varying some twenty fold in magnitude. At infinite dilution in benzene it was strictly of the first order.

The effect of the pressure on the decomposition in the solution was investigated by Walling and Peton (1957)[16] and others[17,18]. It was found that at low pressure, a pressure-retarded unimolecular decomposition predominates, but a radical chain mechanism, which is facilitated by compression, become the more important at high pressures.

Free radical scavengers such as iodine were investigated by Hammond[19] and others[20,21]. Hammond obtained two moles of benzoic acid per mole of benzoyl peroxide, when the latter was decomposed in moist carbon tetrachloride in the presence of iodine as scavenger, and in the decomposition of benzoyl peroxide in a number of solvents, the peroxide decomposition was first order with respect to peroxide and was independent of the iodine concentration.

A number of radical scavengers[22-24] have been investigated, but the unreliability of most of them renders the results obtained of doubtful validity. "Galvinoxyl"[25] (II); [2,6-di-t-butyl-α-(3,5-di-t-butyl-4-oxo-2,5,-cyclohexa-2,5-dienylidene)-4-tolyl-oxy-radical] has, however been demonstrated as an efficient acceptor for o wide variety of radicals.



(II)

The "primary" dissociation of the peroxide is then followed by the spontaneous decarboxylation (5), and the resulting phenyl radical causes nuclear substitution in aromatic solvents.

(5) $PhCO{\cdot}O{\cdot} \longrightarrow Ph{\cdot} + CO_2$

B. Further Mechanistic Features

(1) The nuclear substitution reaction, evidence of σ-radicals, and the nature of residue.

There are three schemes which have been considered to explain the mechanism of the nuclear substitution in aromatic solvents.

a) The abstraction-addition mechanism

This involves the abstraction of hydrogen from the solvent molecule by aryl or aryloxy-radicals, followed by dimerisation of the resulting solvent radicals or by their combination with other radicals.

(6) $Ar{\cdot} + Ar'H \longrightarrow ArH + Ar'{\cdot}$

(7) $Ar'{\cdot} + Ar'{\cdot} \longrightarrow Ar'\text{-}Ar'$

(8) $Ar{\cdot} + Ar'{\cdot} \longrightarrow Ar\text{-}Ar'$

In this scheme a symetrical biaryl is produced by reaction (7) as well as the unsymmetrical biaryl from (8), but the fact that no symmetrical biaryls are found in the product in detectable quantities in these reactions with benzene derivatives, and the high activation energy required for the dissociation of the aromatic C-H bond, effectively eliminate this mechanism.

b) <u>The addition-abstraction mechanism</u>

This mechanism involves the formation of an addition complex between the phenyl-radical and the substrate, followed by the loss of a hydrogen atom, probably by interaction of the addition complex with another radical or other oxidising agent, in a fast, kinetically insignificant stage.

$$(9) \qquad \mathrm{Ar}\cdot + \mathrm{Ar'H} \longrightarrow \underset{\text{(III)}}{\left[\mathrm{Ar'}\!<\!\begin{array}{l}\mathrm{H}\\ \mathrm{Ar}\end{array}\right]\cdot}$$

$$(10) \qquad \mathrm{Ar{\cdot}Ar'H}\cdot + \mathrm{R}\cdot \longrightarrow \mathrm{Ar\text{-}Ar'} + \mathrm{R\text{-}H}$$

c) <u>The synchronous mechanism</u>

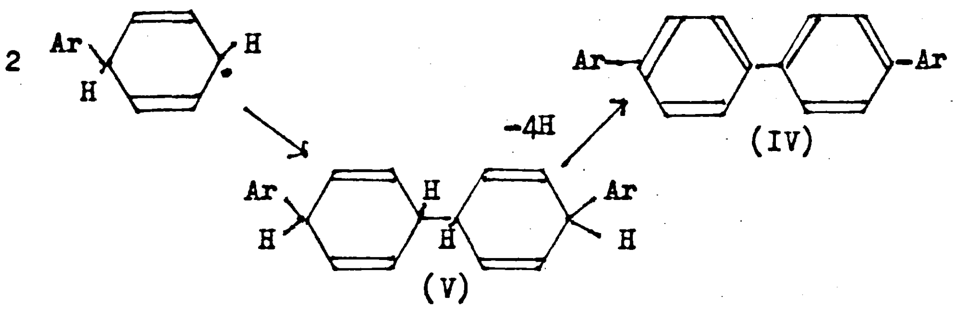
This is a mechanism which involves synchronous approach of the attacking aryl radical and recession of the ejected hydrogen atom.

$$(11) \qquad \mathrm{Ar}\cdot + \mathrm{Ar'H} \longrightarrow \left[\mathrm{Ar'}\begin{array}{l}\cdots\mathrm{Ar}\\ \cdots\mathrm{H}\end{array}\right]\cdot \rightarrow \mathrm{Ar\text{-}Ar'} + \mathrm{H}\cdot$$

Of mechanisms (b) and (c),(c) appears unlikely for two reasons, firstly in view of some of the side-products which have been isolated in the arylation reactions, and secondly mechanism (c) should be subjected to a kinetic isotope effect, whereas in fact the isotope effect is low or nil.

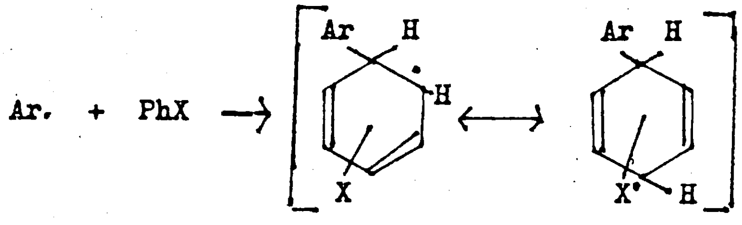
The evidence in favour of mechanism (b) is the existence of the intermediate radical (III) of reaction (10), i.e. arylcyclohexadienyl radical or "σ-complex " which has been postulated independently by Lynch and Pausacker (1957)[26] and by Walling (1957)[27]; the former found *p*-quaterphenyls from the arylation of benzene, whose origin can be most readily explained by assuming that phenylcyclohexadienyl radicals appearing as products of reaction (9) above couple in the canonical form shown to give tetrahydro-*p*-quaterphenyls (IV) which are then dehydrogenated to *p*-quaterphenyls (V).

(12)



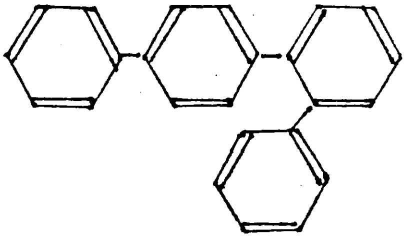
This path to the *p*-quaterphenyls has been confirmed by actual isolation[28] of the 1',4',1",4"-tetrahydro-*p*-quaterphenyl by carrying out the reactions of benzoyl peroxide with benzene at relatively high dilutions. Dimerisation of the σ-complex can also lead to the formation of a number of isomeric and stereoisomeric derivatives of tetrahydroquaterphenyls with union of the nuclei at both 2- and 4-position because of the delocalisation of the unpaired electron. Chemical

(13)



dehydrogenation using tetrachloro-o-benzoquinone[29,30] applied to the total reaction products revealed the isomeric quaterphenyls (V),(VI) and (VII) from the phenylation of benzene with benzoyl peroxide.

(14)



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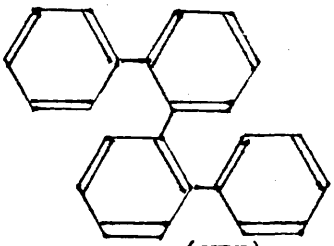
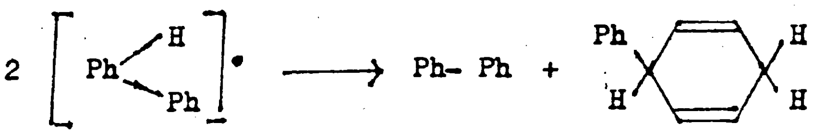


(VII)

Razuvaev, Zateev and Petukhov (1960)[31] allowed benzoyl peroxide to decompose in benzene-1-^{14}C and obtained a small amount of p-terphenyl labelled in only one benzene nucleus, together with a much greater quantity of p,p'-quaterphenyl labelled in two nuclei, thus showing that almost all the tetranuclear products are formed by the dimerisation of σ-complex rather than by further phenylation of biphenyl and terphenyl.

On the other hand, DeTar and Long[28] succeeded in isolating one of the hydroaromatic dimers, as well as 1,4 dihydrobiphenyl (VIII), from the benzoyl peroxide - benzene reaction, using low concentrations of peroxide to ensure the presence of insufficient oxidising agent, for the dehydrogenation of the σ-complex. Dihydrobiphenyl is one of the products of disproportionation of the phenylcyclohexadienyl radical (equation 15), thus proving the existence of phenylcyclohexadienyl

(15)



(VIII)

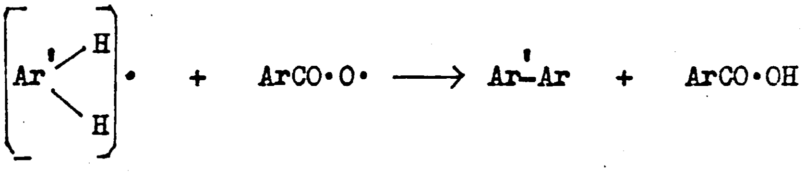
radical which behaves as a perfectly normal free-radical with sufficient resonance stabilisation in the cyclohexadienyl system for reaction with solvent benzene to be energetically unfavourable. Moreover the direct observation of substituted cyclohexadienyl radicals by e.s.r. in a flow system[32] further supports the above conclusion.

Although mechanism (b) proved to be the most likely one, it presents at least two questions, One is whether or not equation (9) is freely reversible; the other is the nature of the hydrogen-abstracting agent "R" in equation (10).

In general the lack of a kinetic isotope effect is used to substantiatr the irreversibility of equation (9). An isotope effect will be observed if either the reversal of the addition step or the step forming side-products competes with the hydrogen abstraction step. This test has been applied by Milytinskaya, Bagdasaryan and Izrailevich (1957)[33] to the arylation of some deuterated aromatic compounds, by measurement of deuterium content of the biaryl, by Convery and Price (1958)[34] to the phenylation of 2,4-dinitrotritiobenzene and by Chag Shih, Hey and Williams (1959)[35], who decomposed benzoyl peroxide in tritiobenzene. All above results indicated that there was no isotope effect within experimental error. Eliel, Meyerson, Welvart and Wilen (1960)[36] who decomposed a variety of peroxides in benzene-d and benzene-benzene-d_6 mixture found that in some peroxides the isotope effects calculated from product deuterium content are in excess of unity. However the benzene-benzene-d_6 mixture recovered from a chlorophenylation remained unchanged in isotopic composition, indicating that the addition of chlorophenyl radical to benzene to form an arylcyclohexadienyl radical is not freely reversible under the conditions of arylation. The product isotope effect is, therefore, ascribed to a competition between arylcyclohexadienyl radicals which go on to produce biaryl and radicals which are diverted into side product (such as dimers), this competition being subject to isotopic discrimination. However Kobayashi and co-workers[37] have reported that aromatic phenylation in DMSO (dimethyl sulphoxide) at room temperature does exibit a significant isotope effect which may reflect some unsuspected effect of DMSO on free-radical behaviour.

The nature of the hydrogen-abstracting reagent "R" has been quite puzzling. Since it is known that the arylation of benzene with a peroxide $(ArCO\cdot O)_2$ gives much acid ArCO·OH and little hydrocarbon ArH, it appeared that "R" is lagely ArCO·O· rather than Ar· . However this seemed rather strange, as it was not clear why so many ArCO·O· radicals should "wait around" for reaction (9) to occur so that they can then participate in reaction (10). A "cage process"[38] involving geminate Ar· and ArCO·O· reacting co-operatively with substrate has been suggested as a possibility.

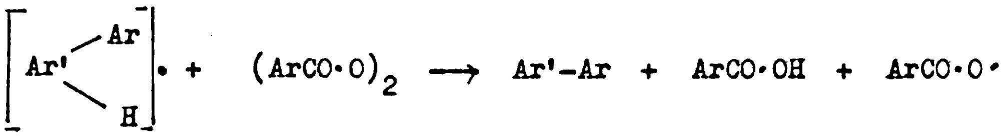
(16)



$$\left[\mathrm{Ar'}\!\langle^{H}_{H}\right]\cdot \;+\; \mathrm{ArCO\cdot O\cdot} \longrightarrow \mathrm{Ar'\!-\!Ar} \;+\; \mathrm{ArCO\cdot OH}$$

Gill (1963)[39] demonstrated that reaction (16), if it occurs at all, does not account for more than 5% of the products of the reaction in benzene.

An alternative is that "R" in reaction (10) is not actually ArCO·O· atall, but an induced decomposition involving diaryl peroxide occur[40,41]. The stoicheiometry of this reaction is represented by the equation (17): -

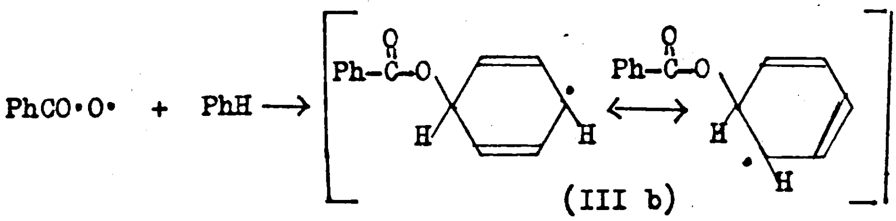
(17) 

$$\left[Ar'\langle^{Ar}_{H}\right]\cdot + (ArCO\cdot O)_2 \longrightarrow Ar'\text{-}Ar + ArCO\cdot OH + ArCO\cdot O\cdot$$

(2) Benzoyloxylation

Hey, Perkins and Williams (1964)[42] who decomposed benzoyl peroxide in benzene at varying initial peroxide concentration, showed the marked variation in the yields of some products over in the low concentration ranges. Extrapolation to infinite dilution, when no induced decomposition can occur, suggests that in such circumstances the yield of benzoic acid would be zero, and the yield of biphenyl and dihydrobiphenyl are equal, at a value of 0.24±0.04 mole/mole peroxide. This means that under such circumstances biphenyl and dihydrobiphenyl are formed almost exclusively by reaction (15). Small quantitues of some of these products accompanied the phenyl benzoate, whose extrapolated yield at zero peroxide concentration is about 0.03 mole/mole peroxide. Davies, Hey and Williams (1961)[43] showed that the formation of phenyl benzoate could occur by either :

(i) Aroyloxylation of benzene in steps analogous to equation (9) and (10) but with Ar• replaced by PhCO•O• . In this case, the first step may be reversible[44], or

(18) 

(III b)

(19) (III b) $\longrightarrow$ PhCO•OPh

(ii) Decomposition of the peroxide induced by a benzoyloxy-radical :

$$(20)\quad PhCO{\cdot}O{\cdot} + (PhCO{\cdot}O)_2 \longrightarrow CO_2 + PhCO{\cdot}OPh + PhCO{\cdot}O{\cdot}$$

Evidence for a duality of mechanism of ester formation comes from analogy with reactions of benzoyl peroxide with substituted benzenes, when unsubstituted phenyl benzoate accompanied the benzoyloxylation products. The relative importance of these different pathways to phenyl benzoate may vary to different extents with peroxide concentration.

At infinite dilution the remainder of the peroxide may de accounted for as tetrahydroquaterphenyls. Thus, at infinite dilution, the reagent is almost entirely accounted by processes (4),(5),(9),(12) and (15).

At finite concentrations, the variations in yields of products, other than phenyl benzoate, must be considered in conjunction with the increasing incidence of induced decomposition of the peroxide. The variation in the rate from one solvent to another is due to different chain termination.

The chain-termination which is most common for the decomposition of benzoyl peroxide is the dimerisation and disproportionation of σ-complexes, and it occurs in benzene[45], alkylbenzenes[41], fluorobenzene[46] and chlorobenzene[47] at low initial concentration of peroxide. This type of chain-termination gives two concurrent reactions of order 1 and 1.5 in peroxide respectively :

$$(21)\qquad -d[P]/dt = k_1[P] + k_2[P]^{3/2}$$

where P is the peroxide, and k_1 and k_2 are constants. The term $[P]^{3/2}$ arises from the induced decomposition; such a rate relationship may be deduced for a reaction scheme involving (4).(5),(9),(12),(15) and (17).

The chain-termination by combination of two similar radicals which are formed directly from the peroxide i.e. two benzoyloxy-radicals leads to 0.5 order chain reaction (22).

$$(22) \qquad -d[P]/dt \;=\; k_1[P] + k_3[P]^{1/2}$$

This type of termination however is most unlikely for the decomposition of benzoyl peroxide, since the stationary concentration of benzoyloxy-radical is low compared with σ-radical.

Another type of chain termination is by combination of two dissimilar radicals, such as a σ-complex and a benzoyloxy-radical as in reaction (16), and leads to a first order chain reaction (23), which

$$(23) \qquad -d[P]/dt \;=\; k_1[P] + k_1'[P]$$

is observed in the decomposition of benzoyl peroxide in bromobenzene at all peroxide concentrations, and in chlorobenzene at high peroxide concentration[47].

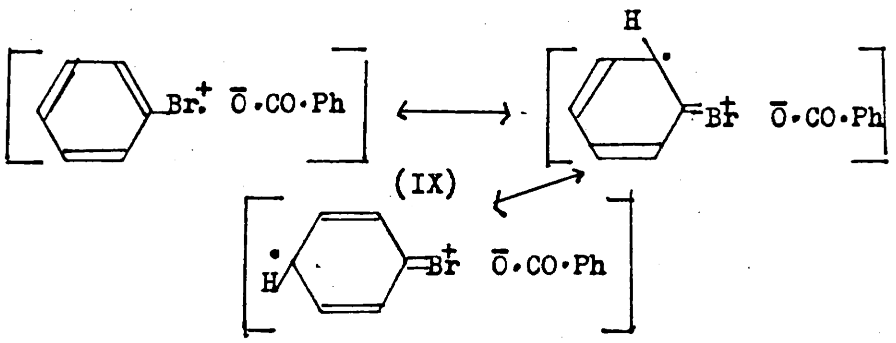
The overall reaction of benzoyl peroxide in chlorobenzene can be represented as equation (24): -

$$(24) \qquad -d[P]/dt \;=\; k_1[P] + k_2[P]^{3/2} + k_1'[P]$$

where at low concentration of peroxide i.e. $\mathrm{IPI}_0 \leqslant 0.11$M, the decomposition is of 1.5 order, whereas at higher concentration $\mathrm{IPI}_0 \geqslant 0.12$M the decomposition becomes first order, although the kinetic analysis is probably insensitive to intermediate reaction order, particularly if the difference from either limiting value is small. In any case, it indicates a change in the termination reaction from (12) and (15) to (16) at this concentration. The formation of dihydrobiphenyls and a large yield of residue at low $[PI]_0$ is consistent with the prediction, from the kinetics, that termination is entirely by reaction (12) and (15). On the other hand, the decomposition in bromobenzene obeys the first order law for the induced reaction at all peroxide concentrations, and the product analysis showes the low yield of residue and the apparent absence of dihydrobiaryls, indicating that the reactions (12) and (15) are unimportant in this solvent. Also, the high biaryl and benzoic acid yields indicate that these products are formed in both propagation (17) and termination (16) reactions. However the decrease in biaryl yield at low $[PI]_0$ values indicates that at these concentrations, reactions (12) and (15) assume some minor importance.

The main differences in behaviour of fluorobenzene, chlorobenzene and bromobenzene were thought to arise from the increases in stationary concentration of benzoyloxy-radicals along this series which was caused by the increasing extent of the formation of charge-transfer complexes of type (IX) between these radicals and the solvent. Such

(25)



(IX)

complexes are formed more readily with bromobenzene because the stability of these complexes should vary in the order $PhF < PhCl < PhBr$, since the electropositivity and polarisability of halogens vary in this sense. Therefore on this basis it would be predicted that the reaction in iodobenzene should be analogous to that in benzene. While the kinetics of the reaction in iodobenzene have not been investigated, the low yield of residue which is formed in this reaction[48] supports this view.

Hence the study of kinrtics and product analysis for the reaction between benzoyl peroxide and benzene led to the sequence of reaction shown bellow.

(a) $(PhCO{\cdot}O)_2 \longrightarrow 2\ PhCO{\cdot}O{\cdot}$ (26)

(b) $PhCO{\cdot}O{\cdot} \longrightarrow Ph{\cdot} + CO_2$

(c)* $PhCO{\cdot}O{\cdot} + PhH \longrightarrow [PhCO{\cdot}OPhH]{\cdot}$

(d) $Ph{\cdot} + PhH \longrightarrow [PhPhH]{\cdot}$

(e)* $PhCO{\cdot}O{\cdot} + (PhCO{\cdot}O)_2 \longrightarrow PhCO{\cdot}OPh + CO_2 + PhCO{\cdot}O{\cdot}$

(f) $Ph{\cdot} + (PhCO{\cdot}O)_2 \longrightarrow PhCO{\cdot}OPh + PhCO{\cdot}O{\cdot}$

(g)* $[PhCO{\cdot}OPhH]{\cdot} + (PhCO{\cdot}O)_2 \longrightarrow PhCO{\cdot}OPh + PhCO{\cdot}OH + PhCO{\cdot}O{\cdot}$

(h) $[PhPhH]{\cdot} + (PhCO{\cdot}O)_2 \longrightarrow Ph{-}Ph + PhCO{\cdot}OH + PhCO{\cdot}O{\cdot}$

(i)* $[PhCO{\cdot}OPhH]{\cdot} + PhCO{\cdot}O{\cdot} \longrightarrow PhCO{\cdot}OPh + PhCO{\cdot}OH$

(j)* $[PhPhH]{\cdot} + PhCO{\cdot}O{\cdot} \longrightarrow Ph{-}Ph + PhCO{\cdot}OH$

(k)* $2\ [PhCO{\cdot}OPhH]{\cdot} \longrightarrow PhCO{\cdot}OPhH_2 + PhCO{\cdot}OPh$

(l) $2\ [PhPhH]{\cdot} \longrightarrow PhPhH_2 + Ph{-}Ph$

(m)* $2\ [PhCO{\cdot}OPhH]{\cdot} \longrightarrow (PhCO{\cdot}OPhH)_2$

(n) $2\ [PhPhH]{\cdot} \longrightarrow (PhPhH)_2$

* indicates reactions which are of minor importance, because of the low stationary concentration of benzoyloxy-radical in bemzene.

C. Nature of Phenyl and Benzoyloxy Radicals

In an investigation with phenyl radical prepared by the reaction between sodium and iodobenzene in a variety of matrices at 77°K. Bennett, Miles and Thomas (1965)[123] have revealed that the unpaired electron remains in the sp^2-orbital of the carbon atom at which bond scission has occured, also the e.s.r. spectrum of phenyl radical has coupling constants with ortho-. meta- and para-protons are about 1.8, 0.6 and 0.2 mT[124] respectively. This contrasts with situation for π-radicals where delocalisation leads to the splitting constants being the order : para $>$ ortho $\gg$ meta. The mechanism of interaction in the phenyl radical must involve the sigma-bonds of the aromatic nucleus. This lack of resonance stabilisation is reflected in the high reactive nature of the phenyl radical.

The near zero ρ values of the meta -and para - position of the Hammett slope[125] (0.09 for meta-, 0.31 for meta and para together) indicate the almost neutral nature of phenyl radicals. This is because phenyl radical is of a σ-type and poor polar character, the transition state for phenylation would be therefore more similar to a σ-complex, with very slight contribution of polar forms. On the other hand, benzoyloxy radicals are electrophilic in nature[126].

D. Quantitative Studies of Phenylation

(a) Competitive reactions

If it is assumed that the formation of a σ-complex is the rate determining step, then the relative rates of substitution at various sites in the substrate molecule are reflected by experimentally determined partial rate factors.

When benzoyl peroxide is allowed to decompose in a monosubstituted derivative of benzene, the homolytic phenylation process produces a mixture of three monosubstituted biphenyls. The partial rate factors may be denoted by F<u>o</u>–, F<u>m</u>– and F<u>p</u>–, which can be defined as numerical expressions of reactivity at the <u>o</u>–, <u>m</u>– and <u>p</u>– positions respectively in the monosubstituted benzene derivative, compared with the reactivity of any one position in benzene.

These factors can be determined by the analysis of the substitution products, firstly, from the ratio of the total rate of substitution in the monosubstituted substrate compared to that in benzene, given by $\frac{PhX}{PhH} K$, and secondly, from the relative proportions in which the <u>ortho</u>–, <u>meta</u>– and <u>para</u>– isomers are formed in the arylation of the monosubstituted benzene. Expressions leading to the partial rate factors for monosubstituted benzene are given below:

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

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

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

where ω, μ and π are the isomer ratios for the <u>ortho</u>–, <u>meta</u>– and <u>para</u>– isomers respectively.

The method of determining relative rates is based on the competition between two substrates present in large excess, and the extent to which the group present in the substitution product originating from the substrate permits calculation of the rate ratio.

Such work has received careful attention from Hey, Williams and co-workers in England, DeTar[130], Dannley[49–52] and Rondestvedt[117], and their co-workers in America, Huisgen and his school in Germany[131] and Simamura[132] in Japan.

Table (1) illustrates a number of results obtained by decomposing benzoyl peroxide at 80° in a number of simple aromatic substrates.

Table (1)

Relative rates and partial rate factors for the phenylation of aromatic compound with benzoyl peroxide at 80°.

Substrates	Relative Rate (PhH = 1)	Isomer Ratio (%)			Partial Rate Factors		
		o-	m-	p-	Fo	Fm	Fp
$PhNO_2$	2.94	62.5	9.8	27.7	5.7	0.86	4.9
PhF	1.03	54.1	30.7	15.2	1.7	0.95	0.86
PhCl	1.06	50.1	31.6	18.3	1.6	1.00	1.2
PhBr	1.29	49.3	33.3	17.4	1.9	1.3	1.3
PhI	1.32	51.7	31.6	16.7	2.0	1.3	1.3
PhMe	1.23	66.5	19.3	14.2	2.5	0.71	1.0
PhEt	0.90	53	28	19	1.4	0.76	1.0
$PhPr^i$	0.64	31	42	27	0.6	0.81	1.0
$PhBu^t$	0.64	24	49	27	0.46	0.94	1.0
PhPh	2.94	48.5	23.0	28.5	2.1	1.0	2.5
PhCN	3.37	60	10	30	6.5	1.1	6.5

From above table, it can be seen that neither the ratio nor the partial rate factors differ greatly from unity, and in the absence of steric factors, all substituents activate the nucleus slightly towards attack by phenyl radicals, quite independently of their polar characteristics.

Although all three isomers are formed in appreciable amounts, again in the absence of steric effects, the *ortho-* isomer is formed in greatest amount. For compounds containing the strongly activating groups, i.e nitrobenzene, benzonitrile and biphenyl, the partial rate factors for the *ortho-*, and *para-* positions are considerably higher than that of the *meta-* position, which is close to unity in all three cases. Thus it is the *ortho-* and *para-* positions which are mainly affected by the above mentioned groups. In the other compounds, again in the absence of steric effects, all the partial rate factors are fairly close to unity, that for the *ortho-* position being the highest, and for the *meta-* position usually being the lowest. However the selective transmission of the activation to the *ortho-*, and *para-* positions appears to be less marked than with the strongly activated compounds.

(b) Validity of partial rate factors.

The assumption made in the formation of partial rate factors is that the rate of the formation of binuclear products is directly related to the rate of formation of the various σ- complexes. The validity of this assumption could not be contested, if the phenylation reaction proceeds in one step, but as shown before the reaction proceeds in two steps. Thus if the σ- radicals are not all oxidised to biaryl and selectively diverted from direct oxidation e.g. by dimerisation or disproportionation of σ- complexes to other non-biaryl products, this will render the fundamental assumption no longer valid.

This postulation has been previously criticised but no definite conclusions have been drawn.

Eliel Meyerson and Wilen (1960)[36] have questioned the validity of partial rate factors as a true measure of reactivities at various positions in aromatic rings, and as a result of their work with deuterated benzene some isotopic discrimation was revealed, and attributed to the competition between the reaction involving hydrogen abstraction from the σ– complexe and side reactions leading to non-biaryl products.

Walling (1957)[27], Lynch and Pausacker (1957)[26] previously criticised the concept without experimental evidence and subsequently further doubts were raised on the true validity of partial rate factors by Eberhardt and Eliel (1962)[55], who found that the presence of oxygen trebled the yield of biaryl.

(i) Effect of oxygen

Morrison, Cazes, Samkoff and Howe (1962)[56] investigated the effect of oxygen further and proposed a general mechanism based on having oxygen present during the decomposition of benzoyl peroxide in an aromatic solvent

$$\begin{array}{llcll}
(a) & (ArCO\cdot O)_2 & \longrightarrow & 2\ ArCO\cdot O\cdot & \\
(b) & ArCO\cdot O\cdot & \longrightarrow & Ar\cdot \ + \ CO_2 & \\
(c) & Ar\cdot \ + \ Ar'H & \longrightarrow & [ArAr'H]\cdot & \\
(d) & [ArAr'H]\cdot \ + \ \text{ox. agent} & \longrightarrow & Ar\text{–}Ar' & (27) \\
(e) & 2[ArAr'H]\cdot & \longrightarrow & (ArAr'H)_2 & \\
(f) & 2[ArAr'H]\cdot & \longrightarrow & ArAr'H_2 \ + \ Ar\text{–}Ar' & \\
(g) & ArAr'H_2 \ + \ \text{ox. agent} & \longrightarrow & Ar\text{–}Ar' &
\end{array}$$

The presence of oxidising agents is seen as increasing the reaction rates of steps (d) and (g), at the expense of steps (e), (f) and other side reactions. The result is that more benzoyloxy-radicals are available for subsequent phenylation.

In a systematic attempt to clarify the situation Morrison and co-workers re-determined the partial rate factors in a number of aromatic systems both in the presence and absence of oxygen.

Their results are shown in Table (2), and it clearly showed that although the presence of oxygen increased the conversion of arylcyclohexadienyl radical to biaryl by as much as three fold, there was no significant change in the isomer ratios or relative reactivities. Thus, on this bases it can be said that the side reaction of σ- complexes are non-selective and the rate data in the absence of oxygen do provide reliable information concerning the relative reactivities at the o-, m- and p- sites towards homolytic arylation.

Table (2)

Arylation of C_6H_5X in Presence and absence of oxygen

Substrate	Oxygen	Yield of Biaryl m/m peroxide	Isomer Ratio (%) o-	m-	p-	Total Rate PhH = 1
PhOMe	-	0.50	69.8	14.7	15.6	1.99
PhOMe	+	1.35	69.8	14.5	15.8	2.01
PhBr	-	0.33	56.2	27.3	16.5	1.14
PhBr	+	1.58	55.2	28.8	16.0	1.11
$PhNO_2$	-	0.19	63.2	9.7	27.1	2.95
$PhNO_2$	+	0.68	62.8	9.7	25.7	2.89

It is known that phenyl radicals are not very reactive towards oxygen[127]. Therefore the oxygen is thought to abstract hydrogen from σ- intermediate, presumably by the formation of a hydroperoxide radical, which could bring about the oxidation of another σ- radical.

$$\begin{array}{ll} (a) & PhC_6H_6 + O_2 \longrightarrow Ph\cdot C_6H_6 + HO_2 \\ (b) & PhC_6H_6 + HO_2 \longrightarrow H_2O_2 + Ph\cdot C_6H_6 \end{array} \qquad (28)$$

Hydrogen peroxide has been detected in these reactions [128]. Theoretically two moles of biphenyl per mole of benzoyl peroxide could be formed in the presence of oxygen. The benzoic acid formed in this reaction is unaffected by oxygen. Some phenol is also formed in this reaction, with higher yields at lower temperature[128].

The above observation is attributed to the higher solubility of the gas at lower temperature and more efficient trapping of phenyl radicals by it.

$$Ph\cdot + O_2 \longrightarrow Ph\cdot O\cdot O\cdot \longrightarrow PhOH \qquad (29)$$

(ii) Effect of nitro-compounds and electron acceptors

The effect that the presence of nitro-compound in reactions involving benzoyl peroxide as phenylating source increases the yield of biaryl was first brought to attention by Auggod and Williams (1957)[57]. It was later shown that only a catalytical amount of nitro-compound was necessary and while the yields of biaryl and aroic acid were greatly increased, the formation of residues and dihydrobiaryls were greatly suppressed and the nitro-compound was almost totally recoverable at the completion of the reaction.

The results of the effect of nitro-compounds on the decomposition of benzoyl peroxide in benzene are given in Table (3).

Table (3)

Yields of benzoic acid and biphenyl from the decomposition of 1g. of benzoyl peroxide in 100ml. of benzene at 80° in presence of additive.

		Yield (m/m peroxide)	
Additives (mg)		Benzoic acid	Biphenyl
$PhNO_2$	(100)	0.75	0.65
$PhNO_2$	(300)	0.93	0.83
PhNO	(12)	0.92	0.86
PhNH OH	(7)	0.99	0.88
PhNH OH	(20)	0.96	0.78
PhN(NO)Me	(100)	0.53	0.61
Nil		0.22	0.36

Although the above phenomenon is explicable in terms of the nitro-compound being a "hydrogen atom carrier"[100] it has been shown that the effective catalyst is the corresponding nitroso-compound[101], which is formed by reduction of the nitro-compound.

$$\begin{array}{lllll}
\text{(a)} & PhNO + Ph\cdot & \longrightarrow & Ph_2NO\cdot & \\
\text{(b)} & Ph_2NO\cdot + [PhArH]\cdot & \longrightarrow & Ph\text{–}Ar + Ph_2N\cdot OH & \\
\text{(c)} & Ph_2N\cdot OH + (PhCO\cdot O)_2 & \longrightarrow & PhCO\cdot O\cdot + PhCO\cdot OH + Ph_2NO & (30) \\
\text{(d)} & Ph_2N\cdot OH + PhCO\cdot O\cdot & \longrightarrow & PhCO\cdot OH + Ph_2NO &
\end{array}$$

In whatever capacity the nitro-group operates, its application can be used to test the validity of the assumption concerning the fate of the σ- complexes. This involves the measurement of the isomer ratios formed from a given substrate in the presence of nitro-compound.

Hey, Perkins and Williams (1963)[58] applied in the case of fluorobenzene, their results which are given in Table (4) indicate that the ratio of isomers is not seriously affected by residue formation. and the yield of biaryl being increased from 0.48 to 0.8 of a mole per mole of peroxide used

Table (4)

Isomeric fluorobiphenys obtained from the decomposition of benzoyl peroxide (3g) in fluorobenzene (100ml).

Substrate	Yield of Fluorobenzene (m/m peroxide)	Isomer Ratio o -	m -	p -
None	0.48	54.1	30.7	15.2
m-Dinitrobenzene (0.5g)	0.8	53.8	32.6	13.6

Other electron acceptors also catalyse the oxidation of σ- complexes by producing benzoyloxy-radicals.

Reaction between benzoyl peroxide and benzene in the presence of a number of electron acceptor molecule have been reported by Hall[59]. The results on Table (5) show that all the electron acceptors with the exception of nitromethane bring about a large increase in the yield of biphenyl and benzoic acid, but there appears to be no simple relationship between the effectiveness of the additives and their electron affinities.

Table (5)

Effect of additives on the decomposition of benzoyl peroxide in benzene at 80°.

Electron Acceptor X	Concentration of X (mole/lit.x10^3)	Concentration of Peroxide (mole/lit.x10^2)	Product Biphenyl (mole/mole Peroxide)	Product Benzoic Acid (mole/mole Peroxide)
None	-	8.33	0.28	0.42
None	-	5.50	0.28	0.50
Nitrobenzene	10.7	8.33	0.70	0.67
m-Dinitrobenzene	8.0	8.33	0.92	0.9
sym-Trinitrobenzene	6.7	5.50	0.95	0.94
Nitromethane	22.0	8.33	0.30	0.28
Tetranitromethane	6.7	5.50	0.69	0.77
Tetracyanoethylene	10.7	8.33	0.74	0.85
p-Chloranil	6.7	5.50	1.00	0.96
p-Chloranil	5.5	8.33	0.92	0.75
Iodine	6.7	5.50	0.54	0.61

(iii) The effect of transition metal ions.

Since Sandmeyer in 1884 observed that aryl halides could be produced by the cuprio halide reduction of aryl diazonium salts, there has been considerable interest in the use of metal salts, both as reactants and catalysts, in organic chemistry. In the free-radical field, oxidation-reduction systems comprising peroxides and salts of metals exhibiting variable valency are well known as vinylic polymerisation initiators. The free radicals produced in such systems can react with the solvents, or can dimerise, disproportionate or be oxidised or reduced by the metal ions, the peroxide themselves can undergo rearrengements or can react catalytically with the solvent.

Böeseken (1925)[50] studied the effects of aluminium chloride and ferric chloride on the decomposition of benzoyl peroxide in benzene, and observed that the aluminium salt (1 mole) caused reaction at 0^{o} to produce one mole of benzoic acid, one mole of phenyl benzoate and no carbon dioxide per mole of peroxide. He suggested that the reaction took place according to equation (31).

$$(31)\quad (C_6H_5CO{\cdot}O)_2 \; + \; C_6H_5(AlCl_3)_3 \longrightarrow C_6H_5CO{\cdot}OH \; + \; C_6H_5CO{\cdot}OC_6H_5$$

The best known example of the use of metal salts to generate free radicals is the use of Fenton's reagent as a mild oxidising agent. The mechanism of the catalytic decomposition of hydrogen peroxide by iron salts has been postulated by Haber and Weiss[61] to involve as one of the chain carrying steps one-electron reduction of the peroxide by ferrous salt :-

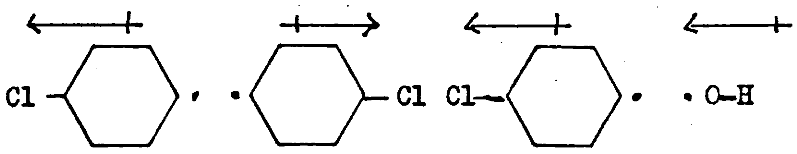
$$(32)\quad ROOH \; + \; Fe^{2+} \longrightarrow HO{\bullet} \; + \; OH^- \; + \; Fe^{3+}$$

Merz and Waters (1949)[62] and later Coffman (1958)[63] used Fenton's reagent in aqueous solution, to bring about the dimerisation of free radicals formed by the action of hydroxy-radicals on monofunctional aliphatic and aromatic compounds. Under appropriate condition of dilution and pH, a wide variety of compounds undergo oxidative coupling by hydroxy-radicals at ordinary temperatures. In this process the abstraction of hydrogen atom (not necessarily activated) bound to carbon is followed by the dimerisation of the radicals so formed : -

$$\begin{array}{llcl} \text{(a)} & RH + HO\cdot & \longrightarrow & R\cdot + H_2O \\ \text{(b)} & R\cdot + H_2O_2 & \longrightarrow & ROH + \cdot OH \\ \text{(c)} & R\cdot + HO\cdot & \longrightarrow & ROH \\ \text{(d)} & 2R\cdot & \longrightarrow & R-R \end{array} \qquad (33)$$

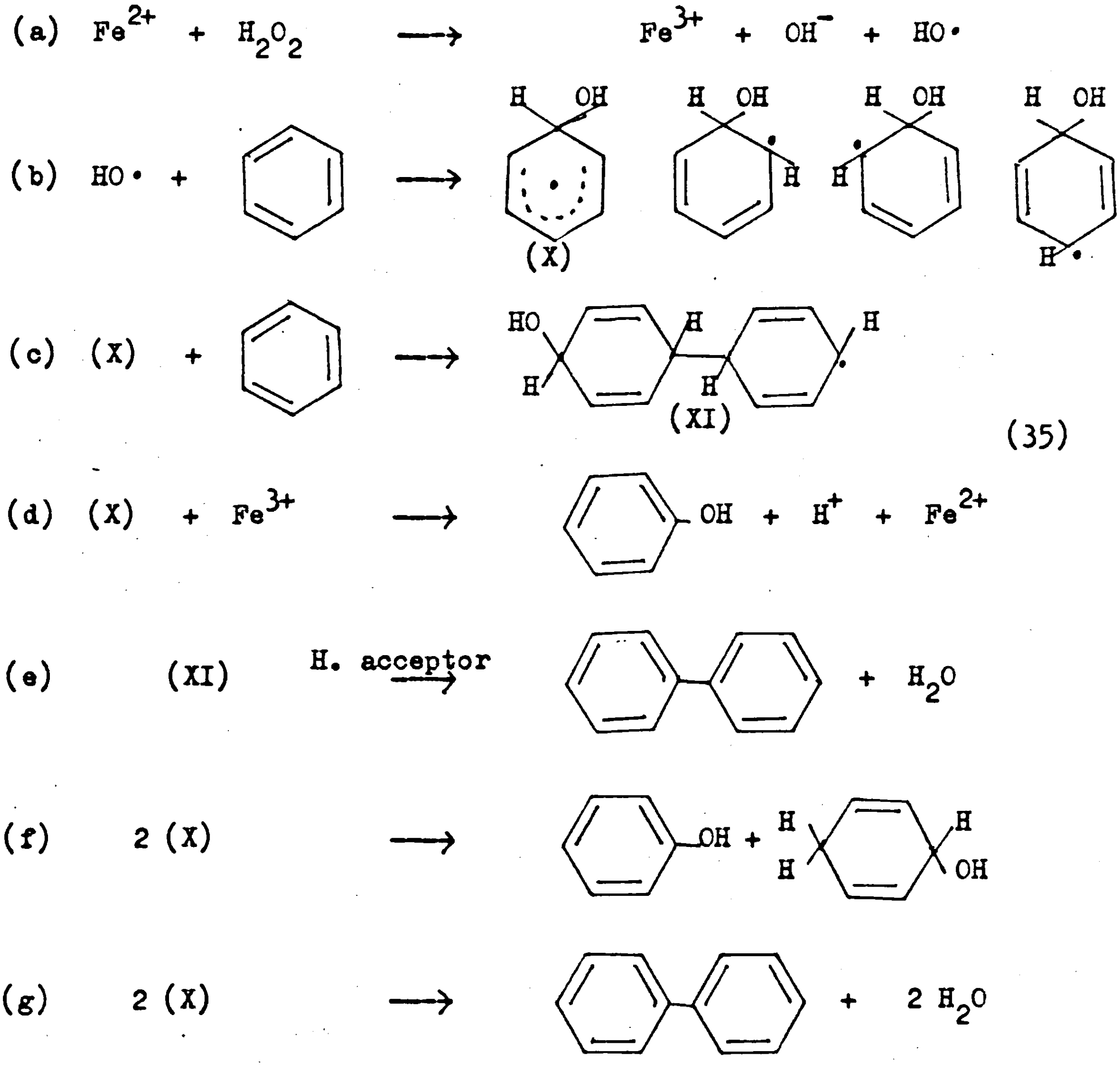
In this way biphenyl was obtained by benzene and bibenzyl from toluene together with the respective phenols, but no biaryls were detected in the corresponding reactions with chlorobenzene and nitrobenzene. This was attributed to the fact that the radicals generated in both cases would be dipoles, owing to their substituents, and that their combination in pairs would have to overcome electrostatic repulsions between like charges, a circumstance which would not arise in their reactions with hydroxy radicals.

(34)



Such reactions with Fenton's reagent were shown not to be chain reactions, and each mole of reacted aliphatic or aromatic compound required one mole of hydroxy radicals.

The oxidation of benzene and toluene by Fenton's reagent was re-investigated in some detail by Smith and Norman (1963)[64] and the conclusion was drawn that free radicals were not produced in these reactions, owing to the absence of a hydrogen isotope effect in the formation of both phenol and biphenyl when benzene and hexadeuterobenzene are separately oxidised. In the suggested mechanism, a hydroxyl-radical first adds to benzene to form a resonance-stablized adduct (35b), which then dimerises (35g) disproportionates (35f), or is oxidised by ferric ion or oxygen to produce the final products biphenyl (35e) and phenol (35d)



(35)

Kharasch and his students[65] in a series of papers beginning in 1958 found that traces of copper usually as cuprous chloride or bromide, and to some extent other transitional metals, profoundly altered the couse of reaction between organic peroxide and a variety of organic substrates. In the reaction of benzoyl peroxide with olefins, he showed that, in the presence of cuprous salts, the tary residue is greatly decreased. The vield of benzoic acid is enhanced and there is an increase in the degree of unsaturated adduct obtained. This suggested that cuprous salts facilitated the termination reaction. With hindsight, these observations were explicable by the oxidation of the radical by copper salts. From these studies, Kharasch arrived at the conclusion that a carbon radical could form a free radical complex with oxygen, nitrogen, hydrogen and even with a carbon-hydrogen bond in the presence of a copper salt.

(36) $R\cdot + R'H + Cu^{+} \longrightarrow [CuRR'H]^{+\cdot}$

Recently, Kochi[66] has classified the oxidation effected by metal salt into ligand-transfer(a) and electron-transfer (b) by analogy with inner sphere and outer sphere mechanism developed by Taube[104] to describe redox reaction in inorganic systems.

(a) $R\cdot + CuCl_2 \longrightarrow RCl + CuCl$

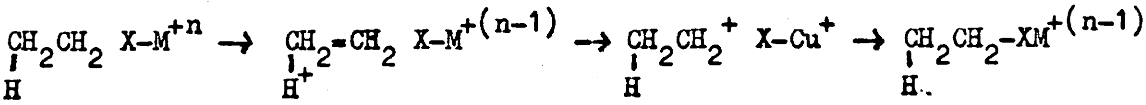
(b) $R\cdot + Cu^{2+} \longrightarrow R^{+} + Cu^{+}$

Ligand transfer mechanisms involve transfer of a group or an atom e.g. chlorine in (a) from the metal complex to the radical through a bridge transition state. Halides and pseudohalides are good transfer agents, sulphate and perchlorate are not good bridging ligans, while carboxylate, alkoxide and hydroxide are of intermediate activity[69]. The metal ions Fe(III), Cr(VI), Pt(IV) and Pb(IV) have been used in the preliminary studies[66]. The electron transfer mechanism involves a direct transfer of electrons from the radical to the metal ion with the production of a carbonium ion which undergoes subsequent reaction to give stable products. The product composition can also be used to provide evidence of the intermediacy of carbonium ion. Thus the oxidation of cyclobutyl radicals by Pb(IV) gives the same mixture of acetates as thar obtained in solvolysis proceeding the carbonium ion[67].

The ease of oxidation of a radical to a carbonium ion depends on the oxidation potential of both the radical and the oxidant. The oxidation potential of the radical is largely controlled by the ability of the group attached to the tervalent carbon to stabilise the developing positive charge. In accordance with this, p-methoxybenzoyl radicals are much more readily oxidised by Pb(IV) than benzyl radicals[68], owing to the stabilizing effect of the methoxy group on the p-methoxy benzyl cation. Any stabilizing effect the methoxy group had on the radical would be less. These results suggest that there is considerable development of carbonium ion character in the transition state in electron-transfer oxidation of radicals.

Kochi[66] argued that classification of these two processes into discrete categories was arbitrary. It was conceivable that the reactions proceeded through related transition states in which the resonance contributions from electron transfer and ligand transfer varied not only with the structure of the free radical, but also with the identity of the metal species and counter-ion. He proposed the following generalised transition state for these oxidation reactions.

(37)



$$\underset{\displaystyle H}{CH_2}CH_2\ X\text{–}M^{+n} \rightarrow \underset{\displaystyle H^+}{CH_2}\text{=}CH_2\ X\text{–}M^{+(n-1)} \rightarrow \underset{\displaystyle H}{CH_2}CH_2^{+}\ X\text{–}Cu^{+} \rightarrow \underset{\displaystyle H\cdot}{CH_2}CH_2\text{–}XM^{+(n-1)}$$

Walling [67b] has proposed a mechanism for the copper-catalysed reaction of peresters with hydrocarbons similar to that evoked by Kochi.

$$\begin{array}{lllll}
\text{(a)} & CH_3CO\cdot OOBu^t + Cu^+ & \longrightarrow & CH_3CO\cdot O^- + Cu^{2+} + t\text{-}BuO\cdot & \\
\text{(b)} & t\text{-}BuO\cdot + RH & \longrightarrow & t\text{-}BuOH + R\cdot & \\
\text{(c)} & R\cdot + Cu^{2+} & \longrightarrow & R^+ + Cu^+ & (38) \\
\text{(d)} & R^+ + CH_3CO\cdot O^- & \longrightarrow & RO\cdot OC\cdot CH_3 \quad \text{or} & \\
\text{(e)} & R\cdot + Cu^{2+}O\cdot OC\cdot CH_3 & \longrightarrow & RO\cdot OC\cdot CH_3 + Cu^+ &
\end{array}$$

A number of other steps to the sequence would also be involved, to compete with the main sequence, influence its total rate, and account for various by-products. These include thermal decomposition of the original peroxide: -

$$\text{(f)} \quad CH_3CO\cdot O\cdot OC(CH_3)_3 \longrightarrow (CH_3)_3CO\cdot + CH_3CO\cdot O\cdot \longrightarrow CH_3\cdot + CO_2 ,$$

reduction of the intermediate alkoxy-radical: -

$$\text{(g)} \quad (CH_3)_3CO\cdot + Cu^+ \longrightarrow (CH_3)_3CO\cdot + Cu^{2+} ,$$

β-scission of the alkoxy-radical probably followed by oxidation of the resulting methyl-radical: -

$$\begin{array}{ll}
\text{(h)} & (CH_3)_3CO\cdot \longrightarrow CH_3CO\cdot CH_3 + CH_3\cdot \\
 & CH_3\cdot + Cu^{2+} + CH_3CO\cdot O^- \longrightarrow CH_3O\cdot COCH_3 + Cu^+ ,
\end{array}$$

and coupling (or disproportionation) of alkyl radicals: -

$$\text{(i)} \qquad 2R\cdot \longrightarrow R\text{-}R$$

The influence of step 38 (h) is shown by the observation that the reaction of t-butyl perbenzoate in an inert solvent (benzene) yields methyl benzoate in 34% yield[65d].

Catalysis of the reaction by copper salts is inoperative if the peroxide reacts with the cuprous salt in the absence of substrates, which can act as hydrogen donors towards oxy-radicals. In these cases no carbon radical is formed (with the exception of fragmentation products of the oxy-radical), and no route is available for regeneration of cuprous catalyst. The predominant route of the reaction in these circumstances is the thermal decomposition of peroxide[70].

In order to maintain catalysis it is necessary to form intermediates which are oxidised by cupric salts. For every radical termination reaction, such as radical-radical dimerisation which occurs without involving cupric salts, a corresponding peroxide molecule must undergo thermal dissociation. Intermediate cases in which generated radicals are oxidised by cupric salts in competition with their mutual annihilation (or reaction with an oxy-radical) represent mixed thermal and catalytic processes.

The effects of copper benzoate and cobalt naphthenate on the decomposition of benzoyl peroxide in benzene and chlorobenzene have been studied by Hey, Liang and Perkins (1969)[71], and from their results shown in Tables (6) and (7) it can be seen that the yields of biaryl and aroic acid were increased by the presence of additives.

Table (6)

Products from the decomposition of benzoyl peroxide (1g) in benzene (100ml) at 80° in the presence of additives.

Additives (mg)	Biphenyl (m/m peroxide)	Benzoic Acid (m/m peroxide)
Nil	0.36	0.22
Cupric Benzoate (50)	0.88	1.06
Cobalt Naphthenate (130)	0.66	0.92
Copper bronze	0.83	0.90

Table (7)

Products from the decomposition of benzoyl peroxide (1g) in chlorobenzene or an equimolar benzene-chlorobenzene mixture at 80° in the presence of cupric benzoate or air.

Solvent (100ml)	Additive	Products (m/m Peroxide)		Isomer ratio			PhCl/PhH
		Benzoic Acid	Biaryl	*o*-	*m*-	*p*-	
PhCl	Nil	0.42	0.45	53.5	25.8	20.7	—
PhCl/PhH	Nil	not determined	0.46	54.3	24.7	21.0	1.13
PhCl	$(PhCO \cdot O)_2Cu$	″	0.78	58.9	23.1	18.0	—
PhCl/PhH	″	″	0.79	58.0	24.1	17.9	1.47
PhCl	Nil(under air)	0.35	ca. 1.0	55.5	27.3	17.2	—
PhCl/PhH	″	not determined	ca.0.95	55.4	27.4	17.2	1.30

A mechanism analogous to Kochi and Walling's scheme was suggested: -

$$\begin{array}{lll} \text{(a)} & (PhCO \cdot O)_2 + Cu^+ \longrightarrow & PhCO \cdot OCu^+ + PhCO \cdot O \cdot \\ \text{(b)} & PhCO \cdot O \cdot \longrightarrow & Ph \cdot + CO_2 \\ \text{(c)} & Ph \cdot + PhH \longrightarrow & \sigma - \text{complex} \\ \text{(d)} & \sigma - \text{complex} + PhCO\ OCu^{2+} \longrightarrow & Ph\text{-}Ph + PhCO \cdot OH + Cu^+ \end{array} \qquad (39)$$

Kochi and Gillion (1964)[72] have observed the effect of copper acetate on the decomposition of di-*o*-phenylbenzoyl peroxide in acetic acid-benzene solutions which were shown to give almost quantitative yields of *o*-phenyl benzoic acid and benzocumarin, compered with yields of *ca* 40% in the absence of copper ion. No cage or dimerisation products from the decomposition of the peroxide or products of radical chain transfer reactions were observed in the presence of cupric salts.

Benzoyloxylation of toluene by benzoyl peroxide in the presence of cupric chloride have been reported by Kovacic and Kurz[73], with acetanitrile as solvent. Tolyl benzoates were found in fair yield (ca. 0.4 mole/mole peroxide) and the typical electrophilic substitution pattern (56% o-; 18% m-; 26% p-) led to suggestion that the reactive species is $PhCO_2^+$ formed by reaction (40): -

$$(40) \qquad PhCO\cdot O\cdot \; + \; Cu^{2+} \longrightarrow PhCO\cdot O^+ \; + \; Cu^+$$

the full scheme being consistent with following sequence; -

$$\begin{array}{lll} (a) & Cu^+ \; + \; (PhCO\cdot O)_2 \longrightarrow Cu^{2+}O\cdot OCPh \; + \; PhCO\cdot O\cdot & (41) \\ (b) & PhCO\cdot O\cdot \; + \; ArH \; + \; Cu^{2+}O\cdot OCPh \longrightarrow ArO\cdot OCPh \; + \; PhCO\cdot OH \; + \; Cu^+ & \end{array}$$

An alternative path, consisting of reversible attack on the aomatic substrate by a benzoyloxy-radical, with subsequent oxidation of the resulting complex by cupric ion was also observed.

$$(42) \qquad PhCO\cdot O\cdot \; + \; ArH \longrightarrow PhCO\cdot OA\vec{r}H\cdot \xrightarrow{Cu^{2+}} PhCO\cdot OAr \; + \; H^+ \; + \; Cu^+$$

Dailly (1960)[74] carried out the decomposition of benzoyl peroxide in various aromatic solvents, in the presence and in the absence of ferric benzoate, and it was shown that ferric benzoate was, a convenient additive, causing very great increases in biaryl yields. It was suggested that Fe (III) ion catalysed the oxidation of σ-complex by benzoyloxy radicals, hence preventing their dimerisation. The following mechanism was proposed to explain the observed catalytic effect of Fe(III) ion.

$$\begin{array}{lllll}
(a) & (PhCO\cdot O)_2 & \longrightarrow & 2\ PhCO\cdot O\cdot & \\
(b) & PhCO\cdot O\cdot & \longrightarrow & Ph\cdot + CO_2 & \\
(c) & Ph\cdot + PhH & \longrightarrow & [Ph\cdot PhH]\cdot & \\
(d) & [Ph\cdot PhH]\cdot + PhCO\cdot O\cdot & \longrightarrow & PhCO_2H + Ph\cdot Ph & (43) \\
(e) & [Ph\ PhH]\cdot + Fe^{3+} & \longrightarrow & Ph\cdot Ph + H^{+} + Fe^{2+} & \\
(f) & PhCO\cdot O\cdot + Fe^{2+} & \longrightarrow & PhCO\cdot O^{-} + Fe^{3+} & \\
(g) & PhCO\cdot O^{-} + H^{+} & \longrightarrow & PhCO_2H & \\
(h)^{*} & 2[Ph\cdot PhH]\cdot & \longrightarrow & \text{dimerisation and disproportionation products.} &
\end{array}$$

(h)* - plays a very minor part

In an exhaustive survey on the efficiency of transition metal salts to act as traps for organic free-radicals, Kriens[75] came to a number of generalized conclusions.

For the reaction of 2-cyano-2-propyl radical, generated from 2,2'-azo-bis isobutyronitrile, in benzene solution and in the presence of transition metal chlorides, there was apparently no general relationship between the ability of metal salt to trap radicals and its reduction potential or electronegativity. Also the apparent order of ability to produce the aryl halide product was, $Fe^{3+} > Te^{4+} > Sb^{5+} > Cu^{2+} > Mo^{5+} > V^{4+} > Ti^{4+}$ and for the anions, trapping ability decreased in the order, $Br > Cl > SCN > RCO_2 > CN > OCH_3, CH_3$. This order was thought to reflect the ability of the anion to form a ligand bridge in the transition state. Neutral ligands were said to increase the electron density around the metal cation and to improve its ability to form a transient π-complex with the radical involved, these postulates being consistent with the observed trapping efficiency of the series $CuCl_2\cdot 2Py > FeCl_3\cdot 6H_2O > CuCl_2\cdot 2H_2O > FeCl_3 > CuCl_2$.

Kamita and Ingold[76] have studied the catalytic effects of manganese, copper, nickel, and iron decanoates on the autoxidation of tetralin and have observed that the maximum rate of oxidation is proportional to the square root of the catalyst concentrations. This limit was partially controlled by the catalyst solubility. Their results supported the view that chain initiation in these reactions occured by the slow decomposition of a rapidly formed metal catalys-hydroperoxide complex.

E. Other Sources of Benzoyloxy or Phenyl Radicals.

(1) Lead Tetrabenzoate

Hey, Stirling and Williams (1954)[77] showed that lead tetrabenzoate decompose in aromatic solvents at 125–130°C to give products of phenylation of the solvent. The ratio of isomeric nitrobiphenyls formed by phenylation of nitrobenzene with lead tetrabenzoate was close to that obtained with benzoyl peroxide under similar conditions. Phenyl radicals are considered to be formed from lead tetrabenzoate by reactions (44).

$$\begin{array}{llcll} \text{(a)} & Pb(O\cdot CO\cdot Ph)_4 & \longrightarrow & Pb(O\cdot COPh)_2 + 2PhCO\cdot O\cdot & \\ \text{(b)} & PhCO\cdot O\cdot & \longrightarrow & Ph\cdot + CO_2 & \end{array} \qquad (44)$$

(2) Phenyl Iodosobenzoate

Decomposition of phenyl iodosobenzoate in nitrobenzene at 125° has been shown to result in the formation of isomers of nitrobiphenyls, in a ratio similar to that found from benzoyl peroxide at the same temperature[78,79].

$$\begin{array}{llcl} \text{(a)} & PhI(O\cdot CO\cdot Ph)_2 & \longrightarrow & PhI + 2PhCO\cdot O\cdot \\ \text{(b)} & PhCO\cdot O\cdot & \longrightarrow & Ph\cdot + CO_2 \end{array} \quad (45)$$

The detailed studies of the reactions of phenyl iodosobenzoate by Leffer, Mitchell and Menon (1966)[80] showed that although the reaction is in part a radical reaction, it is by no means a simple extension of the reaction of benzoyl peroxide. With chlorobenzene the yield of phenyl benzoate is higher than in the peroxide reaction and the phenyl moiety of the ester comes exclusively from the iodobenzene frgment of the phenyliodoso dibenzoate and not at all from the decarboxylation of the benzoyloxy-groups. It was observed that the presence of water in small amounts catalysed the decomposition of phenyl iodosobenzoate, and both the rate and the amount decomposed in the fast initial reaction, varied according to the amount of water present. Water led to lower yields of biaryl and phenyl benzoate in the products of the reaction.

(3) Silver Halide Dibenzoate

When silver iodine dibenzoate is heated with nitrobenzene or chlorobenzene at 130°, a mixture of nitrobiphenyls or chlorobiphenyls is obtained in about 20% yield[81]. The isomer ratios found in the mixture of chlorobiphenyls correspond closely to that obtained from the reaction of benzoyl peroxide with chlorobenzene. Decomposition in benzene give 25% yield of biphenyl.

$$AgX(O\cdot CO\cdot Ph)_2 \longrightarrow 2PhCO\cdot O\cdot + AgX \quad (46)$$

(4) Electrolysis of Benzoic Acid

$$\begin{aligned} &(a) \quad PhCO{\cdot}O^{-} \longrightarrow PhCO{\cdot}O{\cdot} + e \\ &(b) \quad PhCO{\cdot}O{\cdot} \longrightarrow Ph{\cdot} + CO_2 \end{aligned} \qquad (447)$$

Unfortunary this method does not lend itself easily to phenylation reactions in non-aqueous media, but the reaction has been successfully used in the phenylation of pyridine[82], which gives results in good agreement with those obtained in phenylation reactions by other methods.

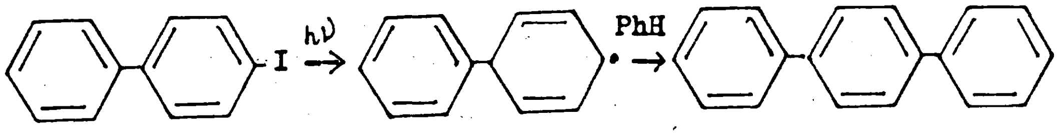
Oxidation of aromatic carboxylic acids has a mechanism allied to that of the electrolysis of aromatic acids, since both processes depend upon the removal of an electron from the carboxylate anion[83,84].

(5) Photolysis of Haloarenes and Organo-Metallic Compounds.

Photolysis of aryl iodides and also aryl bromides in aromatic substrates has been shown by Blair, Bryce-Smith and Pengilly (1959)[85] and Sharma and Kharasch (1968)[86] to generate aryl radicals:

$$ArI \longrightarrow Ar{\cdot} + I{\cdot} \qquad (48)$$

Wolf and Kharasdh (1965)[87] used this technique to prepare p-terphenyl from 4-iodobiphenyl in a yield of 91% :



(49)

In this reaction the yield of p-terphenyl was significantly increased by the presence of oxygen. Photolysis of diphenylmercury, tetraphenyllead, and triphenylbismuth have all been employed to give phenyl radicals[85]. Support for the radical nature of these reactions comes from the isomer distribution of the phenylated products.

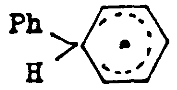
(6) N-Nitrosoacetanilide

The mechanism of the decomposition of this compound has been the subject of much controversy[89,90] because the proposed mechanism fails to take account of the absence of any evidence for the existence of acetoxy radical and absence of hydroaromatic products derived from dimerisation and disproportionation of cyclohexadienyl intermediates. The mechanism generally accepted was that proposed by Ruchardt and Freudenberg[91].

(a) $PhN(NO)Ac \longrightarrow Ph{-}N{=}N{-}OAc \longrightarrow PhN_2^+ + AcO^-$

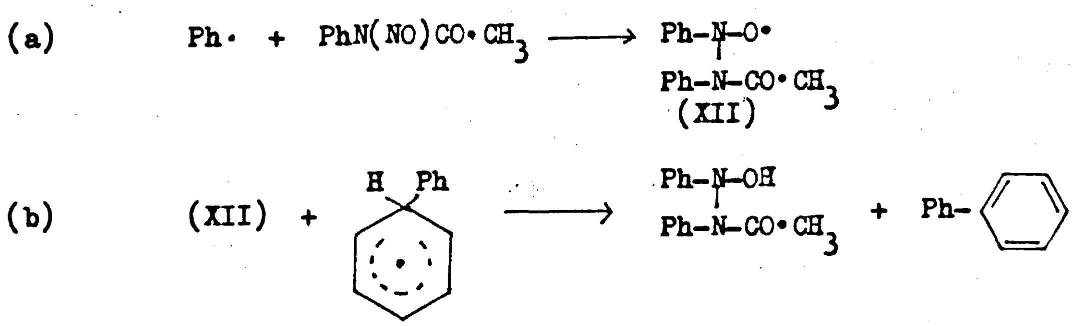
(b) $PhN(NO)Ac + AcO^- \longrightarrow Ph{-}N{-}N{=}N{-}O^- + Ac_2O$

(c) $PhN_2^+ + Ph{-}N{=}N{-}O^- \longrightarrow Ph + N_2 + Ph{-}N{=}N{-}O\bullet$ (50)

(d) $Ph\bullet + PhH \longrightarrow$ 

(e) $[Ph\cdot C_6H_6]\bullet + PhN{-}N{=}N{-}O^- \longrightarrow Ph{-}Ph + Ph{-}N{=}N{-}OH$

The detection of N-(phenylacetamido)phenyl nitroxide radical (XII) by e.s.r. led Perkins and Chalfont[88] to suggest a new mechanism similar to the above scheme, but differing in that N-(phenylacetamido)-phenyl nitroxide radical, formed by addition of phenyl radical to N-nitrosoacetanilide (equation 51) was the key chain carrying radical rather than (phenylazo)oxy radical.



(51)

However, the observation of (phenylazo)oxy radical by e.s.r. together with other evidence, led Cadogan, Paton and Thomson[92] to suggest that the (phenylazo)oxy radical is the more significant chain carrying radical in the decomposition of acylarylnitrosolamine in such solvent.

(7) Aryl Diazonium Salts

Aryl radicals can also be generated from diazonium salts by use of the Gomberg reaction, in which sodium hydroxide is added to a vigorously stirred solution of the cold diazonium salt and the aromatic substrate[133]. This reaction was believed to involve formation of the covalent diazo hydroxide which decomposed to give aryl and hydroxy radicals:-

(52) $$Ar_2^+ + OH^- \longrightarrow Ar{-}N{=}N{-}OH \longrightarrow Ar\cdot + N_2 + HO\cdot$$

Ruchardt and Merz[93] have suggested, however, that the reaction follows an anologous sequence to that proposed for the decomposition of N-nitrosoacetanilide. A somewhat clear modification of the Gomberg reaction, developed by Hey, involves the use of sodium acetate instead of sodium hydroxide, The Gomberg and Gomberg-Hey procedures suffer from the disadvantage that a heterogeneous system is used. This can be overcome by diazotizing the aromatic amine in situ in an organic solvent with amyl nitrite at 60–80°C[94].

A similar mechanism may also be operative in arylation brought about by the acid-catalysed decomposition of 1-aryl-3,3,-dialkyltriazens[95,96] or diazoaminobenzenes[97].

$$\begin{array}{llll}
\text{(a)} & Ar{-}N{=}N{-}NR_2 + H^+ & \rightleftarrows & Ar{-}N{=}N{-}\overset{+}{N}RH_2 \\
\text{(b)} & Ar{-}N{=}N{-}\overset{+}{N}HR_2 & \longrightarrow & ArN_2^+ + R_2NH \\
\text{(c)} & ArN_2^+ + Ar{-}N{=}N{-}NR_2 & \longrightarrow & (ArN{=}N)_2\overset{+}{N}R_2 \\
\text{(d)} & (ArN{=}N)_2\overset{+}{N}R_2 & \longrightarrow & Ar\bullet + N_2 + Ar{-}N{=}N{-}\overset{+\bullet}{N}R_2 \\
\text{(e)} & Ar\bullet + PhH & \longrightarrow & [Ar\bullet PhH]\bullet \\
\text{(f)} & [Ar\bullet PhH]\bullet + Ar{-}N{=}N{-}\overset{+\bullet}{N}R_2 & \longrightarrow & Ar{-}Ph + Ar{-}N{=}N{-}\overset{+}{N}HR_2
\end{array} \qquad (53)$$

In arylations under all the above conditions, the normal chain-propagation step for the formation of aryl radicals may be reduction of the diazonium cation by an arylcyclohexadienyl radical, the resultant arylcyclohexadienyl cation forming the biaryl by loss of a proton[95]:-

$$\begin{array}{llll}
\text{(a)} & ArN_2^+ + [Ar\bullet PhH]\bullet & \longrightarrow & Ar\bullet + N_2 + [Ar\bullet PhH]^{+\bullet} \\
\text{(b)} & [Ar\bullet PhH]^{+\bullet} & \longrightarrow & Ar{-}Ph + H^+
\end{array} \qquad (54)$$

Electron-transfer reduction of diazonium cations is an effective way of generating aryl radicals and is brought about by one-electron reductants:

$$(55) \qquad ArN_2^+ + M^{n+} \longrightarrow Ar\bullet + N_2 + M^{(n+1)+}$$

Thus, Norman and Waters[98] have generated phenyl radicals from the stable benzene diazonium zincichloride with zinc in acetone. The Meerwein reaction, which employs copper(II) chloride in aqueous acetone, proceeded by a radical mechanism. If the reaction is carried out in the presence of an aromatic substrate, arylation of this takes place[69] :

$$\begin{aligned} &(a) \quad 2CuCl_2 + Me_2CO \longrightarrow 2CuCl + MeCOCH_2Cl + HCl \\ &(b) \quad ArN_2^+ + CuCl_2^- \longrightarrow Ar\cdot + N_2 + CuCl_2 \end{aligned} \qquad (56)$$

Similarly aryl radicals are froduced by reduction of diazonium salts wuth ferrocene[100]:

$$(57) \quad ArN_2^+ + FcH \longrightarrow Ar\cdot + N_2 + FcH^+$$

$$\left[FcH = (C_5H_5)_2Fe\right]$$

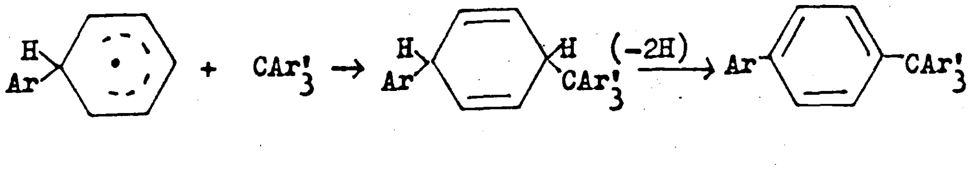
Electrolytic reduction of diazonium salts have been developed as a source of aryl radicals[101]:

$$(58) \quad ArN_2^+ + e^- \longrightarrow Ar\cdot + N_2$$

The decomposition of phenylazotriphenylmethane in benzene solution was first investigated by Hey (1937)[5], who found biphenyl, triphenylmethane and nitrogen amongst the products. Wieland, Shapio and Metzger (1934)[4] obtained o- and p-methylbiphenyl from the decomposition of phenylazotriphenylmethane in toluene, and o- and p-phenylpyridine from its decomposition in pyridine, and on this basis of these results, and further work, notably on Huisgen and Grashey (1957)[102], and Davies Hey and Williams (1956)[103], the decomposition of this compounds in aromatic solvents was formulated as conforming to the general principles of homolytic substitution :

$$\begin{aligned} &(a) \quad Ar{-}N{=}N{-}CAr'_3 \longrightarrow Ar\cdot + N_2 + \cdot CAr'_3 \\ &(b) \quad Ar\cdot + PhH \longrightarrow [Ar\cdot PhH]\cdot \\ &(c) \quad [Ar\cdot PhH]\cdot + \cdot CAr'_3 \longrightarrow Ar{-}Ph + HCAr'_3 \end{aligned} \qquad (59)$$

(d)



The existence of free phenyl radicals in this reaction is established by the observations of Garst and Cole (1963)[104] that the scavengers iodine and carbon tetrabromide are highly efficient in trapping phenyl radicals even when present in very low concentrations, and that hydrogen sbstraction from the side chain of toluene, occurs extensively. A similar conclusion was reached by Russel and Bridger[105], from the results of competitive experiments in which the reactivities of a number of substrates towards hydrogen abstraction by phenyl radicals derived from phenylazotriphenylmethane were measured. These workers also pointed out that the reason for the relative unimportance of side reactions, such as dimerisation of σ- complexes, in phenylation reactions with phenylazotriphenylmethane is probably that the high stationary concentration of trityl radicals which exists, providing a ready route for dehydrogenation of the σ-complexes.

Kinetic studies of this reaction have established that it is nore accurate to represent reaction (59a) as a two-step reaction:-

$$\begin{aligned}
&(a) \quad \mathrm{Ar{-}N{=}N{-}CAr'_3} \longrightarrow \mathrm{ArN_2{\cdot}} + \mathrm{Ar_3C{\cdot}} \\
&(b) \quad \mathrm{ArN_2{\cdot}} \longrightarrow \mathrm{Ar{\cdot}} + \mathrm{N_2}
\end{aligned} \qquad (60)$$

However the absence of any effect of added triphenylmethyl on the rate of decomposition is consistent with one-stage mechanism, or at least showed that if the dissociation is a two-stage, rather than a concerted, process the life time of the arylazo-radicals must be extremely short, so that the first stage is effectively irreversible.

II. EXPERIMENTAL

E.I. Preparation and Purification of Compounds

A. Benzoyl Peroxide

The commercial reagent containing water (30%) was dissolved in a minimum quantity of warm chloroform and the aqueous layer rejected. The solution was rapidly filtered under suction and two volumes of ice-cold methanol were added with stirring, causing precipitation of the crude product which was further purified by repeating the above procedure three times. The purified peroxide was finally filtered and dried in a vacuum dessicator over calcium chloride, m.p. 105°, (lit. m.p. 104-106° [111]).

B. Purification of Solvents

(1) Benzene

a. Commercial "AnalaR" grade benzene was purified by repeated extraction with concentrated sulphuric acid untill extracts were colourless. Then it was washed with saturated sodium hydrogen carbonate and repeatedly with water untill the washings were neutral, and finally distilled after drying ($CaCl_2$), and the middle fraction boiling at 80.5° was collected and stored over calcium sulphate.

b. Commercial sodium dried benzene was also used without further purification, but redistilled just before use, b.p. 80.5°, (lit. b.p. 80.5°).

The following solvents were fractionally distilled twice through a 2-feet column packed with glass helices. The middle boiling fraction was collected. The gas chromatographic analysis revealed no impurities. The literature values are those quoted by Dictionary of Organic Compounds[111] unless otherwise stated.

(2) Fluorobenzene	b.p.	84.8°	760mm	(lit. b.p. 85.2° 760mm)
(3) Chlorobenzene	b.p.	132°	760mm	(lit. b.p. 132° 760mm)
(4) Bromobenzene	b.p.	154°	760mm	(lit. b.p. 155-6° 760mm)
(5) p-Dichlorobenzene	b.p.	173-5°	760mm	(lit. b.p. 174° 760mm)
(6) Benzonitrile	b.p.	188-91°	760mm	(lit. b.p. 190.7° 760mm)
(7) Methylbenzoate	b.p.	198-9°	760mm	(lit. b.p. 199.6° 760mm)

(8) 1,3,5-Trichlorobenzene

The commercial reagent was vacuum distilled (b.p. 97-100°/17mm) and then recrystallised from glacial acetic acid to a constant m.p. 65°C, (lit. m.p. 63.5°)

(9) Benzophenone

The commercial reagent was distilled in vacuum, collecting the fraction at 187-190°/15mm, which solidified into a white solid, m.p. 47-48°C, (lit. m.p. 47.5°)

C. Preparation of Reference Compounds

(1) 2-Chlorobiphenyl

(a) From 2- chloroaniline

2-Chloroaniline (8.0g), and amyl nitrite (10ml) were dissolved in benzene (250ml) and the mixture was allowed to stand at room temperature for 10 mins. Afurther quantity of amyl nitrite (10ml) was then added and the mixture was gently warmed until a steady reaction occured.

After boiling the mixture under reflux for six hours, the bulk of solvent was removed by distillation at atmospheric pressure.

The crude biaryl was distilled at 50–120°/0.1mm and the orange distillate was chromatographed on alumina, and eluted with light petroleum (b.p. 60–80°). After removal of solvent on a rotary evaporator, the residue was distilled in vacuo to yield 2-chlorobiphenyl (b.p. 77-78/0.1mm) as a white crystalline solid m.p. 32-3°, (lit. m.p. 32°)

(b) From 2-aminobiohenyl

2-Aminobiphenyl (21g, 0.125 mole) was diazotized with Analine mixture, and the solution of diazonium chloride was added to a solution of cuprous chloride. After evolution of nitrogen had ceased, the mixture was made alkaline with sodium hydroxide and was then steam-distilled. The organic layer in the distillate was extracted with ether, dried ($MgSO_4$), and filtered. Ether was removed on a rotary evaporator yielding white crystalline 2-chlorobiphenyl, m.p. 32-3°, (lit. m.p. 32°)

(c) From 2-chlorobenzoyl peroxide

2-Chlorobenzoyl peroxide (3.0g) was allowed to decompose in benzene (100ml) at 80° for 72 hours.

The product was steam-distilled and extraction, and purification as above gave 2- chlorobiphenyl m.p. 32-3°

The following compounds are prepared by the analogous method to (a).

(2) 3-Chlorobiphenyl	b.p. 156-60°/6mm ;	Lit. b.p. 150-160°/6mm
(3) 4-Chlorobiphenyl	m.p. 77° ;	Lit. m.p. 77°
(4) 2-Bromobiphenyl	b.p. 158-60°/6mm ;	Lit. b.p. 160°/11mm
(5) 3-Bromobiphenyl	b.p. 170°/17mm ;	Lit. b.p. 169-73°/17mm
(6) 4-Bromobiphenyl	m.p. 88° ;	Lit. m.p. 89°
(7) 2,5-Dichlorobiphenyl	b.p. 170-71°/15mm;	Lit. b.p. 171°/17mm
(8) 2,4,6-Trichlorobiphenyl	m.p. 63° ;	Lit. m.p. 62.5°

(9) 2-Phenylbenzophenone

(a) Preparation of 2-Iodobiphenyl

2-Aminobiphenyl (14g) was dissolved in 5N-hydrochloric acid (50ml) and diazotized at 5-7° by the slow addition of sodium nitrite solution (7.2g, 0.104 mole) in water (20ml). On completion of diazotization the solution was filtered from undissolved solids and slowly poured into a well-stirred solution of potassium iodide (16g, 0.1 mole) in water (20ml) at room temperature. During the vigorous decomposition nitrogen was evolved and iodine was liberated, and a brown unstable precipitate was formed in the solution. The reaction mixture was allowed to stand for 15 minutes at room temperature and was then warmed on the steam bath untill gas evolution ceased.

The cooled solution was shaken with ether (50ml) and the organic layer was separated and washed with 2N-sodium hydroxide, 2N-sodium metabisulphite and water. It was then dried (KCO_3) and the solvent was removed.

Liquid 2-iodobiphenyl was then fractionally distilled under the reduced pressure and was collected at 174°/11mm.

(b) Convertion of 2-Iodobiphenyl into 2-Phenylbenzophenone

A Grignard reagent was prepared from 2-iodobiphenyl prepared as above (14g) and magnesium (1.41g). A solution of benzaldehyde (5.5ml) in benzene (10ml) was added slowly.

When the addition was complete 2/3 of the ether was distilled off and further benzene (25ml) and benzaldehyde (10ml) were added. The mixture was refluxed for 22 hours, after which the complex was made to decompose by the addition of ammonium chloride solution.

The ether-benzene layer was dried, concentrated, and the residue was distilled under reduced pressure. The entire fraction boiling at 195-232°/19mm was collected and was crystallised from methyl alcohol giving white crystals of 2-phenylbenzophenone, m.p. 86° ; (lit. m.p. 90°)

(10) Preparation of 3-Phenylbenzophenone

3-Bromobiphenyl (23.3g), activated magnesium (2.4g) and sodium dried ether (70ml) were allowed to react and the mixture was reflux for 2 hours after vigorous reaction has subsided.

Benzonitrile (6.7g) in ethereal solution was added slowly with stirring. After refluxing (8hours) the product was decomposed with ice and dilute acid, the ether was removed, and the residual ketimine hydrolysed with hot aqueous acid (6 hours). The ketone was obtained by fractional distillation of the product.

It was formed as a pale yellow oil b.p. 264-267°/ 25mm and separated from light petroleum (b.p. 80–100) in colourless crystals, m.p. 79°, (lit m.p. 79°)

(11) Preparation of 4-Phenylbenzophenone

4-Phenylbenzophenone was prepared by adding benzoyl chloride (25g) slowly to a solution of biphenyl (13.8g) in benzene (33ml) in the presence of aluminium chloride cooled in ice-water. After 6 hours crushed ice and benzene were added, the insoluble material was separated and the benzene layer was washed with dilute sodium hydroxide and with water. Evaporation of benzene left a solid residue to which was added the material previously isolated by filtration, and it was then crystallised from light petroleum (b.p. 80–100°); m.p. 102°, (lit.m.p. 104–105° [107]).

(12) Preparation of 2-Methyloxycarbonylbiphenyl

2-Bromobiphenyl (23.3g), activated magnesium (2.4g) and sodium dried ether (70ml) were allowed to react, and the resulting mixture was refluxed for 2 hours after vigorous reaction subsided. After cooling, the reaction mixture were poured into a beaker containing crushed dry-ice. A vigorous reaction occured and Grignard reagent addition compound was set to a stiff mass, it was continuously stirred until all the dry-ice has evaporated. Crushed ice and dilute hydrochloric acid (1:1 by volume) was added with stirring until most of the solid decomposed.

The biphenyl-2-carboxylic acid was extracted, re-precipitated, filtered and recrystallised from ethanol and finally from benzene.

Treatment of this acid with thionyl chloride and then followed by methyl alcohol gave a colourless oil. Repeated distillation of this oil under pressure gave a clear liquid which solidified on standing at 0°.

The resulting solid was recrystallised from light-petroleum (40–60°) to give 2-methyloxycarbonylbiphenyl; m.p. 114°, (lit m.p. 114-5°).

3- and 4-Methyloxycarbonylbiphenyls were also prepared by the above method.

(13)	3-Methyloxycarbonylbiphenyl	m.p. 160° ;	(lit. m.p. 160–1° [111])
(14)	4-Methyloxycarbonylbiphenyl	m.p. 118° ;	(lit. m.p. 117–8° [111])

(15) Preparation of 2-Cyanobiphenyl

A stirred mixture of 2-bromobiphenyl (16g, 0.069 mole), cuprous cyanide (7.8g, 0.08 mole) and dimethylformamide (10.5ml) was refluxed for 6 hours.

The resulting brown mixture was poured into a solution of hydrated ferric chloride (55.2g) and concentrated hydrochloric acid (14ml) in ware (8.3ml). After the reaction mixture had been maintained at 60–70° for 20 minutes to decompose the complex, the layers were separated.

The organic layer was steam distilled, extracted by ether and dried ($MgSO_4$). Evaporation of ether resulted in a yellow oil, which was vacuum distilled and cooled in ice to give 2-cyanobiphenyl; m.p. 33°, (lit.m.p. 37° [108]).

3-,And 4-cyanobiphenyls were also prepared by the above method.

(16)	3-Cyanobiphenyl	m.p. 44° ;	(lit. m.p. 49° [109])
(17)	4-Cyanobiphenyl	m.p. 86° ;	(lit. m.p. 86° [110])

Biphenyl, 2- and 4-fluorobiphenyls were recrystallised to constant m.p. from aqueous ethanol.

(18)	Biphenyl(B.D.H)	m.p. 71° ;	(lit. m.p. 71°)
(19)	2-Fluorobiphenyl(Koch-Light)	m.p. 74° ;	(lit. m.p. 73.5°)
(20)	4-Fluorobiphenyl(Koch-Light)	m.p. 74° ;	(lit. m.p. 74.2°)

D. Purification of Internal Standards

Commercially available compounds were recrystallised and used as internal standard in gas-chromatographic analysis. The literature values are those quoted in Dictionary of Organic Compounds[111].

(1) Bibenzyl(B.D.H) was recrystallised from ethanol; m.p. 52°, (lit. m.p. 52°)

(2) Diphenylmethane was redistilled and collected at b.p. 261-262°, (lit. m.p. 26-7°, b.p. 261-262°)

(3) Naphthalene(B.D.H) was recrystallised from ethanol; m.p. 80°, (lit. m.p. 80.3°)

(4) Triphenylmethane was recrystallised from ethanol; m.p. 94°, (lit. m.p. 94°)

(5) Pentamethylbenzene(Aldrich) was recrystallised from ethanol; m.p. 53°, (lit. m.p. 53°)

E. Preparation and Purification of Catalysts

(1) o-Chloranil

(a) From catechol

This is a modification of Jackman's method[112]. Chlorine gas was passed through a stirred solution of catechol (10g) in glacial acetic acid (50ml). The temperature of the mixture was maintained between 20° and 30°.

After a period of time depending upon the temperature of the mixture and the rate of passage of chlorine, tetrachlorocatechol separated and the mixture became semi-solid.

The solid was removed by filtration, and the filtrate was treated with chlorine untill no more solid separated. After filtration, the solid was combined with the first crop, and washed until colourless with the minimum amount of acetic acid. This product was used for the next stage without any further purification.

The crude tetrachlorocatechol (19g) was dissolved in ethanol (25ml) and was rapidly added to a vigorously stirred mixture of glacial acetic acid (31ml) and concentrated nitric acid.

Some of the catechol was separated during the addition, but subsequently redissolved. When all the tetrachlorocatechol had been added, the mixture was stirred for 1 minute, and then was diluted with ice-cold water (125ml). It was found[30] essential to wait for the colour of the reaction mixture to change (suddenly) from dark red to light red (1-5 minutes after mixing) before quenching it with ice-water. If this precaution was not taken, only an intractable red tar was obtained.

After the mixture had been allowed to stand for 10 minutes the precipitated quinone was removed by filtration and was dried in air. Tetrachloro-1,2-benzoquinone so obtained had m.p. 128-130°; the m.p. could be raised to 130-132° by recrystallisation from carbon tetrachloride, (lit. m.p. 133°[111]).

(b) From pentachlorophenol[113]

Pentachlorophenol (60g "Technical"grade ex. B.D.H) was stirred in suspension with methylene dichloride (120ml) under reflux, concontrated nitric acid (8ml) was added over a period of 1 minute and a further addition (16ml) was made after the initial reaction has subsided.

The mixture was heated under reflux for a further 15 minutes allowed to cool, and water (45ml) added gradually. The mixture was cooled to 10°, and the yellow tetrachloro-p-benzpquinone was filtered off. The methylene dichloride solution was washed with water untill the washings were colourless, dried ($MgSO_4$) and distilled to dryness.

The red solid so obtained was recrystallised from carbon tetrachloride to give scarlet crstals; m.p. 128–130°, (lit. m. p. 133[111]).

(2) p-Chloranil

The yellow precipitate from above (E.1.b) was collected, and recrystallised from toluene. p-Chloranil sublimed without melting on heating, 290°, (lit. m.p. 290° in sealed tube[111]).

(3) Cupric benzoate

Ready available cupric benzoate was used without further purification, but heated in a crucible until constant weigh was reached. The same sample of cupric benzoate was used throughout the experiments.

(4) Cupric p-X benzoate (X = methyl-, chloro- and nitro-group)

Cupric p-mrthylbenzoate was prepared by stirring in a solution containing p-toluic acid (8.9g) in ethanol (560ml) to a solution of cupric acetate (6g) in ethanol (800ml). THe mixture was allowed to stand in an ice-bath until cupric p-methylbenzoate precipitated completely. It was then filtered, washed and dried by heating in a crucible until constant weight was obtained.

Cupric p-chlorobenzoate and cupric p-nitrobenzoate were prepared in a similar manner to those described above by stirring in a solution containing copper acetate (6g) in ethanol (800ml) to a solution of p-chlorobenzoic acid (10.3g) in ethanol (500ml), and a solution of copper acetate (6g) in ethanol (800ml) to a solution of p-nitro benzoic acid (10.1g) in ethanol (630ml) respectively.

(5) Ferric benzoate

Ferric benzoate was prepared in bulk by mixing equimolar solutions of ferric chloride and sodium benzoate. The precipitated ferric benzoate was washed, filtered and dried by heating in a crucible to a constant weight. This single batch of ferric benzoate was used throughout.

(6) Cadmiun benzoate

Commercially available cadmiun benzoate was dried by heating in a crucible to a constant weight and used without further purification.

(7) Nitrosobenzene and m-dinitrobenzene

(a) Nitrosobenzene was recrystallised from ethanol-acetone to a constant melting point; m.p. 68°, (lit. m.p. 67.5-68° [111])

(b) m-Dinitrobenzene was recrystallised from ethanol to a constant melting point; m.p. 88°, (lit m.p. 89.57° [111])

E. 2. General Outline Of The Experiments

All the experiments unless otherwise stated were conducted as follows : -

Purified solvent (50ml) was placed in a 2 necked reaction flask (100ml) supported in a thermostat containing oil maintained at $80 \pm 1^{\circ}$, and deoxygenated over several hours by passing through it a steady stream of purified nitrogen.

In the experiments where catalysts were used, an accurately weighed quantity of catalyst was introduced into the reaction flask. After shaking thoroughly, the contents of the flask were left one hour to equilibrate, after which time an accurately known quantity of peroxide was added. The contents were thoroughly shaken and the reaction was allowed to proceed to completion for 72 hours in a continuous slow stream of purified nitrogen.

A known amount of the appropriate internal standard was added to the contents of the reaction flask, and the yields of products were estimated as follows : -

(a) Separation of benzoic acid

The solution was poured into a separating funnel (250ml) and the benzoic acid was extracted with saturated sodium hydrogen carbonate solution (6x20ml). The aqueous layer was then acidified by dropwise addition of concentrated hydrochloric acid, and the precipitated benzoic acid extracted with methylene chloride (6x10ml). The methylene chloride solution was then dried ($MgSo_4$), filtered into a weighed round-bottomed flask (100ml), and the solvent was removed by rotary-evaporator until a constant weight was reached.

In a reactions containing metal benzoates as additives, the metal benzoate was filtered and its weight was recorded to make an allowance for the benzoic acid formed from subsequent neutralisation of the metal benzoates dissolved in the reaction mixture. To the filtrate, 50% ortho-phosphoric acid (20ml) was added to hydrolyse the dissolved metallic benzoate. The reaction mixture was washed with water (5x25ml) until the washing was neutral to litmus. After the above pre-treatment of the reaction mixture, the benzoic acid was extracted as described above.

(b) Organic Phase

The original organic layer was dried ($MgSO_4$) and filtered into a round-bottomed flask (100ml). The solvent was removed carefully on a rotary-evaporator checking (g.l.c) the absence of detectable traces of biaryl in the distillate, and the concentrated mixture was analysed by gas-liquid chromatography.

(c) Quantitative and Qualitative Analysis of Reaction Products

The following four columns were employed for qualitative and quantitative analysis of reaction products, and for simplicity they are designated by the code number preceding the description of the column :

Code Number	Description of Column
A. 15. C	8-ft x 1/8 inch outer diameter (O.D.) column packed with 15% Apiezon L.grease on 100-120 mesh Celite (Embacel).
A. 20. C	8-ft x 3/8 inch O.D. packed with 20% Apiezon L. grease on 100-120 mesh Celite (Embacel).
C. 20. C	8-ft x 3/8 inch O.D. column packed with 20% Carbowax on 100-120 mesh Celite.
S. 20. C	8-ft x 1/8 inch O.D. column packed with 20% silicon Elastmometer E 301 on 100-120 mesh Celite

Identification of the reaction products were achieved by comparing the retention times with those of the authentic samples under similar conditions. After the identification of the different components of the reaction products, quantitative analysis by g.l.c. was achieved by method of "internal standardisation".

For each reaction system being studied a standard reference compound was selected, which obviously would not be a product of the reaction, but had a similar chemical structure and did not overlap with the products being studied. Each compound that was to be quantitatively estimated was then individually calibrated against the standard.

This was done by making up a series of five or more solutions containing varying relative concentrations of standard and compound under study. Each solution was injected three times into the gas chromatograph. The relative peak height of compound to standard was calculated, a mean of the three injections was taken. A calibration graph was plotted of relative peak height versus relative mole ratio. From the calibration curves it was seen that the detector response only remained linear so long as the peak heights of standard and compounds were approximately of equal magnitude. When one peak was small relative to the other the detector responce changed from linearity for peak height plot. Peaks broadened rapidly as retention time increased and therefore it was inevitable that, in a reaction system where the biaryl isomers varied considerably in retention time by arranging the concentration of standard so that the peak obtained was of approximately the same magnitude as that of the more volatile isomer, then one found that the peak height of the standard was many times larger than the height of the least volatile isomer. This disadvantage of peak height measurement over peak area measurement could be overcome by the constrution of calibration curves over a wide range of relative concentrations of compounds to standard.

When calibration curves for all compounds in a reaction had been constructed, then it became a simple matter to calculate the quantitative composition of any unknown mixtures of the same compounds containing a known amount of standard. In reactions where g.l.c. peaks overlapped, special correction factors had to be calculated and these will be dealt with in the appropriate section.

It was calculated that all results obtained by this method were accurate to within 2%.

E. 3 The Phenylation Reaction

Hey, Perkins and Williams (1964)[42] have shown that the yields of aroic acid and biaryl depend to a large extent on the initial concentration of aroyl peroxide. Therefore, for a study of the additives to have any relative significance it was necessary to fix on a concentration of peroxide and perform all experiments involving catalysts at this arbitrary value. An initial concentration of 0.083M (1g. peroxide to 50ml solvent) of benzoyl peroxide has been used throughout these studies.

(1) The phenylation reaction of benzene

(a) The decomposition of benzoyl peroxide in benzene

The decomposition of benzoyl peroxide (1g) in benzene (50ml) were carried out by the method as outlined in section E.2 , and allowed to proceed to completion for 72 hours at 80 ± 1°.

At the end of the reaction period, an accurately known amount of diphenylmethane (0.15-0.25g) was added, and the yield of biphenyl was estimated by g.l.c.

The results obtained are tabulated in Table (8). The following experimental conditions were adopted for the g.l.c. analysis.

G.L.C. Analysis Data

Column : A. 15 C

Instrument : Perkin-Elmer F21D

Column temperature : 170°

Carrier gas : Nitrogen

Pressure : 1 Kp/cm^2

Attenuation : x 128

Retention Data - Relative to diphenylmethane

Biphenyl	0.86
Diphenylmethane	1.00

(b) The effects of additives on the decomposition of benzoyl peroxide in benzene.

A variety of catalysts were selected and duplicate reactions were set up containing benzoyl peroxide (1g) in benzene (50ml), and a known amount of the catalyst under study. The reaction scheme as described in section E.2 was closely followed and the reactions were allowed to proceed to completion over 72 hours at 80 ± 1°.

At the end of reaction period a known amount of diphenylmethane (0.15-0.25g) was added and any insoluble catalyst was filtered off. The reaction mixtures were then worked-up according to the general method, except when quinones were also added at the end of the reaction.

In the reaction where quinone was added after the decomposition of benzoyl peroxide was complete, the bulk of the benzene was removed and quinone (1.5-2.0g) was added to the reaction mixture which was refluxed for 24 hours. Tetraline (0.3g) was added, and the solution was refluxed for a further 20 hrs. to convert unreacted quinone to

Table (8)

The decomposition of benzoyl peroxide in benzene in the presence and absence of additives at 80° for 72 hours.

Experiment number	Additives	amount of additives (g)	biphenyl (m/m)	benzoic acid (m/m)
A.1	nil	—	0.3827	0.2474
A.2		—	0.3893	0.2561
A.3		—	0.3926	0.2465
A.1-3 average		—	0.3882	0.2500
A.4	o-chloranil*	1.0	0.5598	0.4927
A.5		1.0	0.5593	0.4884
A.6		1.0	0.5637	0.4877
A.4-6 average		1.0	0.5610	0.4896
A.7	o-chloranil	1.0	0.6599	—
A.8		1.0	0.6634	—
A.9		1.0	0.6630	—
A.7-9 average		1.0	0.6621	—
A.10	p-chloranil*	1.0	0.5072	0.4742
A.11		1.0	0.5083	0.4745
A.12		1.0	0.5091	0.4745
A.10-12 average		1.0	0.5082	0.4744

* indicates the additive added after completion of decomposition of benzoyl peroxide in benzene.

Table (8) continued

Experiment number	additives	amount of additives (g)	biphenyl (m/m)	benzoic acid (m/m)
A.13	nitrosobenzene	0.02	0.8702	0.9583
A.14		0.02	0.8699	0.9545
A.15		0.02	0.8575	0.9534
A.13–15 average		0.02	0.8692	0.9554
A.16	pentafluoronitrosobenzene	0.02	0.9928	0.9259
A.17		0.02	0.9966	0.9265
A.18		0.02	0.9968	0.9258
A.16–18 average		0.02	0.9954	0.9264
A.19	m–dinitrobenzene	0.2	1.0409	0.9260
A.20		0.2	1.0364	0.9255
A.21		0.2	1.0360	0.9259
A.19–21 average		0.2	1.0363	0.9258
A.22	cupric benzoate	0.5	0.8264	0.8081
A.23		0.5	0.8254	0.8049
A.24		0.5	0.8226	0.7993
A.22–24 average		0.5	0.8248	0.8065

Table (8) continued

Experiment number	additives	amount of additives (g)	biphenyl (m/m)	benzoic acid (m/m)
A.25	cupric p-methylbenzoate	0.5	0.6138	0.6685
A.26		0.5	0.6158	0.6693
A.27		0.5	0.6169	0.6692
A.25-27 average		0.5	0.6155	0.6690
A.28	cupric p-chlorobenzoate	0.5	0.9502	0.8853
A.29		0.5	0.9485	0.8839
A.30		0.5	0.9492	0.8846
A.28-30 average		0.5	0.9493	0.8846
A.31	cupric p-nitrobenzoate	0.5	0.8129	0.8054
A.32		0.5	0.8109	0.8034
A.33		0.5	0.8130	0.8065
A.31-33 average		0.5	0.8119	0.8051
A.34	ferric benzoate	0.5	0.7973	0.8097
A.35		0.5	0.8003	0.8195
A.36		0.5	0.8024	0.8293
A.34-36 average		0.5	0.8000	0.8195

the more readily removed quinol. p,p'-Quaterphenyl, which separated from the solution, was removed by filtration. The filtrate was shaken with 2N sodium hydroxide (25ml) and the black solid which was formed was filtered off and was discarded. The organic portion of the filtrate was separated and shaken again with 2N sodium hydroxide (2 x 10ml) and with ether (2 x 20ml). The combined aqueous extracts were washed with benzene (25ml) and this benzene was extracted with water (2 x 10ml), and all the benzene solution were combined and dried ($CaCl_2$). Benzene was distilled from dried solution by rotary-evaporator, and the yield of biphenyl was estimated by g.l.c.

The column, column conditions, and calibration curves previously constructed for section (a) were used for g.l.c. analysis in all cases, and the results from this series of reactions are illustrated in Table (8).

(2) The phenylation reaction of chlorobenzene

(a) The decomposition of benzoyl peroxide in chlorobenzene.

These reactions were performed according to the procedure outlined in section (E.2) and were allowed to proceed to completion for 72 hours at 80 ± 1°, and accurately weighed diphenylmethane (c.a. 0.2g) was added as an internal standard at the end of each reaction.

The yields of chlorobiphenyls were estimated by g.l.c. with the following experimental conditions, all the results are shown in Table (9).

G.L.C. Analysis Data

Column : A. 15 C	Instrument : Perkin-Elmer F21D
Column temperature : 170°	Carrier gas : Nitrogen

Pressure : 1 Kp/cm^2 Attenuation : x 64

Since 3- and 4-chlorobiphenyl were not completely resolved on the column used for analysis, correction factors had to be applied. Owing to the departure from the ideal Gaussian shape, the tail of the 3-chlorobiphenyl peak made a contribution to the peak maximum of the 4-isomer. Analysis of synthetic mixtures also showed that the emergence of the later 4-isomer similarly caused an increase of the signal for the 3-isomer, although to a much smaller extent. Therefore the following analytical procedure was adopted for the estimation of the yields of 3- and 4-chlorobiphenyl : -

Calibration curves were constucted for each isomer individually, by preparing solutions containing varying concentrations of chlorobiphenyl and diphenylmethane. A number of solutions were then made up containing the same concentration of diphenylmethane but different concentrations of both 3-, and 4-chlorobiphenyl relative to each other. Values for the real mole ratio of each isomer relative to the standard were then plotted against the values of mole ratio obtained by the use of the individual calibration curves for each isomer. Measurement of the slope of the two straight lines obtained gave the correction factors which had to be applied for unknown mixtures containing both 3- and 4-chlorobiphenyl. The correction factors were calculated to be 0.98 and 0.89 for the 3-, and 4-isomer respectively. That is the graphical mole ratio must be multiplied by 0.98 to give the real mole ratio for 3-chlorobiphenyl and by 0.89 for the 4-chlorobiphenyl.

Retention Data - (Relative to diphenylmethane)

Compounds	Relative retention times
Diphenylmethane	1.00
2-Chlorobiphenyl	1.37
3-Chlorobiphenyl	2.24
4-Chlorobiphenyl	2.35

(b) The effects of additives on the decomposition of benzoyl peroxide in chlorobenzene.

A series of reactions in duplicate were studied according to the experimental method outlined in section (E.2), and were allowed to proceed to completion over 72 hours at 80 ± 1°. For this series known amounts of the various catalysts were added to pure chlorobenzene (50ml) followed by the addition of benzoyl peroxide (1g) to the reaction when thermal equilibrium had been established.

At the completion of the reaction a known amount of diphenylmethane (0.15-0.25g) was added as the standard for g.l.c. analysis and the reaction mixture was filtered free of deposited catalyst before commencing the nornal work-up procedure. The reactions where quinone was added after completion of the reaction were dealt with in a similar manner to those described for benzene.

The yields of chlorobiphenyls were estimated by g.l.c. with the same experimental conditions and same calibration curve to the section (2a). The results obtained are tabulated as Table(9).

Table (9)

The decomposition of benzoyl peroxide in chlorobenzene in the presence and absence of additives at 80° for 72 hours.

Experiment number	amount of additives (g)	chlorobiphenyl (m/m)	benzoic acid (m/m)	isomer ratio <u>o</u>	<u>m</u>	<u>p</u>
nil						
B.1	—	0.4025	0.3396	54.9	27.0	18.1
B.2	—	0.4028	0.3387	55.0	27.1	17.9
B.3	—	0.4019	0.3378	53.9	27.5	18.6
B.1-3 average		0.4024	0.3387	54.6	27.2	18.2
<u>o</u>-chloranil*						
B.4	1.0	0.5348	—	56.7	25.8	17.5
B.5	1.0	0.5385	—	57.0	25.6	17.4
B.6	1.0	0.5383	—	57.0	25.4	17.6
B.4-6 average		0.5372	—	56.9	25.6	17.5
<u>o</u>-chloranil						
B.7	1.0	0.6368	—	58.4	24.3	17.3
B.8	1.0	0.6349	—	58.2	24.5	17.3
B.9	1.0	0.6357	—	58.3	24.4	17.3
B.7-9 average		0.6358	—	58.3	24.4	17.3

* indicates the additive added after the completion of phenylation.

Table (9) continued

Experiment number	amount of additives (g)	chlorobiphenyl (m/m)	benzoic acid (m/m)	isomer ratio o	m	p
	nitrosobenzene					
B.10	0.02	0.8418	0.8074	56.1	26.0	17.9
B.11	0.02	0.8432	0.8091	55.9	26.1	18.0
B.12	0.02	0.8431	0.8102	56.3	25.6	18.1
B.10–12 average		0.8427	0.8089	56.1	25.9	18.0
	pentafluoronitrosobenzene					
B.13	0.02	0.8053	0.7072	58.1	24.5	17.4
B.14	0.02	0.8048	0.7066	58.3	24.3	17.4
B.15	0.02	0.8046	0.7066	58.2	24.4	17.4
B.13–15 average		0.8049	0.7068	58.2	24.4	17.4
	m-dinitrobenzene					
B.16	0.2	0.7544	0.8001	56.9	25.1	18.0
B.17	0.2	0.7528	0.7904	56.9	25.0	18.1
B.18	0.2	0.7554	0.7834	56.6	25.5	17.9
B.16–18 average		0.7542	0.7913	56.8	25.2	18.0
	cupric benzoate					
B.19	0.5	0.7133	0.8054	57.4	25.3	17.3
B.20	0.5	0.7137	0.8049	57.1	25.7	17.2
B.21	0.5	0.7135	0.8056	57.4	25.2	17.4
B.19–21 average		0.7135	0.8053	57.3	25.4	17.3

Table (9) continued

Experiment number	amount of additives (g)	chlorobiphenyl (m/m)	benzoic acid (m/m)	isomer ratio *o*	*m*	*p*
cupric *p*-methylbenzoate						
B.22	0.5	0.7479	0.7581	58.3	24.2	17.5
B.23	0.5	0.7463	0.7574	58.4	24.2	17.4
B.24	0.5	0.7489	0.7582	58.2	24.2	17.6
B.22-24 average		0.7477	0.7579	58.3	24.2	17.5
cupric *p*-chlorobenzoate						
B.25	0.5	0.8029	0.8719	58.2	24.3	17.5
B.26	0.5	0.8046	0.8723	58.3	24.0	17.7
B.27	0.5	0.8039	0.8724	58.4	24.3	17.3
B.25-27 average		0.8038	0.8722	58.3	24.2	17.5
cupric *p*-nitrobenzoate						
B.28	0.5	0.8381	0.8034	58.2	24.5	17.3
B.29	0.5	0.8379	0.8042	58.4	24.3	17.3
B.30	0.5	0.8383	0.8029	58.3	24.4	17.3
B.28-30 average		0.8381	0.8035	58.3	24.4	17.3
ferric benzoate						
B.31	0.5	0.9451	0.9729	57.8	24.0	18.2
B.32	0.5	0.9448	0.9738	58.2	23.7	18.1
B.33	0.5	0.9457	0.9713	58.0	24.0	18.0
B.31-33 average		0.9452	0.9727	58.0	23.9	18.1

E.4 The Competitive Reactions of Benzoyl Peroxide in Equimolar Benzene/Chlorobenzene Mixture.

(a) The decomposition of benzoyl peroxide in an equimolar mixture of benzene and chlorobenzene in the absence of additive.

Benzoyl peroxide (1.0g) was decomposed in equimolar benzene/chlorobenzene solution (50ml), and the reactions were allowed to proceed to completion over 72 hours at 80 ± 1°, in an atmosphere of nitrogen. At the end of this period a known amount of diphenylmethane (0.2g) was added and the reactions were worked-up as outlined in section (E.2).

The yields of biphenyl and isomeric chlorobiphenyls were calculated by g.l.c. analysis making use of the calibration curves previously constructed for these compounds. The results are given in Table (10).

G.L.C. Analysis Data

Column : A 15 C	Instrument : Perkin-Elmer F21D
Column temperature : 170°	Carrier gas : Nitrogen
Pressure : 1 Kp/cm^2	Attenuation : x 64

(b) The decomposition of benzoyl peroxide in an equimolar mixture of chlorobenzene and benzene in the presence of additive.

A number of catalysts were selected and triplicate reactions were set up each containing benzoyl peroxide (1.0g) in equimolar benzene/chlorobenzene solution (50ml), and a known quantity of the catalyst under study. The reaction scheme as described in section

(E2) was closely followed and the reactions were allowed to proceed to completion over 72 hours at 80 ± 1°.

At the end of reaction a known amount of diphenylmethane (0.15-0.25g) was added, and deposited catalyst was filtered before the yields of products were estimated by g.l.c. with the same experimental conditions as above. The results of this series of experiments are tabulated in Table (10).

(c) The decomposition of benzoyl peroxide in the solution containing varying molar ratios of benzene and chlorobenzene in the presence of ferric benzoate.

In this series of experiments, the molar ratio of substrates is varied while the total volume of solvent was stll remained at 50ml. Benzoyl peroxide (1.0g) was allowed to decompose in these mixture in the presence of ferric benzoate (0.5g) for the duration of 72 hours at 80 ± 1°.

The same work-up procedures were adopted for the reaction mixtures, and the results are summarized in Table (11).

Table (10)

The decomposition of benzoyl peroxide in equimolar benzene–chlorobenzene mixture in the presence and absence of additives at 80° for 72 hours.

experiment number	biaryl (total) (m/m)	PhC_6H_4Cl (m/m)	Ph–Ph (m/m)	${}^{Cl}_{H}K$	isomer ratios o-	m-	p-	p.r.f Fo	Fm	Fp
J. 1	0.5731	0.3054	0.2677	1.14	54.7	27.9	18.3	1.87	0.92	1.26
J. 2	0.5717	0.3046	0.2671	1.14	54.4	27.2	18.4	1.86	0.93	1.26
J. 3	0.5739	0.3056	0.2683	1.14	54.6	27.2	18.2	1.87	0.93	1.23
J. average	0.5729	0.3052	0.2677	1.14	54.6	27.2	18.2	1.87	0.93	1.24
Cu. J. 1	0.8735	0.5248	0.3487	1.50	57.5	25.2	17.3	2.59	1.13	1.56
Cu. J. 2	0.8706	0.5239	0.3467	1.51	57.0	25.7	17.3	2.58	1.16	1.57
Cu. J. 3	0.8728	0.5245	0.3483	1.51	57.4	25.6	17.0	2.60	1.16	1.57
Cu. J. average	0.8723	0.5244	0.3479	1.51	57.3	25.5	17.2	2.60	1.16	1.57

Table (10) continued.

experiment number	biaryl (total) (m/m)	PhC_6H_4Cl (m/m)	Ph-Ph (m/m)	$\frac{Cl}{H}K$	isomer ratios			p . r . f		
					o	m	p	Fo	Fm	Fp
p-Cl. J. 1	0.8114	0.4716	0.3398	1.39	58.2	24.5	17.3	2.43	1.02	1.44
p-Cl. J. 2	0.8138	0.4722	0.3416	1.38	58.6	24.1	17.3	2.43	1.02	1.43
p-Cl. J. 3	0.8141	0.4716	0.3425	1.38	58.4	24.3	17.3	2.42	1.01	1.43
p-Cl. J. average	0.8131	0.4718	0.3413	1.38	58.4	24.3	17.3	2.42	1.01	1.43
Fe. J. 1	0.8662	0.5095	0.3567	1.43	57.4	25.3	17.3	2.46	1.09	1.48
Fe. J. 2	0.8649	0.5098	0.3551	1.43	57.4	25.2	17.4	2.46	1.08	1.50
Fe. J. 3	0.8678	0.5110	0.3568	1.44	58.0	24.8	17.2	2.51	1.07	1.49
Fe. J. average	0.8663	0.5101	0.3562	1.43	57.6	25.1	17.3	2.47	1.08	1.48

Table (11)

The decomposition of benzoyl peroxide in a solution containing various molar ratio of benzene and chlorobenzene in the presence of ferric benzoate at 80° for 72 hours.

experiment number	mole ratio PhCl : PhH	biaryl (total m/m)	PhC_6H_4Cl (m/m)	Ph-Ph (m/m)	${}^{Cl}_{H}K$	isomer ratios			partial rate factor		
						o	*m*	*p*	F*o*	F*m*	F*p*
Fe. V. 1	2 : 1	0.8298	0.6107	0.2191	1.39	57.2	25.0	17.8	2.39	1.04	1.48
Fe. V. 2	2 : 1	0.8321	0.6121	0.2200	1.39	57.3	24.8	17.9	2.39	1.03	1.49
Fe. V. 3	2 : 1	0.8317	0.6111	0.2206	1.39	57.3	24.6	18.1	2.39	1.03	1.51
Fe. V. 1-3 average	2 : 1	0.8312	0.6113	0.2199	1.39	57.3	24.8	17.9	2.39	1.03	1.49
Fe. V. 4	1.5 : 1	0.8056	0.5482	0.2571	1.42	57.6	24.3	18.1	2.45	1.04	1.54
Fe. V. 5	1.5 : 1	0.8101	0.5528	0.2573	1.43	57.7	24.1	18.2	2.48	1.03	1.56
Fe. V. 6	1.5 : 1	0.7987	0.5445	0.2542	1.43	57.7	24.2	18.1	2.48	1.04	1.55
Fe. V. 4-6 ave.	1.5 : 1	0.8048	0.5485	0.2563	1.43	57.7	24.2	18.1	2.48	1.04	1.55

Table (11) continued.

experiment number	mole ratio PhCl : PhH	biaryl (toal m/m)	PhC_6H_4Cl (m/m)	Ph-Ph (m/m)	${}^{Cl}_{H}K$	isomer ratios			partial rate factors		
						o	m	p	Fo	Fm	Fp
Fe. J. 1	1 : 1	0.8662	0.5095	0.3567	1.43	57.4	25.3	17.3	2.46	1.09	1.48
Fe. J. 2	1 : 1	0.8649	0.5098	0.3551	1.43	57.4	25.2	17.4	2.46	1.08	1.50
Fe. J. 3	1 : 1	0.8678	0.5110	0.3568	1.44	58.0	24.8	17.2	2.51	1.07	1.49
Fe. J. 1-3 average	1 : 1	0.8663	0.5101	0.3562	1.43	57.6	25.1	17.3	2.47	1.08	1.48
Fe. V. 7	1 : 1.5	0.7917	0.3730	0.4197	1.33	57.7	24.5	17.8	2.30	0.98	1.42
Fe. V. 8	1 : 1.5	0.7938	0.3718	0.4210	1.32	57.9	24.3	17.8	2.29	0.96	1.40
Fe. V. 9	1 : 1.5	0.7974	0.3733	0.4241	1.32	57.8	24.7	17.5	2.29	0.98	1.39
Fe. V. 7-9 ave.	1 : 1.5	0.7943	0.3727	0.4216	1.32	57.8	24.5	17.7	2.29	0.97	1.40
Fe. V. 10	1 : 2	0.8363	0.3322	0.5041	1.31	57.8	24.4	17.8	2.27	0.96	1.40
Fe. V. 11	1 : 2	0.8358	0.3318	0.5040	1.32	57.6	24.3	18.1	2.28	0.96	1.43
Fe. V. 12	1 : 2	0.8365	0.3290	0.5075	1.31	58.0	24.2	17.8	2.28	0.95	1.42
Fe. V. 10-12 ave.	1 : 2	0.8362	0.3310	0.5052	1.31	57.8	24.3	17.9	2.27	0.95	1.41

E.5 The Phenylation Reaction of Bromobenzene

(a) The decomposition of benzoyl peroxide in bromobenzene.

Reactions were set up each containing benzoyl peroxide (1.0g) and bromobenzene (50ml) according to the experimental method outlined in section (E2), and were allowed to proceed to completion over 72 hours at 80 ± 1°. At the completion of the reaction a known amount of diphenylmethane (0.1-0.2g) was added as the internal standard for g.l.c. analysis.

The yields of bromobiphenyls were estimated by g.l.c. with the following experimental conditions, and the results are tabulated in Table (12).

G.L.C. Analysis Data

Column : A.15.C

Column temperature : 200°

Pressure : 1 Kp/cm^2

Instrument : Perkin-Elmer F21D

Carrier gas : Nitrogen

Attenuation : x 64

Retention Data - (Relative to diphenylmethane)

Compounds	Relative retention times
Diphenylmethane	1.00
2-Bromobiphenyl	2.08
3-Bromobiphenyl	3.16
4-Bromobiphenyl	3.51

(b) The effects of additives on the decomposition of benzoyl peroxide in bromobenzene.

Duplicate reactions were set up containing benzoyl peroxide (1.0g) in bromobenzene (50ml) with known quantity of selected catalyst according to usual experimental method, and were allowed to proceed to completion over 72 hours at 80 ± 1°.

At the end of the reaction a known amount of diphenylmethane (0.15-0.2g) was added as the standard for g.l.c. analysis, and the insoluble catalyst was filtered off. The reaction mixtures were then worked-up according to the usual method. In the reactions where quinone was added after completion of the reaction were dealt in a similar manner to those described for benzene in section E.3(1b).

The yields of bromobiphenyls were estimated by g.l.c. using the same experimental conditions and calibration curves to the above reactions. The resukts from this series of experiments are summarised in Table (12).

Table (12)

The decomposition of benzoyl peroxide in bromobenzene in the presence and absence of additives at 80° for 72 hours.

experiment number	amount of additives (g)	PhC_6H_4Br (m/m)	$PhCO_2H$ (m/m)	isomer ratios o	m	p
nil						
C.1	—	0.7448	0.9559	54.0	30.6	15.4
C.2	—	0.7457	0.9511	54.2	30.5	15.3
C.3	—	0.7457	0.9531	54.4	30.1	15.5
C.1-3 average		0.7454	0.9536	54.2	30.4	15.4
o-chloranil*						
C.4	1.0	0.7525	—	54.0	30.4	15.6
C.5	1.0	0.7541	—	53.7	30.8	15.5
C.6	1.0	0.7479	—	54.3	30.3	15.4
C.4-6 average		0.7515	—	54.0	30.5	15.5
o-chloranil						
C.7	1.0	0.8174	—	55.8	28.8	15.4
C.8	1.0	0.8172	—	55.9	29.3	14.8
C.9	1.0	0.8152	—	55.4	29.2	15.4
C.7-9 average		0.8166	—	55.7	29.1	15.1

* indicates the additive added after the completion of phenylation.

Table (12) continued

experiment number	amount of additives (g)	PhC_6H_4Br (m/m)	$PhCO_2H$ (m/m)	isomer ratios		
				o	m	p
nitrosobenzene						
C.10	0.02	0.7918	1.0855	54.7	29.4	15.9
C.11	0.02	0.7932	1.0794	55.0	29.2	15.8
C.12	0.02	0.7934	1.0835	55.0	29.3	15.7
C.10–12 average		0.7928	1.0828	54.9	29.3	15.8
pentafluoronitrosobenzene						
C.13	0.02	0.8242	0.8403	53.8	29.9	16.3
C.14	0.02	0.8238	0.8408	54.0	29.7	16.1
C.15	0.02	0.8234	0.8435	54.2	29.8	16.0
C.13–15 average		0.8238	0.8415	54.0	29.8	16.2
m-dinitrobenzene						
C.16	0.2	0.8498	0.8849	54.9	27.7	15.4
C.17	0.2	0.8492	0.8853	54.9	29.6	15.5
C.18	0.2	0.8511	0.8836	54.6	29.8	15.6
C.16–18 average		0.8500	0.8846	54.8	29.7	15.5
cupric benzoate						
C.19	0.5	0.7502	0.9450	58.6	27.8	13.6
C.20	0.5	0.7479	0.9582	58.4	27.8	13.8
C.21	0.5	0.7462	0.9432	57.9	27.7	14.4
C.19–21 average		0.7481	0.9488	58.3	27.8	13.9

Table (12) continued

experiment number	amount of additives (g)	PhC_6H_4Br (m/m)	$PhCO_2H$ (m/m)	isomer ratios		
				o	*m*	*p*
cupric *p*-methylbenzoate						
C.22	0.5	0.7627	0.8479	56.2	28.7	15.1
C.23	0.5	0.7599	0.8453	56.4	28.5	15.1
C.24	0.5	0.7625	0.8484	56.3	28.6	15.1
C.22-24 average		0.7617	0.8472	56.3	28.6	15.1
cupric *p*-chlorobenzoate						
C.25	0.5	0.8679	0.9077	56.0	28.6	15.4
C.26	0.5	0.8662	0.8997	56.0	28.3	15.7
C.27	0.5	0.8660	0.9043	56.3	28.2	15.5
C.25-27 average		0.8667	0.9039	56.1	28.4	15.5
cupric *p*-nitrobenzoate						
C.28	0.5	0.7835	0.8566	57.3	27.8	14.9
C.29	0.5	0.7837	0.8572	57.3	27.8	14.9
C.30	0.5	0.7842	0.8566	57.4	27.9	14.7
C.28-30 average		0.7838	0.8568	57.3	27.8	14.9
ferric benzoate						
C.31	0.5	0.9631	0.9833	54.7	29.6	15.9
C.32	0.5	0.9623	0.9837	54.3	29.3	16.4
C.33	0.5	0.9597	0.9831	53.9	29.3	16.8
C.31-33 average		0.9617	0.9834	54.3	29.4	16.3

E.6 The Competitive Reactions of Benzoyl Peroxide in Equimolar Benzene/Bromobenzene Mixture

(a) The decomposition of benzoyl peroxide in an equimolar mixture of bromobenzene and benzene in the absence of additives.

Benzoyl peroxide (1.0g) was allowed to decompose in an equimolar mixture of benzene and bromobenzene (50ml) over 72 hours at 80 ± 1°, in an atmosphere of nitrogen. At the end of this period a known amount of diphenylmethane (0.15-0.2g) was added and the reactions were worked-up as described in section (E2).

The calibration curve for biphenyl against diphenylmethane was constructed at 200°, and the yields of biphenyl and the isomeric bromobiphenyls were calculated by g.l.c. analysis making use for the above calibration curve and the calibration curves previously constructed for bromobiphenyl. The results of this experiment are given in Table (13).

G.L.C. Analysis Data

Column : A.15.C
Column temperature : 200°
Pressure : 1 Kp/cm^2
Instrument : Perkin-Elmer F21D
Carrier gas : Nitrogen
Attenuation : X 64

Retention Data - (Relative to diphenylmethane)

Compound	Relative retention time
Biphenyl	0.86
Diphenylmethane	1.00

2-Bromobiphenyl	2.08
3-Bromobiphenyl	3.16
4-Bromobiphenyl	3.51

(b) The decomposition of benzoyl peroxide in an equimolar mixture of bromobenzene and benzeme in the presence of additives.

Triplicate reactions were set up each containing benzoyl peroxide (1.0g) in an equimolar benzene/bromobenzene solution (50ml), and a known quantity of catalyst under study. The reactions were allowed to proceed to completion in the usual manner over 72 hours at 80 ± 1°.

At the end of reaction deposited catalyst was filtered off and a known amount of diphenylmethane (0.15-0.2g) was added, and the yields of products were estimated as previously. The results are tabulated as Table (13).

(c) The decomposition of benzoyl peroxide in the solution containing varying molar ratios of benzene and bromobenzene.

A series of experiments with the relative concentrations of bromobenzene and benzene varying from 2:1 to 1:2 were carried out. Each reactions were carried out by allowing benzoyl peroxide (1.0g) to decompose in a total volume of 50ml. solvent mixture for 72 hours at 80 ± 1°. The analysis and work-up of the reaction mixtures were similar to those used in the competitive reaction of equimolar mixture of the bromobenzene and benzene.

The results are summarised in Table (14).

Table (13)

The decomposition of benzoyl peroxide in equimolar benzene-bromobenzene mixture in the presence and absence of additives at 80° for 72 hours.

experiment number	biaryl (total) (m/m)	PhC_6H_4Br (m/m)	Ph-Ph (m/m)	${}^{Br}_{H}K$	isomer ratios			p . r . f		
					o	m	p	Fo	Fm	Fp
K. 1	0.7445	0.4433	0.3012	1.47	54.2	30.5	15.3	2.30	1.35	1.35
K. 2	0.7405	0.4409	0.2996	1.47	54.0	30.6	15.4	2.38	1.35	1.36
K. 3	0.7490	0.4494	0.2996	1.47	54.4	30.4	15.2	2.40	1.35	1.34
K. average	0.7413	0.4412	0.3001	1.47	54.2	30.5	15.3	2.39	1.35	1.35
Cu. K. 1	0.8059	0.4783	0.3276	1.46	57.4	27.8	14.8	2.51	1.22	1.28
Cu. K. 2	0.7943	0.4714	0.3229	1.46	57.0	28.4	14.6	2.50	1.24	1.28
Cu. K. 3	0.7837	0.4651	0.3186	1.46	57.2	28.4	14.4	2.51	1.24	1.26
Cu. K. average	0.7935	0.4716	0.3219	1.46	57.2	28.2	14.6	2.51	1.24	1.28

Table (13) continued.

experiment number	biaryl (total) (m/m)	PhC_6H_4Br (m/m)	Ph-Ph (m/m)	$^{Br}_{H}K$	isomer ratios o	 m	 p	p . r . f Fo	 Fm	 Fp
p-Cl. K. 1	0.7626	0.4448	0.3178	1.40	56.1	28.4	15.5	2.36	1.19	1.30
p-Cl. K. 2	0.7653	0.4450	0.3203	1.39	55.5	28.9	15.6	2.31	1.21	1.30
p-Cl. K. 3	0.7704	0.4503	0.3201	1.41	56.4	27.9	15.7	2.38	1.18	1.32
p-Cl. K. average	0.7661	0.4467	0.3194	1.40	56.0	28.4	15.6	2.35	1.19	1.31
Fe. K. 1	0.9086	0.5478	0.3580	1.53	54.3	29.6	16.1	2.49	1.34	1.48
Fe. K. 2	0.9086	0.5483	0.3603	1.52	54.7	29.3	16.0	2.49	1.34	1.46
Fe. K. 3	0.9066	0.5479	0.3587	1.53	54.5	29.6	15.9	2.50	1.36	1.46
Fe. K. average	0.9070	0.5480	0.3590	1.53	54.5	29.5	16.0	2.30	1.35	1.47

Table (14)

The decomposition of benzoyl peroxide in a solution containing various molar ratio of benzene and bromobenzene in the absence of additives at 80° for 72 hours.

experiment number	mole ratio PhBr : PhH	biaryl (total m/m)	PhC_6H_4Br (m/m)	Ph-Ph (m/m)	${}^{Br}_{H}k$	isomer ratios			partial rate factors		
						o	m	p	Fo	Fm	Fp
K. V. 1	2 : 1	0.9012	0.6779	0.2233	1.52	54.7	29.6	15.7	2.48	1.35	1.43
K. V. 2	2 : 1	0.9009	0.6762	0.2247	1.51	54.7	29.7	15.6	2.48	1.35	1.41
K. V. 3	2 : 1	0.8994	0.6775	0.2219	1.53	55.0	29.2	15.8	2.52	1.34	1.45
K. V. 1-3 average	2 : 1	0.9005	0.6772	0.2233	1.52	54.8	29.5	15.7	2.49	1.35	1.43
K. V. 4	1.5 : 1	0.8943	0.6178	0.2765	1.49	54.7	30.2	15.1	2.45	1.35	1.35
K. V. 5	1.5 : 1	0.8921	0.6152	0.2769	1.48	54.3	30.5	15.2	2.43	1.35	1.35
K. V. 6	1.5 : 1	0.8881	0.6133	0.2748	1.49	54.5	30.2	15.3	2.44	1.35	1.37
K. V. 4-6 average	1.5 : 1	0.8915	0.6155	0.2760	1.49	54.5	30.3	15.2	2.44	1.35	1.34

Table (14) continued.

experiment number	mole ratio PhBr : PhH	biaryl (total m/m)	PhC_6H_4Br (m/m)	Ph-Ph (m/m)	$\frac{Br}{H}K$	isomer ratios			partial rate factors		
						o	m	p	Fo	Fm	Fp
K. 1	1 : 1	0.7445	0.4433	0.3012	1.47	54.2	30.5	15.3	2.30	1.35	1.35
K. 2	1 : 1	0.7405	0.4409	0.2996	1.47	54.0	30.6	15.4	2.38	1.35	1.36
K. 3	1 : 1	0.7490	0.4494	0.2996	1.47	54.4	30.4	15.2	2.40	1.35	1.34
K. 1-3 average	1 : 1	0.7413	0.4412	0.3001	1.47	54.2	30.5	15.3	2.39	1.35	1.35
K. V. 7	1 : 1.5	0.8391	0.3733	0.4658	1.20	55.2	28.9	15.9	1.99	1.04	1.14
K. V. 8	1 : 1.5	0.8364	0.3712	0.4652	1.20	55.1	28.8	16.1	1.98	1.04	1.16
K. V. 9	1 : 1.5	0.8369	0.3721	0.4648	1.20	55.3	29.0	15.7	1.99	1.04	1.13
K. V. 7-9 average	1 : 1.5	0.8374	0.3722	0.4652	1.20	55.2	28.9	15.9	1.99	1.04	1.14
K. V. 10	1 : 2	0.9255	0.3085	0.6170	1.00	53.9	30.8	15.3	1.62	0.92	0.92
K. V. 11	1 : 2	0.9243	0.3054	0.6189	0.99	54.3	30.3	15.4	1.61	0.90	0.91
K. V. 12	1 : 2	0.9237	0.3047	0.6190	1.98	54.1	30.7	15.2	1.60	0.90	0.89
K. V. 10–12 average	1 : 2	0.9245	0.3062	0.6183	0.99	54.1	30.6	15.3	1.60	0.91	0.91

E.7 The Phenylation Reactions of Fluorobenzene in The Presence and Absence of Additive.

A series of reactions were carried out in fluorobenzene following the experimental method as described in section (E2), in the presence and absence of catalyst, and were allowed to proceed to completion over 72 hours at 80 ± 1^{o}.

A known quantity of catalyst was added to fluorobenzene (50ml), and when equilibrium was established a calculated amount of benzoyl peroxide (1.0g) was added. Reactions containing the same concentration of benzoyl peroxide but without the presence of added catalyst was also carried out. All experiments were performed in triplicate.

At the completion of the reaction a known amount of pentamethylbenzene (0.15–0.2g) was added, and the reactions were worked-up in the standard manner.

Gas chromatography however, provided an incomplete analysis of the products of this series of reactions. Biphenyl and 2-fluorobiphenyl were easily resolved and their yields were estimated against the internal standard. However the available stationary phases of differing characteristics could not resolve 3- and 4-fluorobiphenyl.

Calibration curves of biphenyl, 2-fluorobiphenyl and 4-fluorobiphenyl against pentamethylbenzene were then constructed. The analysis of synthetic mixtures containing all three isomers of fluorobiphenyl showed that a summation of the amount of 3- and 4-fluorobiphenyl in the mixtures was obtained by the use of the calibration curve for pure 4-fluorobiphenyl, since the responses of the 3- and 4-isomers were quantitatively identical.

The results for the reactions conducted in fluorobenzene are shown in Table (15).

G.L.C. Analysis Data

Column : A.20.C

Column temperature : 160°

Pressure : $1 Kp/cm^2$

Instrument : Perkin-Elmer F21D

Carrier gas : Nitrogen

Attenuation : x 64

Retention Data - (Relative to pentamethylbenzene)

Compounds	Relative retention time
Pentamethylbenzene	1.00
Biphenyl	1.67
2-Fluorobiphenyl	1.34
3-Fluorobiphenyl	1.51
4-Fluorobiphenyl	1.51

Table (15)

The decomposition of benzoyl peroxide in fluorobenzene in the presence and absence of additives at 80° for 72 hours.

experiment number	catalyst (g)	PhPhF (m/m)	PhCOOH (m/m)	Ph-Ph (m/m)	isomer ratio	
					o-	m + p-
D. 1	nil	0.6233	0.2524	0.091	48.2	51.8
D. 2		0.6214	0.2498	0.083	48.0	52.0
D. 3		0.6213	0.2508	0.084	48.4	51.6
D. average	nil	0.6220	0.2500	0.086	48.2	51.8
Cu. D. 1	cupric benzoate	0.8916	0.8635	0.035	52.3	47.2
Cu. D. 2	(0.5)	0.8921	0.8641	0.036	52.9	47.1
Cu. D. 3		0.8929	0.8644	0.043	52.7	47.3
Cu. D. ave	cupric benzoate	0.8922	0.8640	0.038	52.9	47.2
Fe. D. 1	ferric benzoate	0.8281	0.8420	0.032	55.1	44.9
Fe. D. 2	(0.5)	0.8288	0.8400	0.034	54.1	45.9
Fe. D. 3		0.8304	0.8479	0.036	54.0	46.0
Fe. D. ave	ferric benzoate	0.8291	0.8433	0.034	54.4	45.6

E.8 The Competitive Reactions of Benzoyl Peroxide in Equimolar Benzene-Fluorobenzene Mixture in the Presence and Absence of Additives.

A series of competitive reactions, each containing benzoyl peroxide (1.0g) in equimolar solution of benzene and fluorobenzene (50ml) were carried out in triplicate, in the presence and absence of catalyst, and were allowed to proceed to completion over 72 hours at 80 ± 1°.

A known quantity of pentamethylbenzene (0.15–0.2g) was added and the reactions were worked-up as in section (E2).

The yields of biaryls were estimated by the use of g.l.c. with the same experimental conditions and by using the same calibration curve as for previous experiments.

The results of this series of experiments are given in Table (16), the partial rate factors of meta- and para-fluorobiphenyls were calculated as a brief guide by using the meta- : para- ratio (1.98 : 1) determined by Lewis and Williams[46] who satisfactory estimated the amount of each isomer by the use of quantitative infra-red spectroscopy.

Table (16)

The decomposition of benzoyl peroxide in equimolar benzene-fluorobenzene mixture in the presence and absence of additives at 80° for 72 hours.

experiment number	biaryl (total) (m/m)	PhC_6H_4F (m/m)	Ph-Ph (m/m)	${}^{F}_{H}K$	isomer ratio		p . r . f		
					o	m + p	F_o	F_m	F_p
L. 1	0.6205	0.3222	0.2983	1.08	48.0	52.0	1.56	1.12	1.13
L. 2	0.6180	0.3209	0.2971	1.08	48.1	51.9	1.56	1.12	1.13
L. 3	0.6176	0.3207	0.2969	1.08	48.4	51.6	1.57	1.11	1.18
L. average	0.6186	0.3212	0.2974	1.08	48.2	51.8	1.56	1.11	1.18
Cu. L. 1	0.7776	0.4363	0.3413	1.28	52.6	47.4	2.02	1.20	1.22
Cu. L. 2	0.7807	0.4383	0.3424	1.28	53.0	47.0	2.04	1.19	1.21
Cu. L. 3	0.7798	0.4378	0.3420	1.28	53.1	46.9	2.04	1.19	1.21
Cu. L. average	0.7794	0.4375	0.3419	1.28	52.9	47.1	2.03	1.19	1.22

Table (16) continued.

experiment number	biaryl (total) (m/m)	PhC_6H_4F (m/m)	Ph–Ph (m/0	^F_HK	isomer ratio $\underline{o}$	 $\underline{m}+\underline{p}$	p . r . f Fo	 Fm	 Fp
Fe. L. 1	0.7990	0.4407	0.3583	1.23	55.0	45.0	2.03	1.10	1.11
Fe. L. 2	0.8016	0.4415	0.3601	1.23	54.8	45.2	2.02	1.11	1.12
Fe. L. 3	0.7997	0.4403	0.3594	1.23	55.1	44.9	2.03	1.10	1.11
Fe. L. average	0.8001	0.4408	0.3593	1.23	55.0	45.0	2.03	1.10	1.11

E.9 The Decomposition of Benzoyl Peroxide in p-Dichlorobenzene in the Presence and Absence of Metal Benzoates.

A series of experiments were carried out in p-dichlorobenzene following the usual experimental procedures in the presence and absence of additives.

Benzoyl peroxide (1.0g) was added to a deaereated solution of p-dichlorobenzene (50g) and allowed to decompose over 72 hours at 80°.

Separate experiments were also carried out , each containing metal benzoate (0.5g) and the same peroxide concentration as above.

Bibenzyl (0.5g) was added as the internal standard in this system. A calibration graph of relative peak height against relative mole ratio was constructed for 2,5-dichlorobiphenyl with bibenzyl, and the yield of 2,5-dichlorobiphenyl was estimated using the following analytical conditions :-

G.L.C. Analysis Data

Column : C.20.C

Column temperature : 200°

Pressure : 1 Kp/cm^2

Instrument : Perkin-Elmer F21D

Carrier gas : Nitrogen

Attenuation : x 64

Retention Data - (Relative to bibenzyl)

Compounds	Relative retention times
Bibenzyl	1.00
2,5-dichlorobiphenyl	2.05

The results are given in Table (17).

Table (17)

The decomposition of benzoyl peroxide in p-dichlorobenzene in the presence and absence of additives at 80° for 72 hours.

experiment number	catalyst (g)	2,5-dichlorobiphenyl (m/m peroxide)
E. 1	nil	0.6646
E. 2		0.6643
E. 3		0.6641
*E. average	nil	0.6643
Cu. E. 1	cupric benzoate	0.8890
Cu. E. 2	(0.5)	0.8882
Cu. E. 3		0.8887
*Cu. E. average	cupric benzoate	0.8884
Fe. E. 1	ferric benzoate	0.9747
Fe. E. 2	(0.5)	0.9721
Fe. E. 3		0.9746
*Fe. E. average	ferric benzoate	0.9738
p-Cl. E. 1	$Cu(p\text{-}ClC_6H_4CO_2)_2$	0.9559
p-Cl. E. 2	(0.5)	0.9570
p-Cl. E. 3		0.9560
*p-Cl. E. average	$Cu(p\text{-}ClC_6H_4CO_2)_2$	0.9563

E.10 The Competitive Reactions of Benzoyl Peroxide in Equimolar p-Dichlorobenzene and Benzene, Bromobenzene or Chlorobenzene in the Presence and Absence of Additives.

(a) The competitive reactions of benzoyl peroxide in equimolar benzene-p-dichlorobenzene in the presence and absence of additive.

Benzoyl peroxide (1.og) was allowed to decompose in an equimolar mixture of p-dichlorobenzene (25g) and benzene (15ml) with and without additives.

At the end of the reaction bibenzyl (0.3–0.5g) was added and the yields of 2,5-dichlorobiphenyl and biphenyl were calculated by the use of g.l.c. using the analytical conditions described above. An additional calibration graph was constructed for biphenyl.

Retention Time of Biphenyl Relative to Bibenzyl

Biphenyl	0.54
Bibenzyl	1.00

The results of this series of reaction are given on Table (18a).

(b) The competitive reactions of benzoyl peroxide in equimolar p-dichlorobenzene-chlorobenzene in the presence and absence of additives.

Benzoyl peroxide (1.0g) was allowed to decompose in an equimolar mixture of chlorobenzene (17.3ml) and p-dichlorobenze (15g) with or without additive according to the standard experimental procedures for the competitive reactions.

At the completion of reaction, diphenylmethane (0.1g) and bibenzyl (0.3g) were added as internal standards to determine the yields of chlorobiphenyls and 2,5-dichlrobiphenyl respectively.

A.15.C column was used with the same g.l.c. analytical condition described in section (E.3.b) for chlorobiphenyls and column C.20.C with the analytical condition described in section (E.9) for the determination of the yield of 2,5-dichlorobiphenyl.

The results are given on Table (18b)

(c) The competitive reactions of benzoyl peroxide in equimolar p-dichlorobenzene-bromobenzene in the presence and absence of additives.

Similar competitive reactions to those described above were carried out using p-dichlorobenzene-bromobenzene mixtures.

Benzoyl peroxide (1.0g) was allowed to decompose in an equimolar mixture of p-dichlorobenzene (15g) and bromobenzene (17.8ml) in the presence and absence of additive for 72 hours at 80 ± 1°.

At the completion of reaction, diphenylmethane (0.1g) and bibenzyl (0.3g) were added as internal standards. The yields of isomeric bromobiphenyls were estimated by the use of the A.15.C column and with experimental conditions similar to those described in section (E.5.a). The yields of 2,5-dichlorobiphenyl were estimated by the use of the C.20.C column with the analytical conditions described in section (E.9).

The results of this series of experiments are given in Table (18c).

Table (18 a)

The decomposition of benzoyl peroxide in equimolar p-dichlorobenzene-benzene system in the presence and absence of additives at 80°.

experiment number	additives (g)	biaryl (total m/m)	$PhC_6H_3Cl_2$ (m/m)	Ph-Ph (m/m)	$K^{p\text{-}Cl_2}_{H}$
M. 1	nil	0.7563	0.4709	0.2854	1.65
M. 2		0.7561	0.4692	0.2869	1.64
M. 3		0.7564	0.4706	0.2851	1.65
M. average	nil	0.7560	0.4702	0.2858	1.65
Cu. M. 1	cupric benzoate	0.9578	0.6540	0.3038	2.13
Cu. M. 2	(0.5)	0.9492	0.6449	0.3043	2.12
Cu. M. 3		0.9501	0.6460	0.3041	2.12
Cu. M. ave.	cupric benzoate	0.9494	0.6453	0.3041	2.12
Fe. M. 1	ferric benzoate	0.9628	0.6397	0.3231	1.98
Fe. M. 2	(0.5)	0.9558	0.6354	0.3204	1.98
Fe. M. 3		0.9492	0.6300	0.3192	1.97
Fe. M. ave.	ferric benzoate	0.9559	0.6350	0.3209	1.98

Table (18 b)

The decomposition of benzoyl peroxide in equimolar p-dichlorobenzene-chlorobenzene system in the presence and absence of additives at 80°.

experiment	biaryl	$Ph\cdot C_6H_3Cl_2$	$Ph\cdot C_6H_4Cl$	$K^{Cl}_{\underline{p}-Cl_2}$	isomer ratio(PhCl)		
number	(total m/m)	(m/m)	(m/m)		o	m	p
nil							
N. 1	0.5975	0.3058	0.2917	0.95	54.4	27.0	18.6
N. 2	0.5979	0.3064	0.2915	0.95	54.6	27.3	18.0
N. 3	0.5984	0.3065	0.2919	0.95	54.7	27.3	18.0
N. average	0.5979	0.3062	0.2917	0.95	54.6	27.3	18.1
cupric benzoate (0.5g)							
Cu. N. 1	0.8263	0.4848	0.3415	0.70	57.1	25.7	17.2
Cu. N. 2	0.8300	0.4862	0.3438	0.71	57.4	25.4	17.2
Cu. N. 3	0.8297	0.4852	0.3445	0.71	57.0	25.6	17.3
Cu. N. ave.	0.8286	0.4854	0.3432	0.71	57.2	25.6	17.3
ferric benzoate (0.5g)							
Fe. N. 1	0.8167	0.4734	0.3433	0.73	57.2	25.7	17.1
Fe. N. 2	0.8118	0.4718	0.3400	0.72	57.4	25.3	17.3
Fe. N. 3	0.8118	0.4706	0.3412	0.72	57.7	25.1	17.2
Fe. N. ave.	0.8134	0.4719	0.3415	0.72	57.4	25.4	17.2

Table (18 c)

The decomposition of benzoyl peroxide in equimolar p-dichlorobenzene-bromobenzene system in the presence and absence of additives at 80°.

experiment number	biaryl (total m/m)	$Ph\cdot C_6H_3Cl_2$ (m/m)	$Ph\cdot C_6H_4Br$ (m/m)	${}^{Br}_{p\text{-}Cl_2}K$	isomer ratio(PhBr) o	m	p
nil							
O. 1	0.7694	0.4766	0.2928	0.61	54.9	29.4	15.7
O. 2	0.7663	0.4760	0.2903	0.61	54.4	29.9	15.7
O. 3	0.7652	0.4753	0.2899	0.61	54.8	29.5	15.7
O. average	0.7670	0.4760	0.2910	0.61	54.7	29.6	15.7
cupric benzoate (0.5g)							
Cu. O. 1	0.8774	0.5203	0.3564	0.68	57.3	27.8	14.9
Cu. O. 2	0.8783	0.5212	0.3571	0.69	57.3	27.7	15.0
Cu. O. 3	0.8782	0.5209	0.3573	0.69	57.1	27.8	15.1
Cu. O. ave.	0.8777	0.5208	0.3569	0.69	57.2	27.8	15.0
ferric benzoate (0.5g)							
Fe. O. 1	0.9206	0.5410	0.3796	0.70	54.4	28.8	16.8
Fe. O. 2	0.9211	0.5427	0.3784	0.70	54.2	29.8	16.0
Fe. O. 3	0.9192	0.5407	0.3785	0.70	54.5	29.0	16.5
Fe. O. ave.	0.9203	0.5415	0.3788	0.70	54.4	29.2	16.4

E.11 The Decomposition of Benzoyl Peroxide in 1,3,5-Trichlorobenzene in the Presence and Absence of Ferric Benzoate.

A series of reactions each in triplicate was conducted according to the experimental method outlined in section (E.2). The reactions were allowed to proceed to completion during 72 hours at 80 ± 1°. For this series a known amount of ferric benzoate (0.25-0.3g) was added to pure 1,3,5-trichlorobenzene (25g) followed by the addition of benzoyl peroxide (0.5g) to the reaction when thermal equilibrum had been established. Separate experiments were also carried out without additives.

At the completion of the reaction a known amount of bibenzyl (0.2-0.25g) was added as an internal standard for g.l.c. analysis, and the reaction mixture was filtered free of deposited ferric benzoate (where the catalyst was used) before commencing the normal work-up procedure.

The yiel of 2,4,6-trichlorobiphenyl was estimated by the use of g.l.c. with the following experimental conditions :-

G.L.C. Analysis Data

Column : C.20.C	Instrument Perkin-Elmer F21D
Column temperature : 200°	Carrier gas : Nitrogen
Pressure : 1 Kp/cm^2	Attenuation : x 64

Retention Data - (Relative to bibenzyl)

Compounds	Relative retention times
Bibenzyl	1.00
2,4,6-Trichlorobiphenyl	2.38

The results obtained are tabulated as Table (19).

Table (19)

The decomposition of benzoyl peroxide in 1,3,5-trichlorobenzene in the presence and absence of additives at 80° for 72 hours.

experiment number	catalyst (g)	2,4,6-trichlorobiphenyl (m/m peroxide)
F. 1	nil	0.8603
F. 2		0.8671
F. 3		0.8703
F. average	nil	0.8661
Fe. F. 1	ferric benzoate	0.9571
Fe. F. 2	(0.5)	0.9559
Fe. F. 3		0.9561
Fe. F. average	ferric benzoate	0.9564

E.12 The Competitive Reactions of Benzoyl Peroxide in Equimolar 1,3,5-Trichlorobenzene and Benzene or Chlorobenzene in the Presence and Absence of Ferric Benzoate.

(a) The competitive reactions of benzoyl peroxide in equimolar benzene-1,3,5-trichlorobenzene in the presence and absence of ferric benzoate.

These reactions were performed, each containing benzoyl peroxide (1.0g) in anequimolar mixture of benzene (15ml) and 1,3,5-trichlorobenzene (30.7g) with a known amount of added ferric benzoate (0.5g). The reactions were allowed to proceed to completion during 72 hours at 80 ± 1°, in an atmosphere of nitrogen. At the end of this period a known amount of the internal standard, bibenzyl (0.3–0.4g), was added and the reactions were worked-up as outlined in section (E.2).

The yields of biphenyl and 2,4,6-trichlorobiphenyl were calculated by g.l.c. analysis making use of the calibration curves previously constructed for these compounds.

A set of triplicate experiments was performed with benzoyl peroxide (1.0g) in equimolar benzene (15ml)- 1,3,5-trichlorobenzene (30.7g) in the absence of added ferric benzoate.

The results are tabulated in Table (20a)

Table (20 a)

The decomposition of benzoyl peroxide in equimolar benzene and 1,3,5-trichlorobenzene mixture in the presence and absence of additives at 80°.

experiment number	additives (g)	biaryl (total m/m)	$Ph\cdot C_6H_2Cl_3$ (m/m)	Ph-Ph (m/m)	${}^{s-Cl_3}_{H}K$
P. 1	nil	0.9346	0.7786	0.1560	4.99
P. 2		0.9420	0.7846	0.1574	4.98
P. 3		0.9442	0.7867	0.1575	4.98
P. average	nil	0.9372	0.7803	0.1569	4.99
Fe. P. 1	ferric benzoate	0.9259	0.7679	0.1580	4.86
Fe. P. 2	(0.5)	0.9218	0.7644	0.1574	4.86
Fe. P. 3		0.9228	0.7650	0.1578	4.85
Fe. P. ave.	ferric benzoate	0.9236	0.7658	0.1578	4.86

(b) The competitive reactions of benzoyl peroxide in equimolar chlorobenzene-1,3,5-trichlorobenzene in the presence and absence of ferric benzoate

Benzoyl peroxide (1.0g) was allowed to decompose in an equimolar mixture of chlorobenzene (15.5g) and 1,3,5-trichlorobenzene (25g) with and without ferric benzoate (0.5g) for 72 hours in an atmosphere of nitrogen at 80° according to the normal experimental procedures for the competitive reactions.

At the end of reaction, diphenylmethane (0.1g) and bibenzyl (0.3g) were added as internal standards to determine the yields of chlorobiphenyls and 2,4,6-trichlorobiphenyl respectively.

A.15.C column was used with the g.l.c. analytical conditions described in section (E.3.b) for chlorobiphenyls, and column C.20.C. with the analytical conditions described in section (E.10) for the determination of the yield of 2,4,6-trichlorobiphenyl.

The results from this series of experiments are given in Table (20 b).

Table (20 b)

The decomposition of benzoyl peroxide in equimolar 1,3,5-trichlorobenzene-chlorobenzene system in the presence and absence of additives at 80°.

experiment number	biaryl (total m/m)	$Ph\cdot C_6H_2Cl_3$ (m/m)	$Ph\cdot C_6H_4Cl$ (m/m)	${}^{Cl}_{s-Cl_3}K$	isomer ratio(PhCl)		
					o	m	p
nil							
Q. 1	0.8915	0.6987	0.1928	0.28	54.9	27.0	18.1
Q. 2	0.8999	0.7001	0.1998	0.28	55.0	27.1	17.9
Q. 3	0.8974	0.7009	0.1965	0.28	55.1	27.1	17.8
Q. average	0.8963	0.6999	0.1964	0.28	55.0	27.0	18.0
ferric benzoate (0.5g)							
Fe. Q. 1	0.9571	0.7340	0.2231	0.30	57.2	25.3	17.5
Fe. Q. 2	0.9575	0.7336	0.2239	0.30	56.9	25.1	18.0
Fe. Q. 3	0.9640	0.7400	0.2240	0.30	57.2	25.5	17.3
Fe. Q. ave.	0.9599	0.7359	0.2240	0.30	57.1	25.3	17.6

E.13 The Decomposition of Benzoyl Peroxide in Methyl Benzoate in the Presence of Metal Benzoates.

The reactions were carried out in methyl benzoate following the normal experimental procedure in the presence and absence of metal benzoate, and were allowed to proceed to completion during 72 hours at 80 ± 1°.

A known quantity of catalyst (cupric benzoate or ferric benzoate) were added to methyl benzoate (50ml) and the solutions were allowed to equilibrate, then benzoyl peroxide (1.0g) was added. Reactions were also carried out using the same peroxide concentration but without added catalyst,

At the end of the reaction a known quantity of bibenzyl (0.2-0.25g) was added to the reaction mixture and were worked-up by the standard procedure.

The yields of methoxycarbonylbiphenyl were estimated by g.l.c. with the following experimental conditions, and the results are given in Table (21).

G.L.C Analysis Data

Column : A.20C

Column temperature : 200°

Pressure : 1 Kp/cm^2

Instrument : Perkin-Elmer F21D

Carrier gas : Nitrogen

Attenuation : x 64

Retention Data - (Relative to bibenzyl)

Compounds	Relative retention times
Bibenzyl	1.00
2-Methoxycarbonylbiphenyl	1.29
3-Methoxycarbonylbiphenyl	3.25
4-Methoxycarbonylbiphenyl	3.63

Table (21)

The decomposition of benzoyl peroxide in methylbenzoate in the presence and absence of additives at 80° for 72 hours.

experiment number	catalyst (g)	$PhC_6H_4CO_2Me$ (m/m)	PhCOOH (m/m)	isomer ratio		
				o-	m-	p-
G. 1	nil	0.6246	0.2508	48.1	20.0	31.9
G. 2		0.6277	0.2514	48.4	19.8	31.8
G. 3		0.6287	0.2514	48.0	19.8	32.2
G. average	nil	0.6266	0.2512	48.1	19.9	32.0
Cu. G. 1	cupric benzoate	0.8102	0.8003	56.9	16.5	26.6
Cu. G. 2	(0.5)	0.7978	0.7976	56.4	16.4	27.2
Cu. G. 3		0.8033	0.7991	56.8	16.1	27.1
Cu. G. ave.	cupric benzoate	0.8013	0.7990	56.6	16.3	27.1
Fe. G. 1	ferric benzoate	0.7749	0.7256	53.2	16.5	30.3
Fe. G. 2	(0.5)	0.7737	0.7249	53.9	16.5	29.6
Fe. G. 3		0.7742	0.7254	53.1	16.7	30.2
Fe. G. ave.	ferric benzoate	0.7741	0.7253	53.4	16.5	30.1

E.14 The Competitive Reactions of Benzoyl Peroxide in Equimolar Benzene-Methyl Benzoate in the Presence and Absence of Metal Benzoates.

Benzoyl peroxide (1.0g) was allowed to decompose in an equimolar mixture of methyl benzoate and benzene (50ml) with and without additives (cupric benzoate or ferric benzoate). The reactions were carried out according to the standard conditions described in section (E.2).

Bibenzyl (0.2-0.25g) was added as an internal standard, the reaction mixture was processed by the standard method and analysed by g.l.c. using the analytical conditions described above. An additional calibration graph of relative peak height against relative mole ratio was constructed for biphenyl with bibenzyl as intarnal standard to determine the yield of biphenyl in these reactions.

Retention Time of Biphenyl Relative to Bibenzyl

Compounds	Relative retention times
Biphenyl	0.54
Bibenzyl	1.00

The results of these reactions are shown on Table (22).

Table (22)

The decomposition of benzoyl peroxide in equimolar benzene–methyl benzoate mixture in the presence and absence of additives at 80° for 72 hours.

experiment number	biaryl (total) (m/m)	$PhC_6H_4CO_2Me$ (m/m)	Ph-Ph (m/m)	$^{CO_2Me}_{H}K$	isomer ratios			p . r . f		
					o	m	p	Fo	Fm	Fp
R. 1	0.8488	0.5561	0.2927	1.90	48.0	19.6	32.4	2.74	1.12	3.69
R. 2	0.8496	0.5546	0.2950	1.88	48.1	20.0	31.9	2.71	1.13	3.61
R. 3	0.8490	0.5552	0.2938	1.89	48.2	19.8	32.0	2.73	1.12	3.64
R. average	0.8492	0.5553	0.2939	1.89	48.1	19.8	32.1	2.73	1.12	3.64
Cu. R. 1	0.9286	0.6261	0.3025	2.07	56.8	16.5	26.7	3.53	1.02	3.32
Cu. R. 2	0.9282	0.6249	0.3033	2.06	56.9	16.5	26.6	3.52	1.02	3.29
Cu. R. 3	0.9281	0.6237	0.3044	2.04	56.1	16.8	27.1	3.48	1.03	3.32
Cu. R. average	0.9284	0.6250	0.3034	2.06	56.6	16.6	26.8	3.50	1.03	3.31

Table (22) continued.

experiment number	biaryl (total) (m/m)	$PhC_6H_4CO_2Me$ (m/m)	Ph-Ph (m/m)	$^{CO_2Me}_{H}K$	isomer ratios			p . r . f		
					o	*m*	*p*	F*o*	F*m*	F*p*
Fe. R. 1	0.9252	0.6198	0.3054	2.03	53.2	16.7	30.1	3.24	1.02	3.67
Fe. R. 2	0.9259	0.6210	0.3049	2.03	53.7	16.5	29.8	3.27	1.00	3.63
Fe. R. 3	0.9266	0.6201	0.3065	2.02	53.9	16.3	29.8	3.27	0.99	3.61
Fe. R. average	0.9259	0.6203	0.3056	2.03	53.6	16.5	29.9	3.26	1.00	3.64

E.15 The Decomposition of Benzoyl Peroxide in Benzophenone in the Presence and Absence of Metal Benzoates.

A series of experiments each in triplicate were carried out according to the method described in section (e.2) in the presence and absence of additives (cupric benzoate or ferric benzoate).

In each reaction benzoyl peroxide (1.0g) was added to a deaerated solution of benzophenone (50g) and the reactions were allowed to proceed to completion during 72 hours at 80 ± 1°.

Experiments were also carried out using the same concentrations of peroxide as above but in the presence of metal catalysts (0.5g).

Triphenylmethane (0.08–0.1g) was added at the completion of reaction as the internal standard. The A.15.C column was found to be suitable for the quantitative analysis. With this column all the major reaction products are completely separated, and the yields of phenylbenzophenones were estimated by the use of calibration curves constructed for the individual isomeric phenylbenzophenones against triphenylmethane as internal standard,

The analytical conditions together with the retention data are given below: -

G.L.C. Analysis Data

Column : A.15.C
Column temperature : 200°
Pressure : 1 Kp/cm^2

Instrument : Pye 104
Carrier gas : Nitrogen
Attenuation : 50×10^{-2}

Retention Data - (Relative to triphenylmethane)

Compounds	Relative retention times
2-Phenylbenzophenone	0.65
Triphenylmethane	1.00
3-Phenylbenzophenone	3.00
4-Phenylbenzophenone	3.87

The results of these reactions are summarised in Table (23).

E.16 The Competitive Reactions of Benzoyl Peroxide in Equimolar Benzophenone-Benzene in the Presence and Absence of Metal Benzoates.

Benzoyl peroxide (1.0g) was allowed to decompose in an equimolar mixture of benzophenone (22.3g) and benzene (10ml) at 80 ± 1° for 72 hours under a steady stream of nitrogen gas in a thermostat in the presence and absence of additives (cupric benzoate or ferric benzoate).

At the end of the reactions triphenylmethane (0.05–0.08g) was added and the yields of biaryls were estimated using the calibration curves described in previous section (csection E.15) with an additional calibration graph of relative peak height against relative mole ratio for biphenyl with triphenylmethane as an internal standard to determine the yield of biphenyl. The analytical conditions described in section (E.15) were used for g.l.c. analysis of these series of reactions, and the results are given on Table (24).

Table (23)

The decomposition of benzoyl peroxide in benzophenone in the presence and absence of additives at 80° for 72 hours.

experiment number	catalyst (g)	phenylbenzophenone (m/m)	isomer ratio o-	m-	p-
H. 1	nil	0.8262	39.5	21.1	39.4
H. 2		0.8642	41.3	20.4	38.3
H. 3		0.8422	39.2	21.8	39.0
H. average	nil	0.8442	40.0	21.1	38.9
Cu. H. 1	cupric benzoate	0.8853	50.0	17.5	32.5
Cu. H. 2	(0.5)	0.8824	50.5	17.4	32.1
Cu. H. 3		0.8843	49.8	17.9	32.3
Cu. H. ave.	cupric benzoate	0.8840	50.1	17.6	32.3
Fe. H. 1	ferric benzoate	0.9869	47.9	18.1	34.0
Fe. H. 2	(0.5)	0.9862	47.6	18.6	33.8
Fe. H. 3		0.9879	47.6	19.1	33.3
Fe. H. ave.	ferric benzoate	0.9870	47.7	18.6	33.7

Table (24)

The decomposition of benzoyl peroxide in equimolar benzene-benzophenone mixture in the presence and absence of additives at 80° for 72 hours.

experiment number	biaryl (total) (m/m)	PhC_6H_4COPh (m/m)	Ph-Ph (m/m)	$^{PhCO}_{H}K$	isomer ratios			p . r . f		
					o	m	p	Fo	Fm	Fp
S. 1	0.7061	0.5762	0.1299	4.44	39.8	21.2	39.0	2.65	1.41	5.20
S. 2	0.7014	0.5713	0.1301	4.39	39.5	21.0	39,5	2.63	1.39	5.21
S. 3	0.6962	0.5658	0.1304	4.34	41.0	21.1	37.9	2.65	1.38	4.94
S. average	0.6962	0.5711	0.1301	4.39	40.1	21.1	38.8	2.65	1.39	5.10
Cu. S. 1	0.7622	0.6121	0.1501	4.08	50.3	17.6	32.1	3.08	1.08	3.93
Cu. S. 2	0.7655	0.6162	0.1493	4.13	50.0	17.5	32.5	3.11	1.08	4.02
Cu. S. 3	0.7676	0.6179	0.1497	4.13	50.3	18.0	31.7	3.12	1.11	3.93
Cu. S. average	0.7651	0.6154	0.1497	4.11	50.0	17.7	32.1	3.10	1.09	3.96

Table (24) continued.

experiment number	biaryl (total) (m/m)	PhC_6H_4COPh (m/m)	Ph-Ph (m/m)	$^{PhCO}_{H}K$	isomer ratios			p . r . f		
					o	m	p	Fo	Fm	Fp
Fe. S. 1	0.7922	0.6331	0.1591	3.98	47.6	18.6	33.8	2.84	1.11	4.03
Fe. S. 2	0.7940	0.6339	0.1601	3.95	47.9	18.4	33.7	2.84	1.10	4.00
Fe. S. 3	0.7898	0.6314	0.1584	3.98	47.9	18.8	33.3	2.86	1.12	3.98
Fe. S. average	0.7920	0.6328	0.1592	3.97	47.8	18.6	33.6	2.85	1.11	4.00

E.17 The Decomposition of Benzoyl Peroxide in Benzonitrile in the Presence and Absence of Metal Benzoates.

A series of experiments was performed according to the standard procedure. Benzoyl peroxide (1.0g) was allowed to decompose in benzonitrile (50ml) for 72 hours under a stream of nitrogen at 80 ± 1° in the presence and absence of metal benzoates (cupric benzoate or ferric benzoate).

At the end of the reactions, bibenzyl (0.1–0.2g) was added as an internal standard for the quantitative determination of cyanobiphenyls. The relative peak height of cyanobiphenyls to bibenzyl was determined and their yields are determined from the relative peak height against relative mole ratio calibration curves constructed for the individual isomeric cyanobiphenyls.

The analytical conditions together with the retention data are given below, and the results obtained are shown in Table (25).

G.L.C. Analysis Data

Column :	A.15.C	Instrument :	Pye 104
Column temperature :	180°	Carrier gas :	Nitrogen
Pressure :	1 Kp/cm^2	Attenuation :	50 x 10^{-2}

Retention Data – (Relative to bibenzyl)

Compounds	Relative retention times
Bibenzyl	1.00
2-Cyanobiphenyl	1.40
3-Cyanobiphenyl	2.05
4-Cyanobiphenyl	2.20

Table (25)

The decomposition of benzoyl peroxide in benzonitrile in the presence and absence of additives at 80° for 72 hours.

experiment number	catalyst (g)	PhC_6H_4CN (m/m)	Ph-Ph (m/m)	isomer ratio		
				o-	*m*-	*p*-
I. 1	nil	0.7238	0.086	51.9	17.5	30.6
I. 2		0.7212	0.087	52.6	17.2	30.2
I. 3		0.7249	0.088	52.4	17.5	30.1
I. average	nil	0.7233	0.087	52.3	17.4	30.3
Cu. I. 1	cupric benzoate	0.7848	—	57.1	15.1	27.8
Cu. I. 2	(0.5)	0.7824	—	56.9	15.3	27.8
Cu. I. 3		0.7824	—	57.0	15.2	27.8
Cu. I. ave.	cupric benzoate	0.7832	—	57.0	15.2	27.8
Fe. I. 1	ferric benzoate	0.8350	0.030	57.4	15.8	26.8
Fe. I. 2	(0.5)	0.8335	0.026	57.7	15.7	26.6
Fe. I. 3		0.8326	0.028	57.7	15.7	26.6
Fe. I. ave.	ferric benzoate	0.8337	0.028	57.6	15.7	26.7

E.18 The Competitive Reactions of Benzoyl Peroxide in Equimolar Benzene-Benzonitrile in the Presence and Absence of Metal Benzoates.

A number of experiments, each with benzoyl peroxide (1.0g) and a known amount of additive (cupric benzoate or ferric benzoate or none) in an equimolar mixture of benzene (21.5ml) and benzonitrile (24.8ml), were performed in triplicate according to the standard procedure described previously, for the duration of 72 hours at 80 ± 1°.

At the completion of reaction a known quantity of bibenzyl (0.1-0.2g) was added as an internal standard, and the reaction mixture was processed by the standard method. The yields of biphenyl and cyanobiphenyls were estimated using the g.l.c. analytical conditions described in above section. An additional calibration graph of relative peak height against relative mole ratio was constructed for biphenyl with bibenzyl as an internal standard to determine the yield of biphenyl in these reactions.

Retention Time of Biphenyl Relative to Bibenzyl

Compounds	Relative retention times
Biphenyl	0.54
Bibenzyl	1.00

The results of these reactions are shown in Table (26).

Table (26)

The decomposition of benzoyl peroxide in equimolar benzene-benzonitrile mixture in the presence and absence of additives at 80° for 72 hours.

experiment number	biaryl (total) (m/m)	PhC_6H_4CN (m/m)	Ph-Ph (m/m)	${}^{CN}_{H}K$	isomer ratios			p . r . f		
					o	m	p	Fo	Fm	Fp
T. 1	0.8728	0.5739	0.2989	1.92	52.2	17.2	30.6	3.01	0.99	3.53
T. 2	0.8805	0.5810	0.2995	1.94	52.3	17.7	30.0	3.04	1.03	3.50
T. 3	0.8920	0.5843	0.3077	1.90	52.4	17.3	30.3	2.99	0.99	3.50
T. average	0.8817	0.5797	0.3020	1.92	52.3	17.4	30.3	3.01	1.00	3.49
Cu. T. 1	0.9898	0.6259	0.3639	1.72	54.1	16.8	29.1	2.79	0.87	3.00
Cu. T. 2	0.9925	0.6276	0.3649	1.72	54.3	16.5	29.2	2.80	0.85	3.01
Cu. T. 3	0.9913	0.6272	0.3641	1.72	54.5	16.7	28.8	2.81	0.86	2.97
Cu. T. average	0.9932	0.6289	0.3643	1.72	54.3	16.6	29.1	2.80	0.86	2.99

Table (26) continued.

experiment number	biaryl (total) (m/m)	PhC_6H_4CN (m/m)	Ph-Ph (m/m)	${}^{CN}_{H}K$	isomer ratios			p . r . f		
					o	m	p	Fo	Fm	Fp
Fe. T. 1	1.0733	0.6927	0.3806	1.82	57.0	15.4	29.6	3.11	0.84	3.01
Fe. T. 2	1.0713	0.6914	0.3799	1.82	57.2	15.4	27.2	3.12	0.85	2.97
Fe. T. 3	1.0726	0.6923	0.3803	1.82	57.1	15.8	27.1	3.12	0.86	2.96
Fe. T. average	1.0724	0.6921	0.3803	1.82	57.1	15.6	27.3	3.12	0.85	2.98

III. DISCUSSION

D.1 The Decomposition of Benzoyl Peroxide in Benzene, Chlorobenzene and Bromobenzene in the Presence and Absence of Additives at 80°.

(A) The decomposition of benzoyl peroxide in benzene, chlorobenzene and bromobenzene in the absence of additives.

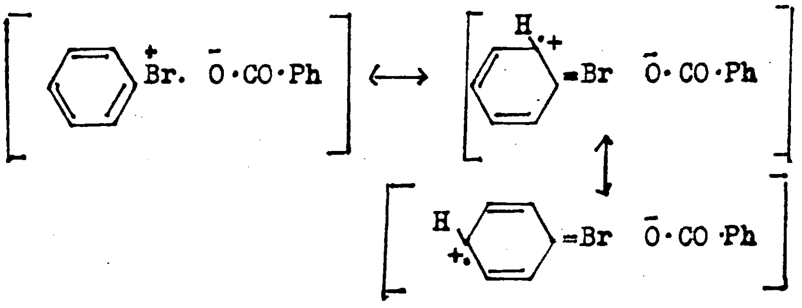
The results of the decomposition of benzoyl peroxide in benzene, chlorobenzene and bromobenzene in the absence of additives are shown in tables (8),(9) and (12)

The mechanisms and kinetics of the thermal decomposition of benzoyl peroxide in these solvents have received the greatest attention by many workers, and in particular the reaction of benzoyl peroxide in benzene, have been subject of extensive kinetic studies. The existence of an induced reaction leading to an order of 1.5 in peroxide, which accompanies the first-order primary homolysis into benzoyloxy radicals, in a number of solvents including some aromatic solvents such as benzene was first brought to light by Nozaki and Bartlett[14]. Further investigations in the reactions of benzoyl peroxide with benzene itself by Gill and Williams [45] established the decomposition of benzoyl peroxide in benzene, obeyed a kinetic law of the form (61) :

$$-d[P]/dt = k_1[P] + k_{3/2}P^{3/2} \qquad (61)$$

The kinetics of this form are given by such a system provided the chains are terminated by a dimerisation or disproportionation reaction involving like radicals, such as two phenylcyclohexadienyl radicals [63 (i) and (j)] .

However, while this picture provides adequately for reactions of benzoyl peroxide in benzene and chlorobenzene, the corresponding reaction in bromobenzene is different. In bromobenzene it is found that it is the reactions between unlike radicals 63(g) which provide the main termination reactions and both dimerisation and disproportionation are much reduced[47], with a consequent increase in the yields of biaryls and benzoic acid as seen in the present work, the yields of bromobiphenyls are much higher than those of biphenyl or chlorobiphenyls. This difference in mechanism is attributed to the greater stability of the benzoyloxy-radical in bromobenzene, probably as the results of the formation of a one-electron transfer complex such as formula (62) with the solvent[47].



(62)

The formation of major products in the decomposition of benzoyl peroxide in benzene in the absence of additives can be accounted for by the sequence of reaction shown below, those marked with an askerisk being of very minor importance when the reaction is conducted at 80°.

(a) $(PhCO\cdot O)_2 \longrightarrow 2\ PhCO\cdot O\cdot$ (63)

(b) $PhCO\cdot O\cdot \longrightarrow Ph\cdot + CO_2$

(c) $Ph\cdot + PhH \longrightarrow [Ph\cdot PhH]\cdot$

(d)* $PhCO{\cdot}O{\cdot} + PhH \longrightarrow [PhCO{\cdot}OPhH]{\cdot}$

(e) $[PhPhH]{\cdot} + (PhCO{\cdot}O)_2 \longrightarrow Ph{\cdot}Ph + PhCO_2H + PhCO{\cdot}O{\cdot}$

(f)* $[PhCO{\cdot}OPhH]{\cdot} + (PhCO{\cdot}O)_2 \longrightarrow PhCO{\cdot}OPh + PhCO_2H + PhCO{\cdot}O{\cdot}$

(g)* $[Ph{\cdot}PhH]{\cdot} + PhCO{\cdot}O{\cdot} \longrightarrow Ph{\cdot}Ph + PhCO_2H$

(h)* $[PhCO{\cdot}OPhH]{\cdot} + PhCO\ O \longrightarrow PhCO{\cdot}OPh + PhCO_2H$

(i) $2\,[Ph{\cdot}PhH]{\cdot} \longrightarrow Ph{\cdot}Ph + PhPhH_2$

(j) $2\,[Ph{\cdot}PhH]{\cdot} \longrightarrow (Ph{\cdot}PhH)_2$

(k)* $2\,[PhCO{\cdot}OPhH]{\cdot} \longrightarrow$ oxygen-containing dimerisation and disproportionation products.

The reaction with chlorobenzene follows a similar pattern but with bromobenzene the reaction corresponding to (g) assumes much greater importance and the reactions corresponding to (i) and (j) become insignificant.

(B) The effects of additives on the decomposition of benzoyl peroxide in benzene, chlorobenzene and bromobenzene.

The presence of oxidising agents such as oxygen,[55,56] nitro-compounds[57,58] and metal benzoates[71,74] during the decomposition of benzoyl peroxide in aromatic solvent is known to increase the yields of products by participating in steps (d) and (g) in the following equation :

(a) $(PhCO{\cdot}O)_2 \longrightarrow 2\,PhCO{\cdot}O{\cdot}$

(b) $PhCO{\cdot}O{\cdot} \longrightarrow Ph{\cdot} + CO_2$ (64)

(c) $Ph{\cdot} + ArH \longrightarrow Ph{\cdot}ArH$

(d) $[Ph\ ArH]{\cdot} + \text{Oxidising agent} \longrightarrow Ph{\cdot}Ar$

(e) $2\,[\mathrm{Ph{\cdot}ArH}]\cdot \longrightarrow (\mathrm{Ph{\cdot}ArH})_2$

(f) $2\,[\mathrm{Ph{\cdot}ArH}]\cdot \longrightarrow \mathrm{Ph{\cdot}Ar} + \mathrm{Ph{\cdot}ArH_2}$

(g) $\mathrm{Ph{\cdot}Ar\,H_2}$ + ox. agent $\longrightarrow \mathrm{Ph{\cdot}Ar}$

The effects of quinones, nitro-compounds and metal benzoates on the decomposition of benzoyl peroxide in benzene chlorobenzene and bromobenzene are shown in Tables (8),(9) and (12).

(1) The effects of quinones on the decomposition of benzoyl peroxide in benzene, chlorobenzene and bromobenzene.

Table (27)

The products of decomposition of benzoyl peroxide in benzene, chlorobenzene and bromobenzene in the presence and absence of quinones at 80°.

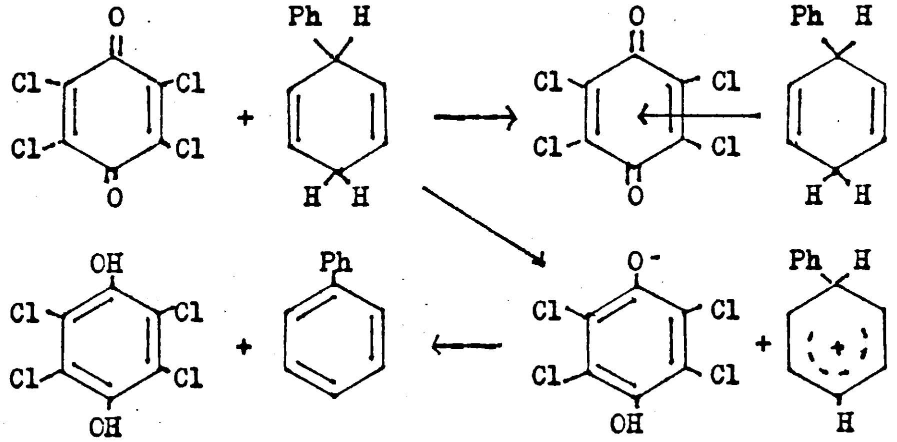
solvents	additives	biaryl (m/m)	benzoio acid (m/m)	isomer ratios		
				o	m	p
benzene	none	0.3882	0.2500		——	
	p-chloranil*	0.5082	0.4744		——	
	o-chloranil*	0.5610	0.4896		——	
chlorobenzene	none	0.4024	0.3387	54.6	24.2	17.2
	o-chloranil*	0.5372	—	56.9	25.6	17.5
	o-chloranil	0.6358	—	58.3	24.4	17.3
bromobenzene	none	0.7454	0.9536	54.2	30.4	15.4
	o-chloranil*	0.7515	—	54.0	30.5	15.5
	o-chloranil	0.8166	—	55.7	29.1	15.1

* indicates the additives being added after the completion of decomposition of benzoyl peroxide.

The results of the decomposition of benzoyl peroxide in benzene, chlorobenzene and bromobenzene in the presence and absence of quinones (o-chloranil or p-chloranil) are summarised above as Table (27).

Quinones comprise the powerful class of organic oxidising agents. The mechanism for dehydrogenation of hydroaromatic compounds proceeds in a two-stage ionic process. The most compelling evidence for the ionic mechanism arises from the occurence of a number of neighboring-group effects similar to those which often accompany unimolecular solvolysis. The initial step in the overall reaction sequence is the formation of charge-transfer complex between donor and acceptors analogous to that postulated in Diels-Alder[94] reaction.

The reaction between tetrahydro-1,4-benzoquinone and 1,4-dihydrobiphenyl is illustrated in equation (65).



(65)

Thus the addition of o- or p-chloranil after the completion of reaction improves the yields of biaryls by oxidising dihydrobiaryls as in (65). This effect was also observed in the present work, where the addition of quinones after the completion of decomposition of benzoyl peroxide in benzene and chlorobenzene resulted in increased yields of biphenyl and chlorobiphenyl respectively, and in the later case the increased yield was accompanied by slight alteration in the isomer ratio in which the o-isomer increased at the expense of m-isomer, while that of the p-isomer seemed to remain unchanged.

However quinone added after the completion of decomposition of benzoyl peroxide in bromobenzene showed no significant increase in the yield of bromobiphenyls, nor was an alteration of isomer ratios observed, indicating the formation of charge-transfer complexes of type (62) between benzoyloxy-radical and bromobenzene which brings about the first order induced reaction observed by Gill and Williams[47], and giving the low yield of residue and apparent absence of dihydrobiphenyls.

Experiments were also carried out in which quinones were present during the decomposition of benzoyl peroxide in benzene, chlorobenzene and bromobenzene.

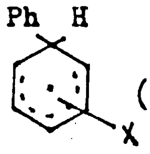
Quinones present during the reaction can also compete for the aryl-cyclohexadienyl radical as well as oxidising the dihydrobiaryls, and should therefore result to the higher yields of biaryl compered with the experiments where quinone was added after the completion of the reaction by eliminating the dimerisation and disproportionation of σ-radicals resulting in high boiling residue. The results given in Table (27) shows a slight increase in the yields of biaryl in all three solvents.

The effects of o-chloranil in the decomposition of benzoyl peroxide in these solvents can be interpreted by the following reaction scheme :

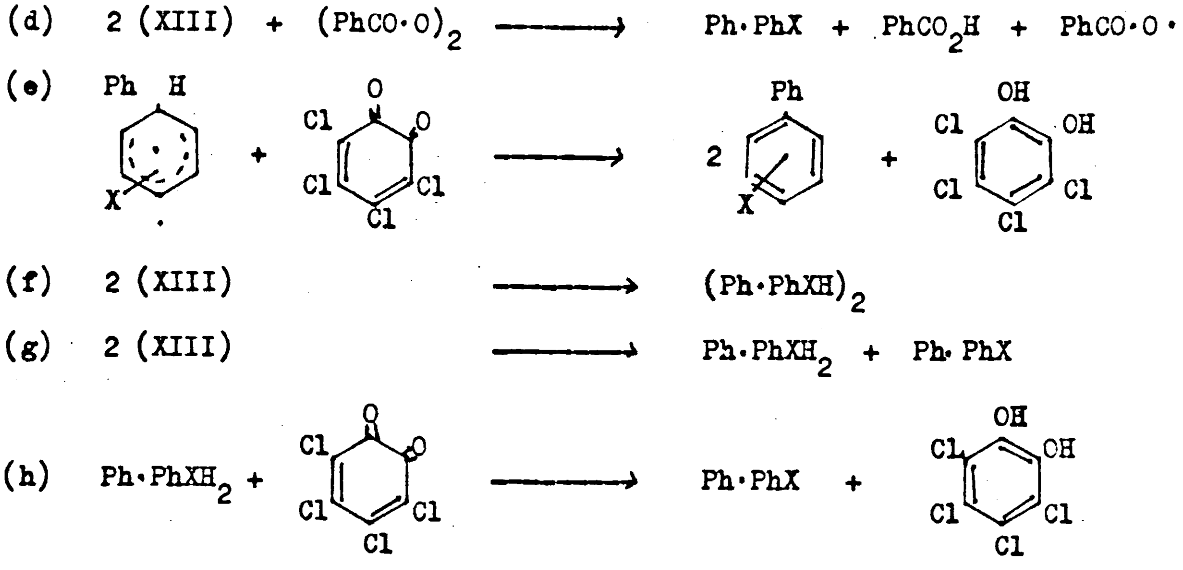
(a) $(PhCO\cdot O)_2 \longrightarrow 2\ PhCO\cdot O\cdot$

(b) $PhCO\cdot O\cdot \longrightarrow Ph\cdot + CO_2$ (66)

(c) $Ph\cdot + PhX \longrightarrow$



(XIII)



(X = H, Cl or Br)

Quinones present during the reaction can be seen as increasing the reaction rates of steps (e) and (h), at the expense of (f) and (g), hence providing more benzoyloxy-radicals for subsequent phenylation.

It was also noted that here again a slight increase in o-isomer occured when o-chloranil was present during the reaction, possible explanation for this observation will be dealt with in the later section.

In the decomposition of benzoyl peroxide in benzene using both o-, and P-chloranil as oxidising agent, the result indicated that o-chloranil is slightly better oxidising agent than the p-isomer.

(2) The effects of nitro-compounds on the decomposition of benzoyl peroxide in benzene, chlorobenzene and bromobenzene.

The effect of the presence of nitro-compounds in phenylation reactions with benzoyl peroxide in increasing the yields of biaryls and aroic acid is referred to as the "nitro-group effect".

This effect is further confirmed by the present results.

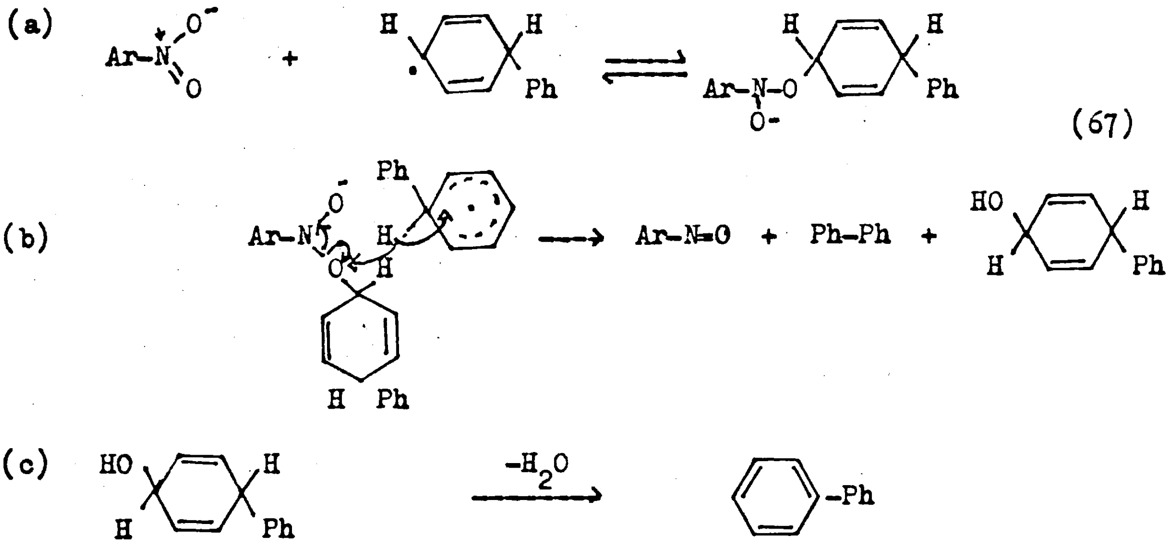
The decomposition of benzoyl peroxide in benzene, chlorobenzene and bromobenzene in the presence of m-dinitrobenzene, nitrosobenzene or pentafluoronitrosobenzene, summarised in Table (28), show a large increase in the yields of biphenyl and chlorobiphenyls and to a lesser extent in bromobiphenyls when nitro-compound was present during the reaction.

Table (28)

The yields of biaryls from the reaction of benzoyl peroxide with benzene, chlorobenzene or bromobenzene in the presence and absence of nitro-compounds at 80°.

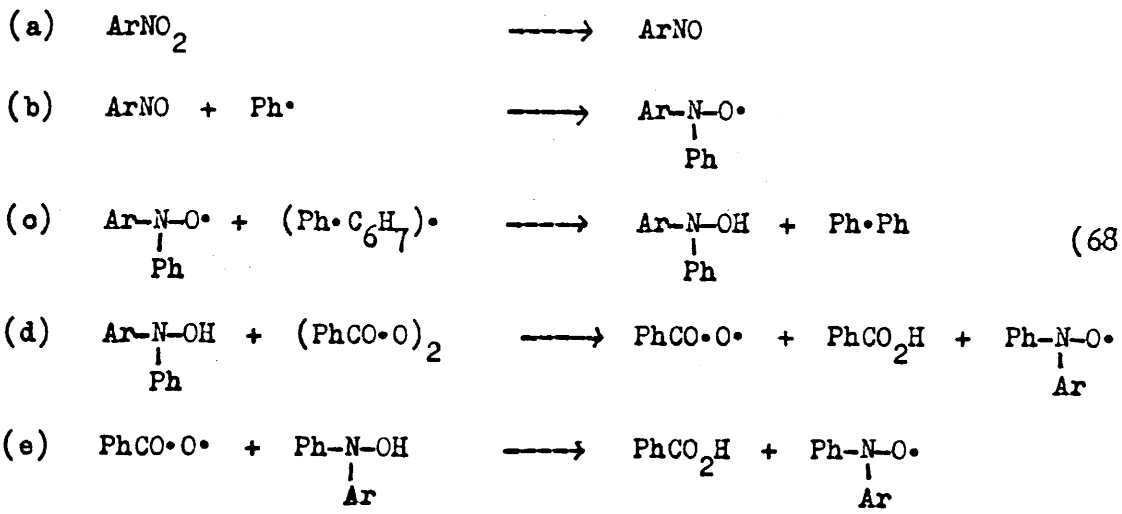
solvents (50ml)	additives (g)	biaryl (m/m)	isomer ratios o	m	p
benzene	none	0.3882	——		
	m-dinitrobenzene (0.18)	1.0362	——		
	nitrosobenzene (0.02)	0.8692	——		
	pentafluoronitrosobenzene (0.02)	0.9954	——		
chlorobenzene	none	0.4024	54.6	27.2	17.2
	m-dinitrobenzene (0.18)	0.7542	52.6	28.6	18.8
	nitrosobenzene (0.02)	0.8427	56.1	25.9	18.0
	pentafluoronitrosobenzene (0.02)	0.8049	58.2	24.4	17.4
bromobenzene	none	0.7454	54.2	30.4	15.4
	m-dinitrobenzene (0.18)	0.8500	54.8	29.7	15.5
	nitrosobenzene (0.02)	0.7928	54.9	29.3	15.8
	pentafluoronitrosobenzene (0.02)	0.8238	54.0	29.8	16.2

It has been shown that the effective catalysts responsible for the conversion of arylcyclohexadienyl radicals to biaryl are the nitroxide radicals formed from the nitroso-compound, which itself arises from the reduction of the nitro-compound[101] based on the observations that nitrosobenzene and phenylhydroxylamine (which is converted into nitrosobenzene) are much more effective than nitrobenzene, and the small amount of nitro-compound recovered at the end of the reaction would, as nitroso-compound, be sufficient to produce the observed effect, and also e.s.r. spectroscopy revealed the presence of a stable radical, a nitroxide, in reactions catalysed by nitro-compounds.



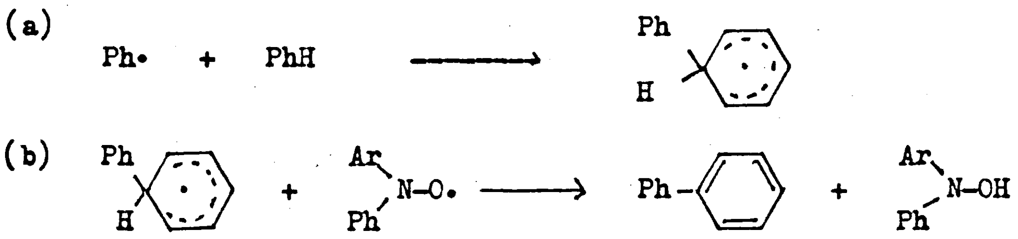
(67)

These stable radicals could then oxidise σ-radicals to form biphenyls, themselves being reduced to the hydroxylamine derivative which then propagates a radical chain by reacting with benzoyl peroxide according to the following scheme (68)



$$
\begin{array}{lll}
\text{(a)} & ArNO_2 \longrightarrow ArNO & \\
\text{(b)} & ArNO + Ph\cdot \longrightarrow Ar{-}\underset{Ph}{\underset{|}{N}}{-}O\cdot & \\
\text{(c)} & Ar{-}\underset{Ph}{\underset{|}{N}}{-}O\cdot + (Ph\cdot C_6H_7)\cdot \longrightarrow Ar{-}\underset{Ph}{\underset{|}{N}}{-}OH + Ph\cdot Ph & (68) \\
\text{(d)} & Ar{-}\underset{Ph}{\underset{|}{N}}{-}OH + (PhCO\cdot O)_2 \longrightarrow PhCO\cdot O\cdot + PhCO_2H + Ph{-}\underset{Ar}{\underset{|}{N}}{-}O\cdot & \\
\text{(e)} & PhCO\cdot O\cdot + Ph{-}\underset{Ar}{\underset{|}{N}}{-}OH \longrightarrow PhCO_2H + Ph{-}\underset{Ar}{\underset{|}{N}}{-}O\cdot &
\end{array}
$$

The observed increase in the yield of biphenyl in the experiments wher nitro-compound was present during the decomposition of benzoyl peroxide in benzene can be explained by nitroxide radicals formed via m-dinitrobenzene, nitrosobenzene or pentafluoronitrosobenzene effectively removing the σ-radicals (69 b), hence reducing their opportunity to dimerise.



(69)

Chalfont, Hey, Liang and Perkins (1971)[102] found in the decomposition of benzoyl peroxide in chlorobenzene that small quantities of nitrosobenzene produced high yields of benzoic acid and chlorobiphenyls, yet nitrobenzene was almost without effect on the reaction. They suggested that chlorine-substituted phenylcyclohexadienyl radicals reduce nitrobenzene to nitrosobenzene much less efficiently than to the unsubstituted radicals. However in the present work, it was found that the presence of m-dinitrobenzene in the phenylation of chlorobenzene increased the yield of chlorobiphenyls almost effectively as that of nitroso-compounds.

A similar picture to the reaction scheme of benzene would explain the increased yields of chlorobiphenyls and benzoic acid in the chlorobenzene reaction.

Chalfont, Hey, Liang and Perkins also noticed with the experiments to which nitrobenzene was added with chlorobenzene that the yields of o-chlorobiphenyl was curiously low; the same trend was observed in present work using m-dinitrobenzene. However the presence of either nitrosobenzene or pentafluoronitrosobenzene in chlorobenzene as in reaction catalysed by o-chloranil increased the yield of o-chlorobiphenyl. This might be due to selective removal of m- and p-chlorinated phenylcyclohexadienyl radical by small quantities of nitrobenzene during reduction to nitrosobenzene as in equation (67).

The increase in the yields of bromobiphenyls in the presence of m-dinitrobenzene, nitrosobenzene or pentafluoronitrosobenzene during the decomposition are less spectacular here than elsewhere because of the already relatively high yield of uncatalysed reaction. The roles played by nitro-compound in bromobenzene can be visualised as in benzene reaction, but to a lesser extent

Nitrosobenzene and pentafluoronitrosobenzene behaved similarly towards increasing the yields and in the effect on the isomer ratios of biaryls. The presence of five strong electron withdrawing fluorine in pentafluoronitrosobenzene which renders the π-system somewhat electron deficient, and also causes the nitro-group to be less electron-rich, showed no visible difference in present experiments.

(3) The effects of ferric benzoate, cupric benzoate and p-substituted cupric benzoates on the decomposition of benzoyl peroxide in benzene, chlorobenzene and bromobenzene.

The discovery of Kharash et al[65] that traces of copper usually as cuprous chloride or bromide, and to some extent other transitional metals, profoundly altered the course of reaction between organic peroxide and a variety of organic substances, has evoked considerable interest in elucidating the mechanism of these important reactions.

Kochi[103] summarised the mechanism of these reactions by postulating two possible classes of reaction; an electron-transfer or 'outer-sphere' mechanism, and a ligand-transfer or 'inner-sphere' mechanism, The predominance of one mechanism over the other, for a particular reaction, is said to depend primarily on the nature of the ligands of the participating metal salts.

The transition metal carboxylates are generally useful as electron-transfer oxidants, and thr reactions are said to proceed through cationic intermediates or transition states.

The results of the decomposition of benzoyl peroxide in benzene, chlorobenzene and bromobenzene in the presence of ferric benzoate, cupric benzoate or cupric X-benzoate ($X = NO_2$, Cl or Me) are shown in Tables (8), (9) and (12). The yields of both biaryl and benzoic acid were increased by the presence of metal benzoates in all three solvents.

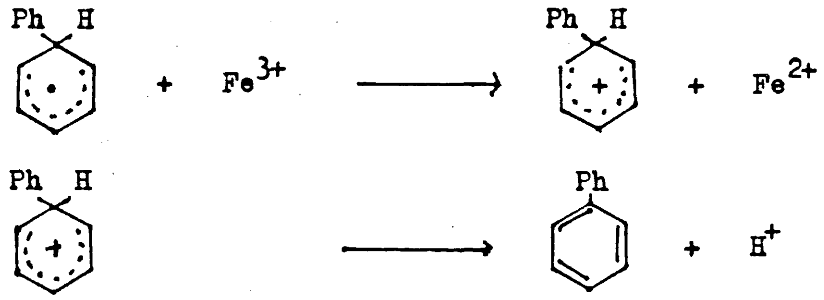
The reaction scheme (70) suggested by Dailly[74] for the reactions in benzene in the presence of ferric benzoate would account for the above observations.

$$
\begin{array}{llll}
(a) & (PhCO{\cdot}O)_2 & \longrightarrow & 2\ PhCO{\cdot}O{\cdot} \\
(b) & PhCO{\cdot}O{\cdot} & \longrightarrow & Ph{\cdot} + CO_2 \\
(c) & Ph{\cdot} + PhH & \longrightarrow & [Ph{\cdot}PhH] \\
(d) & [Ph{\cdot}PhH] + PhCO{\cdot}O{\cdot} & \longrightarrow & Ph{\cdot}Ph + PhCO_2H \\
(e) & [Ph{\cdot}PhH] + Fe^{3+} & \longrightarrow & Ph{\cdot}Ph + H^+ + Fe^{2+} \\
(f) & PhCO{\cdot}O{\cdot} + Fe^{2+} & \longrightarrow & Fe^{3+} + PhCO{\cdot}O^- \\
(g) & PhCO{\cdot}O^- + H^+ & \longrightarrow & PhCO_2H \\
(h) & [Ph{\cdot}PhH] & \longrightarrow & \text{dimerisation and disproportionation products.}
\end{array}
\qquad (70)
$$

Reaction (70e) could be split into two steps (i) and (j), which could well be a concerted process; an initial co-ordination of the σ-complex to ferric ion could be a pre-requisite which is followed by the one-electron transfer from the σ-complex to ferric ion in this oxidation process.

(i)

(j)



The above scheme with step (70h) playing a minor part could explain the observed formation of benzoic acid and biphenyl in equal yields.

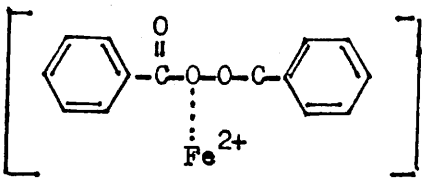
The kinetic studies carried out by Dailly[74] gave the following equation (71) for the decomposition of benzoyl peroxide in benzene in the presence of ferric benzoate over the concentration range of

$$-\frac{d[P]}{dt} = K_1[P] + K_1'[P] \qquad (71)$$

0.165–0.04M, which also happened to be the same as already established kinetio equation for the decomposition of benzoyl peroxide in bromobenzene by Gill and Williams[47] at all concentrations, and in benzene containing 1% nitrobenzene above an initial peroxide of 0.06M[100], suggests that the role of ferric benzoate play in these reactions could be by two separate paths, which may reinforce each other.

Firstly, the catalyst does not initiate or catalyse the peroxide dissociation into radicals, but it does remove peroxide from solution, the extent to which this is done depending on its concentration. This it can only do by co-ordinating with an oxygen atom of a carbonyl group of the peroxide molecule to form a weakly bonded π-complex.

Since the metal carboxylates have intermediate activity as ligand- or electron-transfer oxidants[67b], and Taube[104] states that a system in which the inner and outer orbital states have nearly the same energy combines the virtue that an attached group is strongly polarised from interaction with stable inner orbitals, and thereby activated for certain reactions, with the high lability with respect to substitution which is characteristic of many outer-orbital complexes. Such stability of benzoyloxy-radicals by a polarisation process with the formation of peroxide-derived benzoate anions, is not unreasonable. There are few other examples of analogous π-complex formation reactions in the literature[105,106,107]. Hasegawa and Nishimura[108] provided the evidence for ferrous-oxygen complex bond formation between benzoyl peroxide molecules with ferrous ions, and suggested the structure such as (XIV) for the activated complex which involved a co-ordination of peroxidic oxygen to ferrous ions, probably accompanied by an electron jump from the ion, giving rise to the observed accelerated rate of decomposition of benzoyl peroxide in this system.



(XIV)

The other role of ferric benzoate played in these reactions is the oxidation of σ-radical as in equation (70e) results in the formation of ferrous ions in solution and it is essential that these ferrous ions are oxidised to ferric ions again by some route, in order to avoid the accumulation of ferrous ions in solution resulting from a stoichiometric amount of ferric benzoate required for catalysed decomposition of benzoyl peroxide.

There are two possible ways in which ferrous ions can be converted to ferric ions : -

(A) induced decomposition of benzoyl peroxide by ferrous ions as in equation (72), or

$$Fe^{2+} + (PhCO{\cdot}O)_2 \longrightarrow Fe^{3+} + PhCO{\cdot}O^- + PhCO{\cdot}O{\cdot} \quad (72)$$

(B) direct oxidation of ferrous ion by benzoyl radical resulting in the formation of a benzoate anion which ultimately forms a molecule of benzoic acid as in equation (73).

$$\begin{array}{lllll} \text{(a)} & PhCO\cdot O\cdot + Fe^{2+} & \longrightarrow & Fe^{3+} + PhCO\cdot O^{-} & \\ \text{(b)} & PhCO\cdot O^{-} + H^{+} & \longrightarrow & PhCO_2H & \end{array} \qquad (73)$$

Hey, Liang and Perkins[71] (1967) from their investigation of the effects of copper benzoate (which has a similar structure to that of ferric benzoate) on the decomposition of benzoyl peroxide in benzene and chlorobenzene, without any supporting kinetic data suggested the following mechanism (74), where ferrous ion is oxidised via route (A),

$$\begin{array}{llll} \text{(a)} & (PhCO\cdot O)_2 + Cu^{+} & \longrightarrow & PhCO\cdot OCu^{2+} + PhCO\cdot O\cdot \\ \text{(b)} & PhCO\cdot O\cdot & \longrightarrow & Ph\cdot + CO_2 \\ \text{(c)} & Ph\cdot + PhH & \longrightarrow & [Ph\cdot PhH]\cdot \\ \text{(d)} & [Ph\cdot PhH]\cdot + PhCO\cdot OCu^{2+} & \longrightarrow & Ph\cdot Ph + PhCO\cdot O\cdot + Cu^{+} \end{array} \qquad (74)$$

which is also a well documented induced decomposition of benzoyl peroxide by ferrous ions observed by Hasegawa and Nishimura[108] resulting in accelelated rate of decomposition of benzoyl peroxide. However the fact that the detailed kinetic study of the decomposition of benzoyl peroxide in benzene in the presence of ferric benzoate carried out by Dailly[74] indicated that no autocatalysis nor unimolecular decomposition of peroxide greatly influenced by the metal salt took place and seemed to argue against the possibility of ferrous ion oxidised by ferric species by mechanism (A)

Mechanism (B) involving the direct oxidation of ferrous ion by benzoyloxy radical, which makes the catalyst regenerative by the formation of ferric ions and benzoate anions would be consistent with the results on the kinetics and products.

From the results shown in Table (29) on the effects of ferric benzoate in the decomposition of benzoyl peroxide in chlorobenzene,

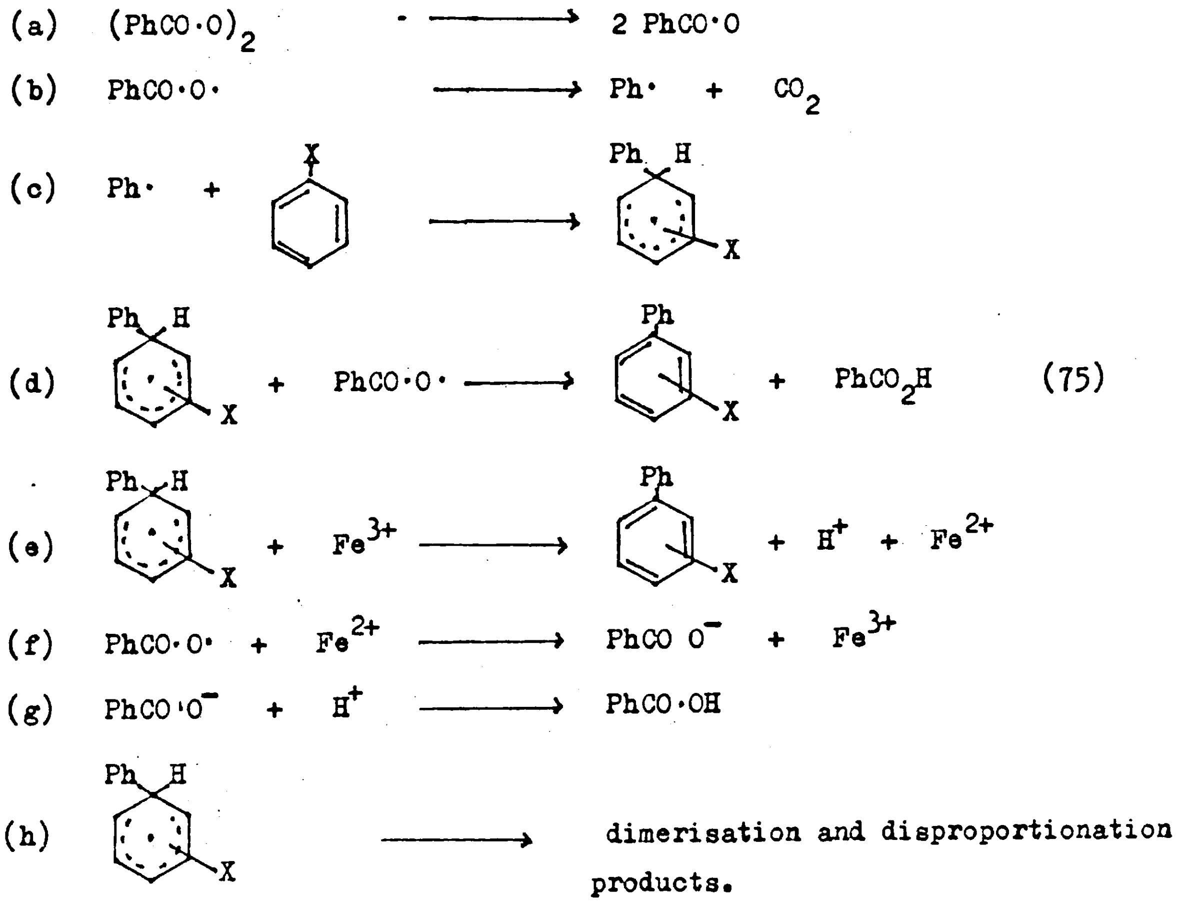
Table (29)

Products from the decomposition of benzoyl peroxide in benzene, chlorobenzene and bromobenzene at 80° in the presence of metal benzoates.

solvents (50ml)	catalyst	biaryl (m/m)	benzoic acid (m/m)	isomer ratios *o*	*m*	*p*
benzene	none	0.3882	0.2500		——	
	cupric benzoate	0.8248	0.8065		——	
	$\mathrm{Cu(}p\text{-}\mathrm{MeC_6H_4CO_2)_2}$	0.6155	0.6690		——	
	$\mathrm{Cu(}p\text{-}\mathrm{ClC_6H_4CO_2)_2}$	0.9493	0.8846		——	
	$\mathrm{Cu(}p\text{-}\mathrm{NO_2C_6H_4CO_2)_2}$	0.8119	0.8051		——	
	ferric benzoate	0.8000	0.8195		——	
chlorobenzene	none	0.4024	0.3387	54.6	27.2	18.1
	cupric benzoate	0.7135	0.8053	57.3	25.4	17.3
	$\mathrm{Cu(}p\text{-}\mathrm{MeC_6H_4CO_2)_2}$	0.7477	0.7579	58.3	24.2	17.5
	$\mathrm{Cu(}p\text{-}\mathrm{ClC_6H_4CO_2)_2}$	0.8038	0.8722	58.3	24.2	17.5
	$\mathrm{Cu(}p\text{-}\mathrm{NO_2C_6H_4CO_2)_2}$	0.8381	0.8035	58.3	24.4	17.3
	ferric benzoate	0.8381	0.8035	58.0	23.9	18.1
bromobenzene	none	0.7454	0.9536	54.2	30.4	15.4
	cupric benzoate	0.7481	0.9488	58.3	27.8	13.9
	$\mathrm{Cu(}p\text{-}\mathrm{MeC_6H_4CO_2)_2}$	0.7617	0.8472	56.3	28.6	15.1
	$\mathrm{Cu(}p\text{-}\mathrm{ClC_6H_4CO_2)_2}$	0.8667	0.9039	56.1	28.4	15.5
	$\mathrm{Cu(}p\text{-}\mathrm{NO_2C_6H_4CO_2)_2}$	0.7838	0.8568	57.3	27.8	14.9
	ferric benzoate	0.9617	0.9834	54.3	29.4	16.3

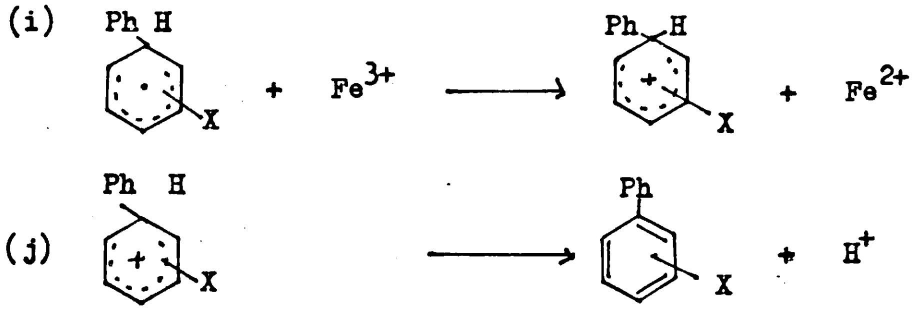
it is evident that the catalitic effect of ferric benzoate in chlorobenzene bears a strong similarity to that obtained in benzene, with high and equivalent yields of chlorobiphenyls and benzoic acid. Consequently a similar mechanism to that proposed in benzene can be assumed to operate. The only significant difference between these reactions is that in chlorobenzene the greater number of products are obtained due to the lower symmetry of the chloro-substituted solvent.

Effects of ferric benzoate on the decomposition of benzoyl peroxide in bromobenzene is less spectacular here because of the already relatively high yields of uncatalysed reaction. However slightly increased yields of bromobiphenyls and benzoic acid in the presence of ferric benzoate can be explained by the following reaction mechanism (75), which also applies to chlorobenzene.



(75)

Reaction (e) could be split into two steps



(where X = Cl or Br)

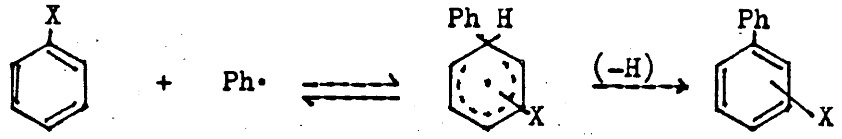
The above discussion of the effect of ferric benzoate on the decomposition of benzoyl peroxide in benzene, chlorobenzene and in bromobenzene is equally applicable to reactions catalysed by cupric benzoate and substituted cupric benzoate. Cupric benzoate, like ferric benzoate is polymeric in structure. Both salts are expected to give similar effects in these reaction because of a marked similarity in the product distribution is observed

The purpose of having various substituent in cupric benzoate was to find out, if the activation of the substituent have any effect in the increases in the yields of the products.

The activation of the substituent increase in the order of $NO_2 > Cl > Me$. While in benzene the yield of biphenyl increased in the order of $Cl > H > NO_2 > Me$, in chlorobenzene the order was $NO_2 > Cl > Me > H$, and in bromobenzene $Cl > NO_2 > Me > H$. Therefore the order made an explanation of increased yield in terms of polar factors unlikely.

As in the previous experiments with substituted benzene in the presence of quinones and nitro-compounds, it is here again noted that the proportion of o-biaryl formed in the presence of both ferric and cupric benzoates are higher than those of uncatalysed reaction. Similar effects of catalysts were observed by Hey, Liang and Perkins[71] in their work on the effect of copper benzoate in chlorobenzene, Dailly[74] on the effect of ferric benzoate in fluorobenzene, toluene and in chlorobenzene and very recently by Lee[109]. There are two possible explanations for the increased yields of o-isomer in the metal catalysed reaction. Firstly -

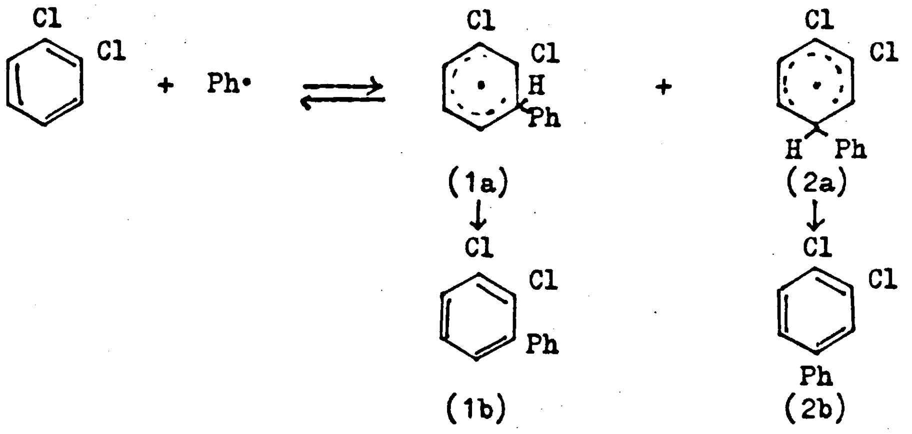
(A) Reaction (75c) ; that is the formation of substituted σ-complex by the addition of phenyl radical to solvent, is reversible



(76)

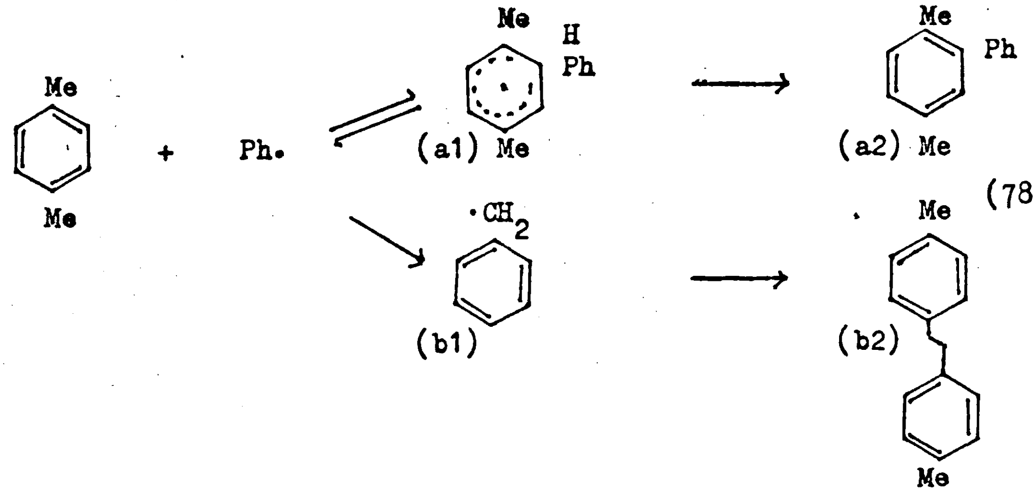
then it is expected the o-substituted phenylcyclohexadienyl radicals will have a greater tendency to dissociate owing to the greater sterric effect associated with a substituent in ortho-position. Consequently the presence of efficient oxidising agents for σ-complexes which inhibit the occurrence of the reverse reaction, would result in the increased yields of ortho-substituted biaryls. However in general, the lack of kinetic isotope effect is used to substantiate the irreversibility of equation (75c). An isotope effect will be observed if either the reversal of the addition step or the step forming side-products competes with hydrogen abstraction step. This test has been applied by many workers,[33,34,35,36] and their results indicated that there was no isotope effect within experimental error. Eliel, Meyerson and Wilen[36], who decomposed a variety of peroxides in benzene-d, and benzene-benzene-d_6 mixture found that, in some peroxides the isotope effects calculated from product deuterium content are in excess of unity. However the benzene-benzene-d_6 mixture recovered from a chlorophenylation remained unchanged in isotopic composition, indicating that the addition of chlorophenyl radical is not fully reversible under the conditions of arylation. Furthermore Eliel, Eberhardt, Simamura and Meyerson[110] compared the arylation of diaroyl peroxide with arylation of nitrosoacetanilides and arylazotriphenylmetanes which does not involve dihydrobiaryl as intermediates and found whereas the decomposition of diaroyl peroxides in benzene-d involves appreciable apparent isotope effects, these effects in the decomposition of nitrosoacetanilides and arylazotriphenylmethanes in benzene-d are very small, well within the range of secondary isotope effects, and therefore further strengthen the above conclusions. Also Saltiel and Curtis[111] who irradiated benzoyl peroxide or benzil in benzene in the presence of oxygen concluded although the addition of benzoyloxy radicals to benzene may be reversible, the addition of phenyl radical to benzene is irreversible, and also Jackson[112], produced thermodynamical data appertaining to reactions of radicals with olefinic and aromatic compounds, and likewise indicated that phenylation is irreversible below 200°.

However Kobayashi and co-workers[37a,b] recently has reported that aromatic phenylation in dimethyl sulphoxide at room temperature does exibit a significant isotope effect which may reflect some unsuspected effect of dimethyl sulphoxide on free-radical behaviour. Also Nonhebel and co-workers[113] recently argued the reversibility of σ-formation. They carried out the decomposition of benzoyl peroxide in o-dichlorobenzene at different temperatures 80° and 100°. The products from the above reaction are 2,3- and 3,4-dichlorobiphenyls. They argued, on steric ground, that 2,3-dichlorobiphenyl is thermodynamically less stable than 3,4-isomer and therefore the ratio of 2,3/3,4 isomer is expected to decrease in increasing temperature.



(77)

Also, if the radical (1a) is more prone to dissociate than radical (2a) then the addition of cupric benzoate, which effects the rapid oxidation of σ-complex to diaryl at the expence of σ-complex dimerising should incease the ratio of (1b)/(2b), and this was precisely what they observed. And since the oxidation potentials of the radicals (1a) and (2a) would be expected to be similar therefore one cannot explain the influence of copper salts on the basis that (1a) would be more readily oxidised, and concluded that the formation of σ-complex may be reversible particularly when the incoming radical enters <u>ortho</u>- to a substituent. However the same observation could be accounted for if one assumes that 2,3-dichlorobiphenyl has a greater tendency to undergo side reaction than 3,4-dichlorobiphenyl with increased temperature.



(78)

They also decomposed benzoyl peroxide in *p*-xylene which gave two products 2,5-dimrthylbiphenyl and 4,4'-dimethylbibenzyl and proposed the above mechanism (78) to explain the increased ratio of (b2)/(a2) with increase in temperature. However, this observation could also be accounted for if the processes (a2) and (b2) have different activation energies. The increase in rate of the two reactions with increase in temperature would then not be the same.

The above discussion provided no clear evidence for interpreting the results obtained in present experiments, i.e increased yields of *o*-biaryls in the presence of catalyst in terms of reversibility of addition of phenyl radicals to solvent molecules.

Another and more likely possible explanation of these effects which has also been suggested by Dailly[74] is by suggesting that -

(B) The rate of *ortho*-substituted σ-complex is very much faster than that of *meta*- or *para*-isomers, so that when dimerisation is a major reaction, as in uncatalysed experiments, then a dispropotionate number of *ortho*-substituted σ-complexes are lost as residue, and *o*-biaryl yield will be decreased by a small, though possibly significant amount. When the residue formation is greatly suppressed, as in metal benzoate catalysed reaction, *o*-substituted σ-complex will not be lost in this way, and a higher percentage of *o*-biaryls will be obtained and that the catalysed results should therefore provide a fairer representation of the homolytic substitution process and lead to more accurate values for the partial rate factors.

D.2 The Competitive Reaction of Benzoyl Peroxide in Equimolar Mixtures of Chlorobenzene and Benzene, and of Bromobenzene and Benzene in the Presence and Absence of Additives.

(A) The decomposition of benzoyl peroxide in equimolar mixture of benzene and chlorobenze or bromobenzene.

Much of the work on the competitive reactions has been concerned with the measurement of "partial rate factors" for the arylation of benzene derivatives. The partial rate factors F*r* for substitution at a position *r*- in a benzene derivative C_6H_5X expresses the charge in the specific rate of substitution at position *r* in the nucleus which arises from the presence of directing group X, that is, it is the ratio of rate of reaction at position *r* in C_6H_5X to that at any one position in benzene, thus for a monosubstituted benzene :

$$6 \; {}^{PhX}_{PhH}K = 2\,F\underline{o} + 2\,F\underline{m} + F\underline{p} \qquad (79)$$

where

$$F\underline{o} = \tfrac{1}{2} \times 6 \times {}^{PhX}_{PhH}K \times \frac{\%\ \underline{ortho}\text{-product}}{100}$$

$$F\underline{m} = \tfrac{1}{2} \times 6 \times {}^{PhX}_{PhH}K \times \frac{\%\ \underline{meta}\text{-product}}{100}$$

$$F\underline{p} = 6 \times {}^{PhX}_{PhH}K \times \frac{\%\ \underline{para}\text{-product}}{100}$$

In order to obtain precise values of partial rate factors, it is necessary to be able to measure accurately the isomer distribution of phenylated compound.

The relative rate and partial rate factor measurements of monosubstituted halogenobenzene of previous and present works are summarised on Table (30).

Table (30)

Total and partial rate factors for phenylation of chlorobenzene and bromobenzene in the absence of additives.

substrate	standard solvent	radical sources	analytical method	$\frac{PhX}{PhH}K$	p.r.f			reference numbers
					F_o	F_m	F_p	
PhCl	$PhNO_2$	Bz_2O_2	titration	1.41		——		7
	$PhNO_2$	Bz_2O_2	titration	1.06	1.6	1.0	1.2	114
	PhH	Bz_2O_2	g.l.c.	1.13	1.8	0.87	0.7	71
	PhH	Bz_2O_2	g.l.c.	1.32	2.17	1.05	1.48	74
	$PhNO_2$	Bz_2O_2	g.l.c.	2.06	3.65	1.55	1.98	115
	p-$C_6H_4Cl_2$	Bz_2O_2	g.l.c.	2.20	3.9	1.65	2.12	115
	PhH	Bz_2O_2	g.l.c	1.14	1.87	0.93	1.24	J.average
PhBr	$PhNO_2$	Bz_2O_2	titration	1.29	1.9	1.3	1.3	114
	$PhNO_2$	Bz_2O_2	g.l.c.	1.82	2.95	1.64	1.78	115
	p-$C_6H_4Cl_2$	Bz_2O_2	g.l.c.	1.90	3.05	1.7	1.92	115
	PhH	$C_6H_5BN_2F_3$	g.l.c.	1.75	2.94	1.42	1.85	116
	PhH	Bz_2O_2	g.l.c.	1.47	2.39	1.35	1.35	K.average

Table (30) reveals some differences in the values obtained by each group; some of these differences can be accounted for by the use of different methods of analysis of the products in competitive reaction. The use of g.l.c. for the analysis in present work is probably more accurate than those values obtained by infra-red methods. Other sources of difference would arise from the choices of standard solvent. The choice of nitrobenzene as a reference solvent was made before the modern chromatographic tecniques, since the nitrobiphenyls present in the total phenylated product lend themselves to ready quantitative determination by titration with titanium (III) chloride or sulphate[114]. Thus, the value of ${}^{PhX}_{PhNO_2}K$ could be obtained, and knowing the value of ${}^{PhNO_2}_{PhH}K$, ${}^{PhX}_{PhH}K$ could be calculated : -

$$ {}^{PhX}_{PhH}K = {}^{PhX}_{PhNO_2}K \times {}^{PhNO_2}_{PhH}K \qquad (80)$$

With the availability of modern chromatographic methods, Davies, Hey, and Summers[115](1971) used p-dichlorobenzene as a reference compound rather than nitrobenzene. This had the advantage of giving only one monophenylation product, and the reactions should be free from the known catalytic influence of nitro-compounds on arylation. The use of reductive titration is eliminated and the formation of a single product, namely 2,5-dichlorobiphenyl, greatly simplified the analysis of the g.l.c. chromatogram.

The use of benzene itself was considered not suitable as a standard solvent for such competitive experiments because of the ready loss of the relatively volatile biphenyl in the work up.

However, the g.l.c. analysis on the excess solvents removed after the competitive reaction by the use of rotary-evaporator revealed no traces of biphenyl, and the results obtained by using benzene itself as a standard solvent followed by g.l.c. analsis should be reliable. Moreover the values obtained[115] by the use of p-dichlorobenzene as a standard solvent are much higher than those results obtained in the present work; this is probably because the earlier values were not determined directly from competitive reactions with benzene but made use of conversion equations such as (80), the reliability of which has been proved doubtful[109] in the absence of additives.

The rate factors of phenylation of chlorobenzene obtained in the present work agrees very well with the values for the uncatalysed reaction of Hey, Liang and Perkins[71]. The value for the phenylation of bromobenzene lies intermediate between those obtained by Hey, Orman and Williams[114], and Galdallah and Elofson[116] who used the electrolysis of benzenediazonium tetrafluoroborate as a source of phenyl radicals.

The same mechanism suggested for the phenylation of benzene and chlorobenzene or bromobenzene on its own would probably apply to the formation of the major products (namely biphenyl, chloro- or bromobiphenyl and benzoic acid) from these competitive reactions, with the additional possibility of dimerisation and disproportionation reactions between phenylcyclohexadienyl radical and chloro- or bromo-substituted phenylcylohexadienyl radicals.

The introduction of chloro- or bromo-group has activated the nucleus for homolytic substitution of nearly neutral phenyl radical, and ortho- and para-positions display the effect better than the meta-position. The reason for this behaviour is that electron-attracting groups can delocalise the unpaired electron onto the group when attack occurs ortho- or para to that group.

No completely satisfactory explanation has been proposed for the dominance of attack at the ortho-position. However, Rondestvedt and Blanchard suggested an explanation[117] based on the inductive effects of the group X. These workers postulated that in the formation of the preliminary π-complex which they envigase as the precursor of the σ-complex, the phenyl radical tends to become associated with sites of high electron density, i.e that the phenyl radical is somewhat electrophilic. Compounds such as chloro- or bromobenzene show the greatest electron density at the substituent itself, and if -I effects of the directing groups are largely inductomeric, then the incoming radical becomes associated in the π-complex largely with the substituent (Cl or Br), giving a complex which can most readily rearrange to the ortho-substituted σ-complex.

Also, there is no satisfactory explanation to account for unreasonably high partial rate factor (1.35) for the relative attack on m-position of bromobenzene, if the phenyl radical is the only species involved in selecting between the competing solvent molecule then partial rate factor for the m-position is expected to be as reactive as one of the six positions of benzene. Therefore it suggests species other than phenyl (benzoyl peroxide or benzoyloxy) radical are involved in the selection process. If the complex is formed between bromobenzene and benzoyloxy-radical or benzoyl peroxide with a weak intermolecular attractive force prior to decarboxylation, then the phenyl radical generated in such conditions would be in closer proximity to bromobenzene molecules than to benzene and hence the probability of them attacking the bromobenzene is higher, therefore leading to a higher reactivity.

The complex formation owing to the greater polarisability and electropositivity of bromine atom on bromobenzene and benzoyloxy radical which result in the formation of the benzoate anion is suggested by Gill and Williams[47]. However so formed benzoate anion is less likely to decarboxylate under experimental condition owing to the greater strength of C(1) - CO bond, so it is more likely the complex formed between bromobenzene and benzoyl peroxide by co-ordinating with oxygen atom of carbonyl group of peroxide molecule, when decarboxylate give the observed high reactivity. In chlorobenzene the polarisability and electropositivity of chlorine atom is less than bromine atom, hence the reactivity at *m*-position showed near to unity.

If the higher reactivity in bromobenzene arises by the above suggestion then, this makes the relative rate and partial rate factors in this reaction invalid as reactivity indices of bromobenzene molecules in the phenylation reaction.

(B) The decomposition of benzoyl peroxide in a system containing various molar proportions of benzene and bromobenzene in the absence of additive.

The relative rate factors for the competitive phenylation reaction containing varying molar ratios of benzene and bromobenzene in the absence of additive are summarised in Table (31).

Table (31)

The effect of varying substrate concentration on the relative rate of bromobenzene in the absence of additive.

mole ratio PhBr : PhH	PhC_6H_4Br (m/m)	Ph-Ph (m/m)	isomer ratios *o*	*m*	*p*	${}^{Br}_{H}K$	p.r.f F*o*	F*m*	F*p*
2 : 1	0.6772	0.2233	54.8	29.5	15.7	1.52	2.49	1.35	1.43
1.5 : 1	0.6155	0.2760	54.5	30.3	15.2	1.49	2.44	1.35	1.36
1 : 1	0.4412	0.3001	54.2	30.5	15.3	1.47	2.49	1.35	1.35
1 : 1.5	0.3722	0.4652	55.2	28.9	15.9	1.20	1.99	1.04	1.14
1 : 2	0.3062	0.6183	54.1	30.6	15.3	0.99	1.60	0.91	0.91

Relative rate factors of 1.52 and 1.49 for the reactions containing bromobenzene and benzene in the molar ratios of 2:1 and 1.5:1 agree quite well with the value (1.47) from the competitive reaction containing equimolar mixture of bromobenzene and benzene in the absence of additive. However, slightly lower values of 1.2 and 0.99 are obtained for the reactions containing the molar ratios of 1:1.5 and 1:2 of bromobenzene and benzene.

The yield of biphenyl when benzoyl peroxide was decomposed in benzene alone without any additive was 0.3882 m/m peroxide. However, in the competitive reactions with bromobenzene when the molar ratios of bromobenzene and benzene are 1:1.5 or 1:2, the yields of biphenyl increased to 0.4652 and 0.6183 m/m peroxide respectively, which might suggest that at these molar ratios the termination by dimerisation of phenylcyclohexadienyl radicals resulting in the formation of side products are reduced, and more biphenyls are formed by the oxidation of more plentiful phenylcyclohexadienyl radicals in solution by benzoyloxy-radicals stablised by complex-formation with bromobenzene.

(C) The effects of ferric benzoate and Cupric benzoate on the decomposition of benzoyl peroxide in an equimolar mixture of benzene and chlorobenzene, and of benzene and bromobenzene.

The summary of the effects of the presence of ferric benzoate and cupric benzoate in the competitive reactions containing equimolar mixture of chlorobenzene and benzene are illustrated on Table (32).

Table (32)

The effects of ferric benzoate and cupric benzoate on the decomposition of benzoyl peroxide in an equimolar mixture of benzene and chlorobenzene.

additives	PhC_6H_4Cl (m/m)	Ph-Ph (m/m)	${}^{Cl}_{H}K$	p.r.f F_o	F_m	F_p	references
none	0.384	0.241	1.32	2.15	1.05	1.48	Dailly (74)
ferric benzoate	0.525	0.313	1.64	2.80	1.25	1.72	
none	0.45		1.13	1.81	0.87	1.40	Hey, Liang & Perkins (71)
cupric benzoate	0.74		1.47	2.56	1.06	1.58	
none	0.3052	0.2677	1.14	1.87	0.93	1.24	Present work
ferric benzoate	0.5101	0.3562	1.43	2.47	1.08	1.48	
cupric benzoate	0.5244	0.3479	1.52	2.60	1.16	1.57	
$Cu(p\text{-}ClC_6H_4CO_2)_2$	0.4718	0.3413	1.38	2.42	1.02	1.43	

The present results, using cupric benzoate in competitive reactions in an equimolar solution of benzene and chlorobenzene, agree very well with the results obtained on similar experiments by Hey, Liang and Perkins,[71] and the results of ferric benzoate catalysed reactions, also agree moderately well with the values reported by Dailly[74].

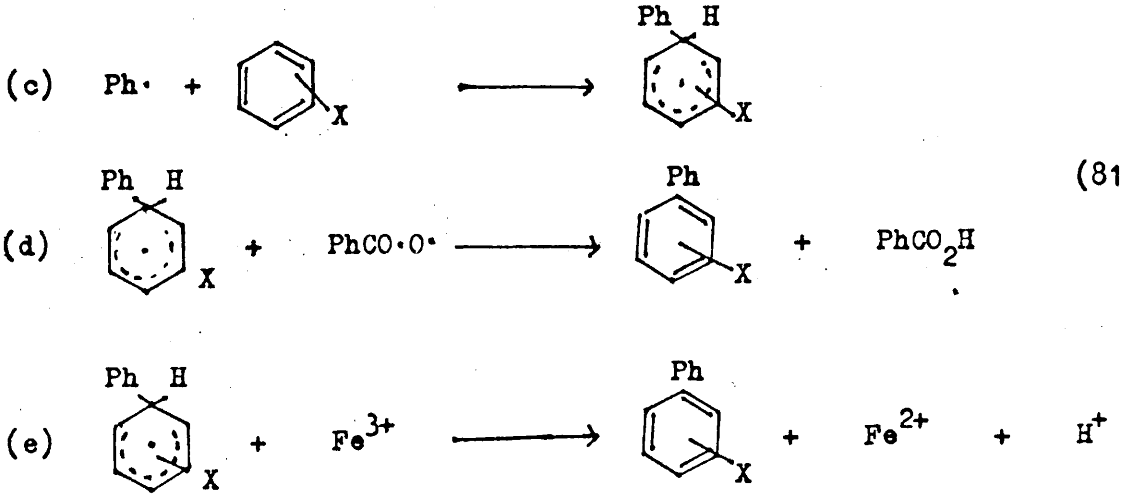
The presence of ferric benzoate or cupric benzoate in a competitive reaction increases both the yields of chlorobiphenyls and biphenyl. However the effects seem to be greater on chlorobenzene than on benzene, consequently higher values of relative rates are obtained when the additives are present during the reaction.

The isomer ratios of chlorobiphenyls in metal benzoate catalysed reactions are almost identical to those values obtained in metal catalysed phenylation reactions of chlorobenzene alone. Therefore it is unreasonable to assume that the effects of metal benzoates in an equimolar solution of benzene and chlorobenzene would be different from the effects they have in reactions in benzene or chlorobenzene alone, unless solvent complexation is important.

Consequently, a similar mechanism suggested to the metal benzoates catalysed reactions in chlorobenzene (75) and benzene (70) alone can account for the formation of biaryls and benzoic acid in the competitive reactions.

(a) $(\mathrm{PhCO{\cdot}O})_2 \longrightarrow 2\ \mathrm{PhCO{\cdot}O}$

(b) $\mathrm{PhCO{\cdot}O{\cdot}} \longrightarrow \mathrm{Ph{\cdot}} + \mathrm{CO_2}$



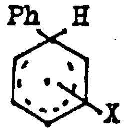
(81)

(f) $PhCO{\cdot}O{\cdot} + Fe^{2+} \longrightarrow PhCO{\cdot}O^- + Fe^{3+}$

(g) $Fe^{2+} + (PhCO{\cdot}O)_2 \longrightarrow Fe^{3+} + PhCO{\cdot}O^- + PhCO{\cdot}O{\cdot}$

(h) $PhCO{\cdot}O^- + H^+ \longrightarrow PhCO_2H$

(i)



$\longrightarrow$ dimerisation and disproportionation products

(where X = H or Cl)

The importance of reaction 81(i) is greatly reduced in these system, and consequently the rate factors obtained in the presence of metal benzoates are more reliable indices of the reactivity of chlorobenzene towards phenylation reactions than those values obtained from uncatalysed reactions.

The summary of the effects of the presence of metal benzoates in the competitive reactions containing equimolar mixture of benzene and bromobenzene are illustrated on Table (33).

Table (33)

The effects of metal benzoate on the decomposition of benzoyl peroxide in an equimolar mixture of benzene and bromobenzene.

additives	relative rate	F*o*	F*m*	F*p*
cupric benzoate	1.46	2.51	1.24	1.28
$Cu(p\text{-}ClC_6H_4CO_2)_2$	1.40	2.35	1.19	1.31
ferric benzoate	1.53	2.50	1.35	1.47
none	1.47	2.39	1.35	1.35

The above Table (33) shows, that the presence of metal benzoates during the competitive reactions of benzene and bromobenzene has little or no effects on the values of relative rates and partial rate factors obtained in uncatalysed reaction.

The mechanism suggested for the competitive reactions of benzene and chlorobenzene in the presence of metal benzoates (equation 81) would account for the formation of bromobiphenyls, biphenyl and benzoic acid in this reaction.

(D) The decomposition of benzoyl peroxide in a system containing various molar proportions of benzene and chlorobenzene in the presence of ferric benzoate.

Table (34)

The effects of varying substrate concentration on the relative rate of chlorobenzene in the presence of ferric benzoate.

mole ratio PhCl : PhH	PhC_6H_4Cl (m/m)	Ph-Ph (m/m)	isomer ratios o	m	p	${}^{Cl}_{H}K$	p.r.f. Fo	Fm	Fp
2 : 1	0.6113	0.2199	57.3	24.8	17.9	1.39	2.39	1.03	1.49
1.5 : 1	0.5485	0.2563	57.7	24.2	18.0	1.43	2.48	1.04	1.54
1 : 1	0.5101	0.3562	57.6	25.1	17.3	1.43	2.47	1.08	1.48
1 : 1.5	0.3727	0.4216	57.8	24.5	17.7	1.32	2.29	0.97	1.40
1 : 2	0.3310	0.5052	57.8	24.3	17.9	1.31	2.27	0.95	1.41

Table (34) shows the relative rates and partial rate factors for the competitive phenylation reactions of varying molar ratios of benzene and chlorobenzene in the presence of ferric benzoate. The consistent values of 1.39, 1.43, 1.32 and 1.31 are observed for the reactions containing chlorobenzene and benzene in the molar ratios of 2:1, 1.5:1, 1:1.5 and 1:2 in the presence of ferric benzoate. These values are higher than those values (1.14) obtained from the corresponding reactions containing an equimolar mixture of the two competing solvent in the absence of additives. On the other hand these values are comparable to that obtained from the reaction containing an equimolar mixture of chlorobenzene and bromobenzene (1.43) in the presence of ferric benzoate. This close similarity of results in catalysed reactions provide a further check for the reliability of the rate values obtained in reactions containing an equimolar mixture of chlorobenzene and benzene in the presence of ferric benzoate.

D.3 The Decomposition of Benzoyl Peroxide in Fluorobenzene in the Presence and Absence of Metal Benzoates.

Table (35) gives the summary of the results of the decomposition of benzoyl peroxide in fluorobenzene in the presence and absence of metal (cupric or ferric) benzoates.

Table (35)

The decomposition of benzoyl peroxide in fluorobenzene in the presence and absence of metal benzoates at 80°.

additives	PhC_6H_4F (m/m)	$PhCO_2H$ (m/m)	Ph-Ph (m/m)	isomer ratios o	m + p
none	0.6233	0.2524	0.091	48.2	51.8
cupric benzoate	0.8922	0.8640	0.038	52.9	47.2
ferric benzoate	0.8291	0.8433	0.034	54.4	45.6

The low yield of benzoic acid compere to the relatively high yields of fluorobiphenyls in the absence of additives suggests, that these products are formed by a similar mechanism to that proposed in the uncatalysed reaction in benzene. The only significant difference between the reactions in benzene and fluorobenzene is in benzene the termination process by reaction (82) occurs to some extent, the

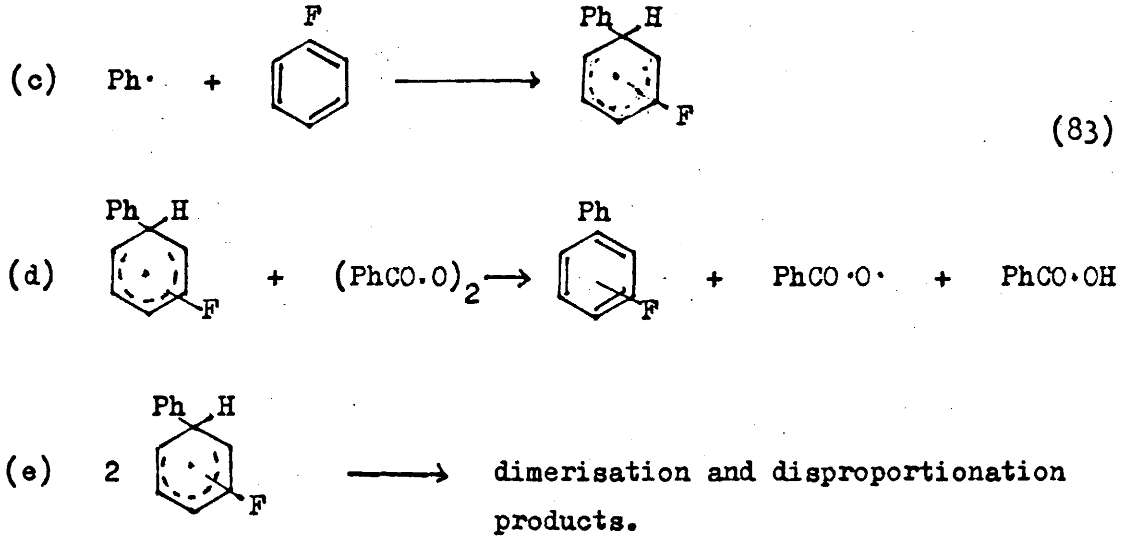
$$\sigma\cdot + PhCO{\cdot}O\cdot \longrightarrow Ph\text{-}Ph + PhCO_2H . \qquad (82)$$

detailed kinetic study of the decomposition of benzoyl peroxide in fluorobenzene by Lewis and Williams[46] revealed that k_{In} is not lower than k_1, indicating that none of peroxide decomposes in a first-order at induced reaction showing that reaction (82) does not take place in this solvent.

The following reaction scheme is proposed, therefore, for the reaction of benzoyl peroxide in fluorobenzene in the absence of metal benzoates.

$$\text{(a)}\quad (PhCO\cdot O)_2 \longrightarrow 2\ PhCO\cdot O\cdot$$

$$\text{(b)}\quad PhCO.O\cdot \longrightarrow Ph\cdot + CO_2$$

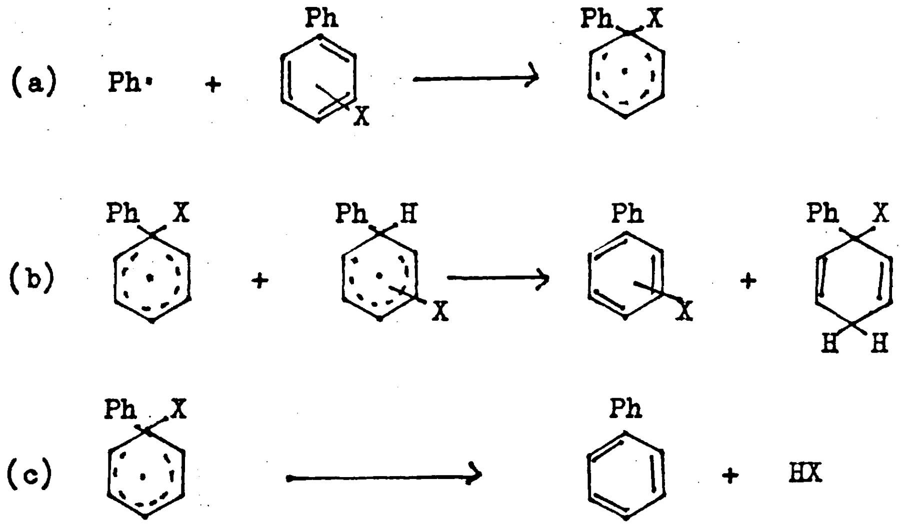


(83)

The catalytic effects of ferric benzoate and cupric benzoate in this solvent bears a strong similarity to that obtained in benzene, chlorobenzene and bromobenzene, with high and equivalent fluorobiphenyls and benzoic acid yields. Consequently a similar mechanism to that proposed in benzene and two halogenated solvents is thought to operate, and many of the arguments discussed previously [Section D.1 (3)], will be relevant to the consideration of the mechanism here.

Biphenyl was detected by g.l.c. in small quantities in the reactions with chlorobenzene, both in the presence and in the absence of metal benzoates, but no comment was made in the previous Section. However more definite yield of biphenyl was obtained in fluorobenzene, although the effect of the catalyst was to cause a marked decrease in the formation of this product.

The formation of biphenyl in chlorobenzene and fluorobenzene in the absence of catalyst is thought[46] to arise by the attack of a phenyl radical on the 1-position of nucleus of the aromatic solvent, followed by reaction with normally substituted σ-complexes and subsequent dehydrohalogenation of the primary products of this process.



(84)

(where X = Cl or F)

The relatively high yield of biphenyl which is formed in fluorobenzene can be understood with the observation that hexafluorobenzene is only a little less active than benzene towards phenylation[122]. Consequently the less suceptibilities of hydrogen- and fluorine-bearing positions to attack by phenyl radicals are of a similar order and biphenyl yield of 16% might be expected in fluorobenzene. The observed yield of 11% in uncatalysed reactions can be accounted for by the influence of a small steric factor. The steric inhibition to attack at the 1-position in chlorobenzene would be expected to be much greater, and the observed smaller yield of biphenyl compere to fluorobenzene is in accordance with this interpretation. As an extention of this point no trace of biphenyl was detected by g.l.c. in the corresponding reaction in bromobenzene.

However in the presence of metal benzoate the yield of biphenyl in fluorobenzene is reduced to 4%. This observation would appesr to reflect the great efficiency with which the metal ions oxidise σ-complexes to the exclusion of side reactions.

D.4 The Competitive Reaction of Benzoyl Peroxide in Equimolar Solution of Benzene and Fluorobenzene in the Presence and Absence of Metal Benzoates.

The results of the yields of fluorobiphenyls and biphenyl are given in Table (16). The relative rates and partial rate factors for phenylation obtained in the present work in the presence and absence of metal (cupric or Ferric) benzoate, together with values obtained by Hey, Orman and Williams[114] are shown in Table (36). The $F_m : F_p$ ratio of fluorobiphenyls given here was calculated from the meta- : para- ratio reported by Lewis and Williams[46] .

The rate factors obtained in the present work in the absence of additive agree reasonably well with those values obtained by Hey, Orman and Williams[114].

Table (36)

Relative rates and partial rate factors of fluorobenzene in the presence and absence of metal benzoates.

additives	relative rates	F_o	F_m	F_p	references
none	1.03	1.70	0.95	0.86	114
none	1.08	1.57	1.11	1.18	L. average
cupric benzoate	1.28	2.03	1.19	1.22	Cu. L. ave.
ferric benzoate	1.23	2.03	1.10	1.11	Fe. L. ave.

The relative rate (1.08) in the uncatalysed reactions indicates that fluorobenzene is slightly more reactive than benzene towards phenylation.

The isomer ratios of fluorobiphenyls in this system in the absence of additives are almost identical to those values obtained in phenylation reactions of fluorobenzene alone. Consequently, a similar mechanism suggested to the uncatalysed reactions in fluorobenzene (83) and benzene (70) alone can account for the formation of biaryls and benzoic acid in this system.

The catalytic effects of ferric benzoate and cupric benzoate in this system bears a strong resembrance to those effects observed in chlorobenzene-benzene system, in increasing the relative rates and F_o values of fluorobiphenyl. Therefore a mechanism suggested for the competitive reactions of benzene and chlorobenzene in the presence of metal benzoates (equation 81), would account for the main products formed in this system.

D.5 The Decomposition of Benzoyl Peroxide in p-Dichlorobenzene and 1,3,5-Trichlorobenzene in the Presence and Absence of Additive

It was noticed that when benzoyl peroxide decomposed in chlorobenzene the proportion of o-chlorobiphenyl formed in the presence of catalysts was higher than in the uncatalysed reaction. Similar changes in isomer ratios were also observed in the competitive reactions of benzene and chlorobenzene, and were accompanied by increased relative rates in catalysed reaction.

The explanations suggested to account for these observations were : -

(a) The first step of homolytic aromatic substitution, namely the formation of σ-complex, may be reversible particularly when the incoming radical enters ortho- to a substituent, or

(b) The rate of dimerisation of the ortho-substituted σ-complex is faster than that of the meta- or para-isomers. Therefore in the uncatalysed reaction where dimerisation is important the loss of the o-isomer may be more significant than the loss of the other isomers.

These complications concerning the isomer ratios arise in mono-substituted benzene derivatives like chlorobenzene because there are three non-equivalent nuclear positions available for the phenylation, thus giving rise to three isomeric chlorobiphenyls. Since there are two o- and two m-positions and one p-, and since the total rate of substitution is the sum of the individual nuclear substitution rates, namely F_o, F_m and F_p, then the total rate for the competitive reaction in chlorobenzene and benzene is given by : -

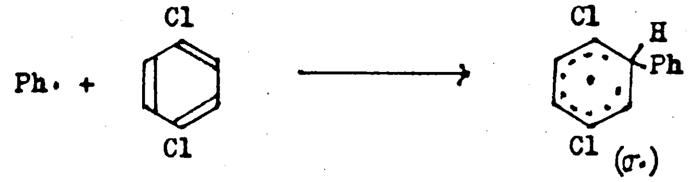
$$6\ {}^{PhCl}_{PhH}K = 2\,F_{\underline{o}} + 2\,F_{\underline{m}} + F_{\underline{p}} \qquad (85)$$

However if the solvent is either The p-dichloro-substituted or the symmetrical trichloro-substituted compound, then for both substances all the nuclear positions available for phenylation are equivalent giving only one phenylated product. Therfore in the reactions of benzoyl peroxide with these solvents no complication arises through relative removal of substituted σ-complex.

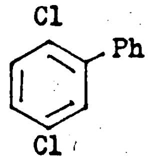
The results of the decompositions of benzoyl peroxide in p-dichlorobenzene and 1,3,5-trichlorobenzene in the presence and absence of catalysts given on Table (37) indicates, that in the absence of catalysts the yields of biaryls from the decompositions of benzoyl peroxide in p-dichlorobenzene (0.6643 m/m peroxide) and in 1,3,5-trichlorobenzene (0.8661 m/m peroxide) are higher than those obtained in chlorobenzene (0.4024 m/m peroxide). A similar mechanism to that of uncatalysed reaction in chlorobenzene is suggested to account for the products formed in uncatalysed experiments in these solvents, with the contribution of reaction (f) being somewhat lesser extent in p-dichlorobenzene than in chlorobenzene, and only a minor contributor in 1,3,5-trichlorobenzene.

(a) $(PhCO{\cdot}O)_2 \longrightarrow 2\,PhCO{\cdot}O{\cdot}$

(b) $PhCO{\cdot}O{\cdot} \longrightarrow Ph{\cdot} + CO_2$

(c) 

(86)

(d) $\sigma\cdot + PhCO{\cdot}O\cdot \longrightarrow$  $+ PhCO{\cdot}OH$

(e) $\sigma\cdot + (PhCO{\cdot}O)_2 \longrightarrow PhC_6H_3Cl_2 + PhCO{\cdot}OH + PhCO{\cdot}O\cdot$

(f) $2\,\sigma\cdot \longrightarrow$ dimerisation and disproportionation products

Table (37)

The decomposition of benzoyl peroxide in p-dichlorobenzene and 1,3,5-trichlorobenzene in the presence and absence of catalysts at 80°.

Solvents	Additives	Biaryl (m/m)	Ref
p-dichlorobenzene	nil	0.6643	E. ave
	cupric benzoate	0.8884	Cu.E.ave.
	ferric benzoate	0.9738	Fe.E.ave.
	$Cu(p\text{-}ClC_6H_4CO_2)_2$	0.9167	pCl.E.ave
1,3,5-trichlorobenzene	nil	0.8661	F. ave
	ferric benzoate	0.9563	Fe.F.ave

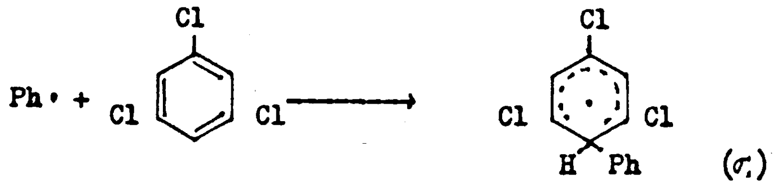
The effects of metal benzoates on the decompositions of benzoyl peroxide in p-dichlorobenzene and 1,3,5-trichlorobenzene are less spectacular here than elsewhere because of the already relatively high yields of the uncatalysed reactions. However the fairly small increases necessary to give the very high yields of biaryls obtained when the metal benzoates were present in the reactions could be accounted for by the following scheme, in which very little termination occurs by reaction (h).

(a) $(PhCO{\cdot}O)_2 \longrightarrow 2\ PhCO{\cdot}O{\cdot}$

(b) $PhCO{\cdot}O{\cdot} \longrightarrow Ph{\cdot} + CO_2$

(87)

(c)



(d) $\sigma{\cdot} + PhCO{\cdot}O{\cdot} \longrightarrow PhC_6H_2Cl_3 + PhCO{\cdot}OH$

(e) $\sigma{\cdot} + Fe^{3+} \longrightarrow PhC_6H_2Cl_3 + H^+ + Fe^{2+}$

(f) $PhCO{\cdot}O{\cdot} + Fe^{2+} \longrightarrow PhCO{\cdot}O^- + Fe^{3+}$

(g) $PhCO{\cdot}O^- + H^+ \longrightarrow PhCO{\cdot}OH$

(h) $2\sigma{\cdot} \longrightarrow$ dimerisation and disproportionation products.

Reaction (e) could be split into two steps

(i) $\sigma{\cdot} + Fe^{3+} \longrightarrow \sigma^+ + Fe^{2+}$

(j) $\sigma^+ + PhCO{\cdot}O^- \longrightarrow PhC_6H_2Cl_3 + PhCO{\cdot}OH$

For p-dichlorobenzene any one positions is o- to one chlorine atom and m- to the other. Similarly in 1,3,5-trichlorobenzene, there are three equivalent positions available for substitution, each of which is o- with respect to two of the substituents and p- with respect to the third. The equations, analogous to equation (85) for the respective total rates of substitutions are : -

$$6\ {}^{p\text{-}C_6H_4Cl_2}_{PhH}K = 4\ F_{o,m} \qquad (88)$$

$$6\ {}^{s\text{-}C_6H_3Cl_3}_{PhH}K = 3\ F_{o,o,p} \qquad (89)$$

It has been shown,[118,119] for heterolytic (electrophilic) substitution the frequency factor in the Arrhenius equation is substantially independent of the nature of the directing substituent. Brown[120] has shown this to be true for a series of similar molecules. If this assumption, that the entropy of activation is constant, can be made for phenylation, the partial rate factor are dependent only on energies of activation, to which several directing substituents can be expected to contribute additively. The partial rate factor of substitution may then be calculated as the product of two or more of the partial rates, each corresponding to one directing group and its position. Then the equations (88) and (89) can be represented as : -

$$\underline{p}\text{-}{}^{C_6H_4Cl_2}_{PhH}K = 1/6\ (4\ Fo\ Fm) \qquad (90)$$

$$\underline{s}\text{-}{}^{C_6H_3Cl_3}_{PhH}K = 1/6\ (3\ Fo^2Fp) \qquad (91)$$

Augood, Hey and Williams[121] tested the validity of the above assumption by comparing the measured values of $\underline{p}\text{-}{}^{C_6H_4Cl_3}_{PhH}K$ and $\underline{s}\text{-}{}^{C_6H_3Cl_3}_{PhH}K$ with the values obtained from equations (90) and (91) by substitution of measured values of F<u>o</u>, F<u>m</u> and F<u>p</u> for chlorobenzene and found that the assumption made with regard to the additivity of the effects of the substitution is valid, at least as a first approximation.

The results of competitive reactions of <u>p</u>dichlorobenzene and <u>s</u>-trichlorobenzene against benzene in the presence and absence of catalysts are given in Table (38). Using these measurements and the appropriate values of F<u>o</u>, F<u>m</u>, and F<u>p</u> for chlorobenzene, measured and theoretical values of K for catalysed and uncatalysed competitive reactions are calculated and the results are illustrated in Table (39).

Table (38)

The decomposition of benzoyl peroxide in equimolar solution of benzene and p-dichlorobenzene, and benzene and 1,3,5-trichlorobenzene at 80°.

Solvents	p-dichlorobenzene			1,3,5-trichlorobenzene	
Additives	Nil	Fe.benz.	Cu.benz.	Nil	Fe.benz
Biaryl (m/m)	0.4702	0.6350	0.6453	0.7833	0.7658
Ph-Ph (m/m)	0.2858	0.3209	0.3041	0.1569	0.1573
Biaryl (total)	0.7560	0.9559	0.9494	0.9402	0.9236
Relative rates	1.65	1.98	2.12	4.99	4.86

Table (39)

Observed and calculated rate factors of p-dichlorobenzene and 1,3,5-trichlorobenzene in the presence and absence of metal benzoate at 80°.

Additives	Nil	Ferric benzoate	cupric benzoate
$\frac{p\text{-}C_6H_4Cl_2}{PhH}$ K (cal.)	1.15	1.76	2.01
$\frac{p\text{-}C_6H_4Cl_2}{PhH}$ K (obs.)	1.65	1.98	2.13
$\frac{s\text{-}C_6H_3Cl_3}{PhH}$ K (cal.)	2.15	4.48	not determined
$\frac{s\text{-}C_6H_3Cl_3}{PhH}$ K (obs.)	4.99	4.86	not determined
partial rate factor	Fo Fm Fp	Fo Fm Fp	Fo Fm Fp
of PhCl used	1.86 0.93 1.24	2.47 1.07 1.47	2.60 1.16 1.57

It can be seen from the above table that the values obtained when the catalysts are present in the reaction agree well with the values predicted by the assumption regarding the additivity of directing group on activation for phenylation reaction, although the agreement is much poorer for the uncatalysed reactions.

It can be seen that the contribution of $F_{\underline{o}}$ value of chlorobenzene is important in equations (90) and (91). This is especially true for 1,3,5-trichlorobenzene when $F_{\underline{o}}$ is squared, and, if given the above assumption, the good agreement of measured and calculated values particularly for this solvent, is further proof that catalysed reactions where *o*-isomers are not being lost by dimerisation of *o*-substituted σ-complexes, give more reliable values for the partial rate factors.

D.6 The Competitive Reactions of Equimolar Mixtures of Chlorobenzene and *p*-Dichlorobenzene, and of Bromobenzene and *p*-Dichlorobenzene, in the Presence and Absence of Metal Benzoates.

The yields of chlorobiphenyls and 2,5-dichlorobiphenyl and the relative rates determined from the competitive reactions of equimolar mixtures of *p*-dichlorobenzene and chlorobenzene are listed in Table (18b). The yields of bromobiphenyls, 2,5-dichlorobiphenyl and relative rates are listed in Table (18c). By making use of the following conversion equations (92) and (93), these ralative rates can be converted into the relative rates with respect to benzene as the standard solvent[7],

$$\genfrac{}{}{0pt}{}{\text{PhX}}{\text{PhH}}K = \genfrac{}{}{0pt}{}{\text{PhX}}{\text{PhY}}K \cdot \genfrac{}{}{0pt}{}{\text{PhY}}{\text{PhH}}K \qquad (92)$$

$$\genfrac{}{}{0pt}{}{\text{PhY}}{\text{PhH}}K = \genfrac{}{}{0pt}{}{\text{PhX}}{\text{PhH}}K \Big/ \genfrac{}{}{0pt}{}{\text{PhX}}{\text{PhY}}K \qquad (93)$$

where PhX and PhY represent the substituted benzene.

The relative rates for chlorobenzene and bromobenzene with respect to benzene as the standard solvent, calculated by the conversion equation, and the measured values from experiments (E.5.b) and (E.6.b) are shown in Table (40).

Table (40)

Measured and calculated relative rates for chlorobenzene and bromobenzene in the presence and absence of metal benzoates.

	nil	cupric benzoate	ferric benzoate
$\frac{\text{PhCl}}{\text{PhH}}$ K (measured)	1.14	1.51	1.43
$\frac{\text{PhCl}}{\text{PhH}}$ K (calculated)	1.57	1.51	1.43
$\frac{\text{PhBr}}{\text{PhH}}$ K (measured)	1.47	1.46	1.53
$\frac{\text{PhBr}}{\text{PhH}}$ K (calculated)	1.01	1.46	1.39

The results obtained by using the conversion equation in the absence of any additive in both chlorobenzene and bromobenzene a disagreed with those determined directly from the competitive reactions between these substrates and benzene. This might ascribed to relative loss of σ-complexes by dimerisation, and the consequent unreliability of the measured relative rates. However good agreement is obtained in the presence of additives, this is especially true for cupric benzoate.

The above finding supports the view[109] that the rate factors determined in the absence of additives are not reliable indices of reactivity, but those determined in the presence of such additives are much superior.

The relative rates obtained for chlorobenzene and bromobenzene both by conversion and directly, in the presence of cupric benzoate are 1.51 and 1.46 respectively, these values make bromobenzene slightly less reactive than chlorobenzene in the phenylation reaction by benzoyl peroxide. This reversal of the order of previously accepted values for chlorobenzene and bromobenzene was also noticed by Davies, Hey and Summers[115] who reinvestigated the phenylation of a series of mono-substituted derivatives of benzene using p-dichlorobenzene as the reference compound. Their total rate values of 2.20 and 1.90 for chlorobenzene and bromobenzene respectively are higher than present findings but in the order.

D.7 The Competitive Reactions of Benzoyl Peroxide in Equimolar Mixtures of Chlorobenzene and 1,3,5-Trichlorobenzene in the Presence and Absence of Ferric Benzoate.

The yields of chlorobiphenyls and 2,4,6-trichlorobiphenyl and the relative rates determined in the competitive reactions in this series are listed in Table (20b). By making use of conversion equations (92) and (93), the relative rates of phenylation of chlorobenzene with respect to benzene as the standard solvent are obtained and are shown in the following Table (41).

Table (41)

Measured and calculated relative rates of chlorobenzene in the presence and absence of ferric benzoate.

Catalyst	$\frac{PhCl}{PhH}$ K (from exp. E.4)	$\frac{PhCl}{PhH}$ K (calculated)
nil	1.14	1.40
ferric benzoate	1.43	1.46

Here again as noticed before in the competitive reactions of benzoyl peroxide in chlorobenzene and p-dichlorobenzene the results obtained by the use of conversion equation and experiments with benzene as the standard solvent showed some discrepancy in the absence of ferric benzoate, while good agreement is obtained in the presence of the additive.

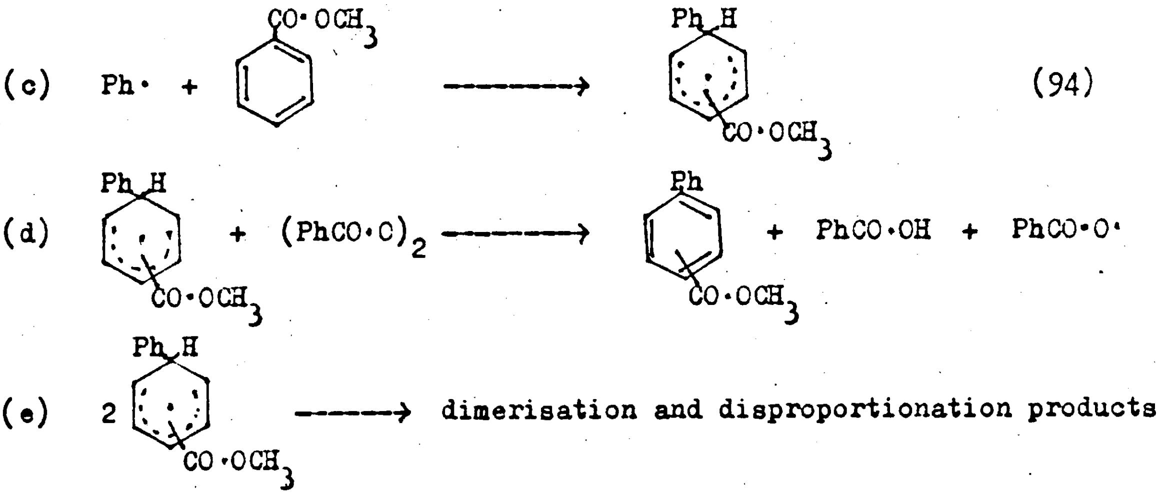
The values obtained by the use of conversion equations both in the presence (1.46) and absence (1.40) of ferric benzoate are in close agreement with the value (1.43) of ferric benzoate catalysed reactions with benzene as standard solvent. This agreement shows that in all these systems, reliable results which are uncomplicated either by loss of σ-complexes or by complexation can be obtained by the use of efficient additive.

D.8 The Decomposition of Benzoyl Peroxide in Methyl Benzoate in the Presence and Absence of Metal Benzoates.

The decomposition of benzoyl peroxide in methyl benzoate in the presence and absence of metal (cupric or ferric) benzoates summarised in Table (42) shows non-equivalent yields of benzoic acid and methyloxycarbonylbiphenyls in the uncatalysed reaction. The low yield of benzoic acid compared with relatively high yields of biaryls suggest the chain-termination process in this solvent is the dimerisation and, particularly disproportionation of σ-complexes, and the products formed in uncatalysed reaction of this solvent can be accounted for by the following mechanism : -

(a) $(PhCO{\cdot}O)_2 \longrightarrow 2\ PhCO{\cdot}O{\cdot}$

(b) $PhCO{\cdot}O{\cdot} \longrightarrow Ph{\cdot} + CO_2$



(94)

The dihydrobiaryls which accompany the biaryls formed by disproportionation would be expected to be readily oxidised to biaryls during working up.

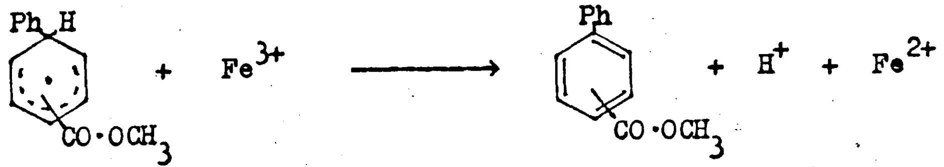
Table (42)

Summary of the decomposition of benzoyl peroxide in methyl benzoate in the presence and absence of metal benzoates.

Additives	$PhC_6H_4CO_2CH_3$ (m/m)	PhCO OH (m/m)	isomer ratio o-	m-	p-
nil	0.6266	0.2512	48.1	19.9	32.0
cupric benzoate	0.8013	0.7990	56.6	16.3	27.1
ferric benzoate	0.7741	0.7253	53.4	16.5	30.1

The effect of the catalysts in methyl benzoate is seen by the increased yields of both biaryl and benzoic acid. The increased yield of methyloxycarbonylbiphenyl is here again accompanied by a substantial increase in the proportion of ortho- isomer (5.3% with cupric- and 8.5% with ferric benzoate). In the catalysed reaction almost equivalent yields of biaryl and benzoic acid are formed suggesting that removal of σ-complexes though dimerisation or disproportionation is no longer important, and the radicals in the solution are removed by the following reactions : -

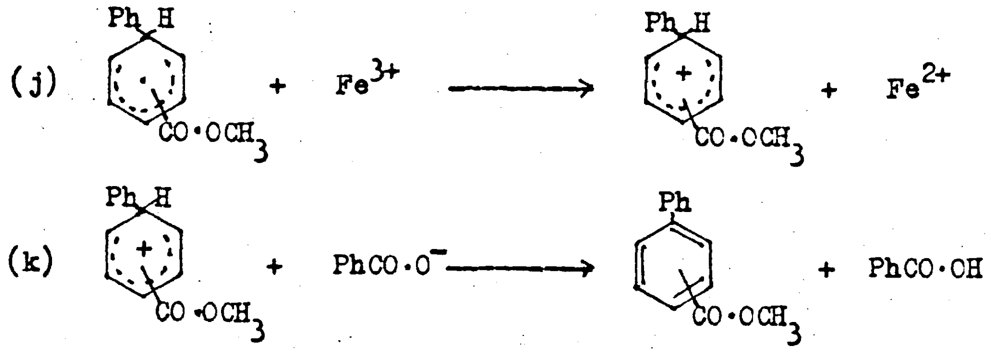
(g)



(h) $PhCO{\cdot}O{\cdot} + Fe^{2+} \longrightarrow PhCO{\cdot}O^- + Fe^{3+}$

(i) $PhCO{\cdot}O^- + H^+ \longrightarrow PhCO{\cdot}OH$

Reaction (g) could be split into two steps



D.9 The Competitive Reaction of Benzoyl Peroxide in Equimolar Mixtures of Benzene and Methyl Benzoate in the Presence and Absence of Metal Benzoates

The relative rates and partial rate factors obtained for metal (cupric or ferric benzoate) catalysed and uncatalysed reactions in the benzene–methyl benzoate system are summarised in Table (43).

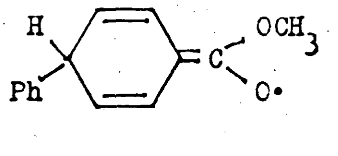
Table (43)

Relative rates and partial rate factors of methyl benzoate in the presence and absence of metal benzoates.

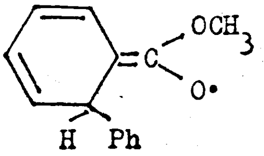
Additives	relative rate	partial rate factor			references
		Fo	Fm	Fp	
nil	1.77	3.04	0.93	2.73	129
nil	1.89	2.73	1.12	3.64	R.ave.
cupric benzoate	2.06	3.50	1.03	3.31	Cu.R.ave
ferric benzoate	2.03	3.26	1.00	3.64	Fe.R.ave.

The introduction of methoxycarbonyl group has activated the ortho- and para- but not the meta- positions by near-neutral phenyl radical both in the presence and absence of catalysts, the partial rate factor for meta-substitution is close to unity, a value expected if the neutral phenyl radical is the only species involve in selecting among the available positions.

The high values of Fo and Fp are due to the stabilisation of the appropriate σ-complexes by delocalisation of the unpaired electron in the methoxycarbonyl group, which makes this possible by virtue of its conjugation with the nucleus. Thus the stabilisation of the σ-complex for para-substitution in methyl benzoate arises from the contribution of canonical forms such as (XV).

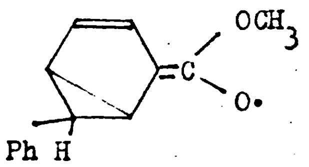


(XV)



(XVI)

Analogous forms can be written for ortho-substitution (XVI), but the corresponding form for meta-substitution requires a formal bond between ortho- and para-position (XVII), and its contribution would therefore be expected to be negligible.



(XVII)

The marked increase of Fo values in catalysed reactions again suggests the selective removal of o-substituted σ-complex when the termination process is the dimerisation or disproportionation of σ-complexes as in uncatalysed reaction. However, introduction of catalysts successfully removes the σ-radicals as biaryls before their dimerisation can take place, thus giving true values for the partial rate factors.

D.10 The Decomposition of Benzoyl Peroxide in Benzophenone in the Presence and Absence of Metal Benzoates.

Table (44)

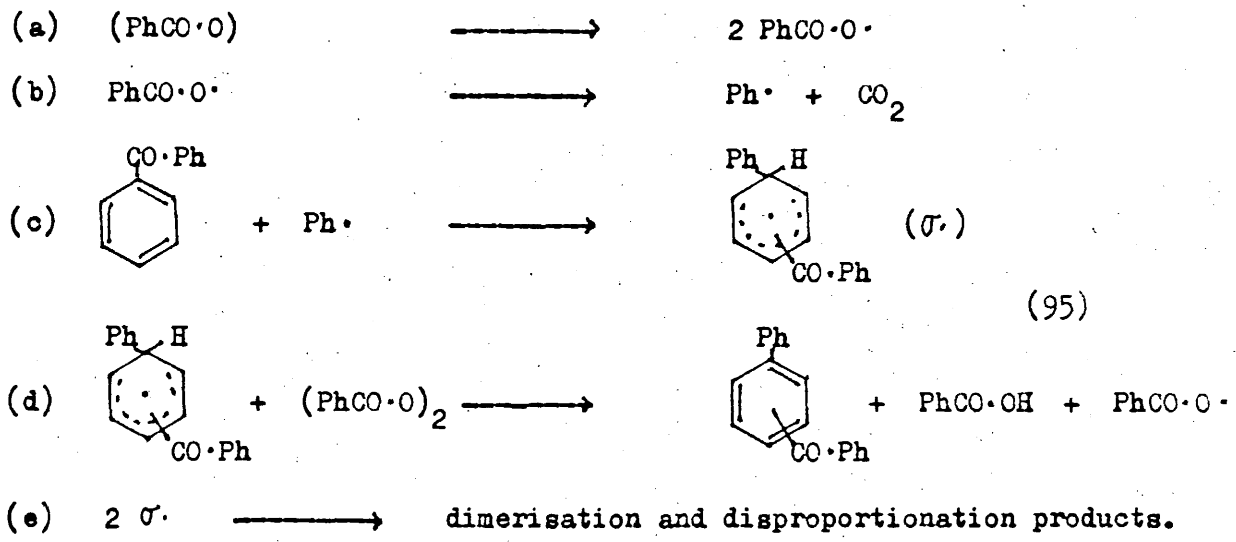
Summary of the decomposition of benzoyl peroxide in benzophenone in the presence and absence of metal benzoates.

Additives	PhC_6H_4COPh (m/m)	PhCO OH (m/m)	isomer ratio o-	m-	p-
nil	0.8442	0.2541	40.0	21.1	38.9
cupric benzoate	0.8840	0.7849	50.1	17.6	32.3
ferric benzoate	0.9870	0.8134	47.7	18.6	33.7

The above Table shows the summary of the results of phenylation reactions of Benzophenone in the presence and absence of metal benzoates.

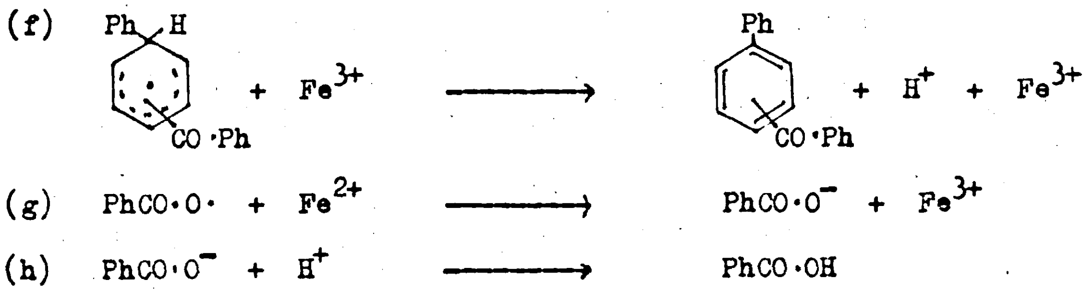
The major products detected in this solvent are isomers of phenylbenzophenone and benzoic acid. High yields of phenylbenzophenone are noticed in both catalysed and uncatalysed reactions, but here again as in methyl benzoate the yield of benzoic acid is low compared with the yields of phenylbenzophenone in the uncatalysed reaction. The presence of metal (cupric or ferric) benzoates resulted in increasing the yield of benzoic acid almost to equivalent proportion to biaryl which in turn had a very little effect in improving the yield, but altered the isomer ratios considerably, again the increase of o-isomer (10.1% with cupric benzoate and 7.7% with ferric benzoate) at the expence of both m- and p-isomers is noticeable.

The phenylbenzophenone and benzoic acid are formed according to the following mechanism; with the termination reaction occuring between σ-radicals in the uncatalysed reaction (95);

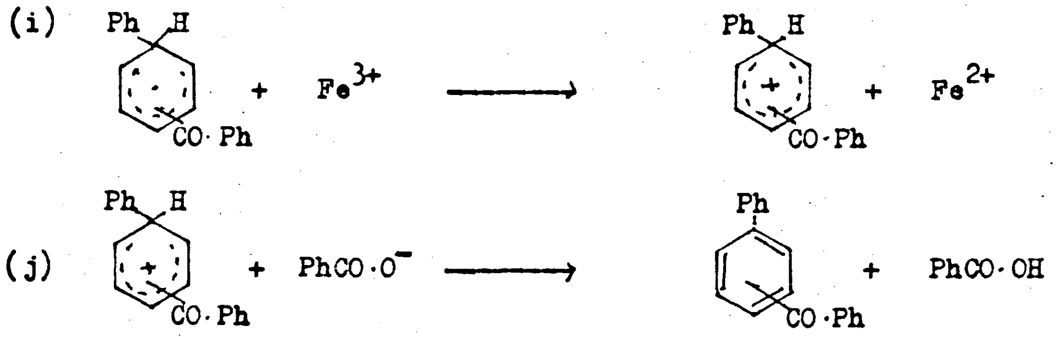


(95)

and metal assisted termination of radicals (95 f.g.h) in the catalysed reaction



σ-radicals could be oxidised to biaryls by metal ions by the following mechanism : -



D.11 The Competitive Reactions of Benzoyl Peroxide in Equimolar Mixtures of Benzene and Benzophenone in the Presence and Absence of Metal Benzoates.

The results for the individual yields of phenylbenzophenone and biphenyl in the competitive experiments in benzene and benzophenone in the presence and absence of metal (cupric or ferric) benzoates are given in Table (24). The relative rates and partial rate factoes for phenylation obtained from the reactions in this system in the presence and absence of additives are summarised in the following Table (45).

Table (45)

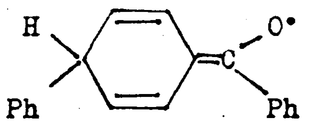
Relative rates and partial rate factors of benzophenone in the presence and absence of metal benzoates.

additives	relative rate	partial rate factors Fo	Fm	Fp	references exp. number
none	4.40	2.65	1.39	5.10	S. average
cupric benzoate	4.12	3.10	1.09	3.96	Cu.S.ave.
ferric benzoate	3.98	2.85	1.11	4.00	Fe.S.ave.

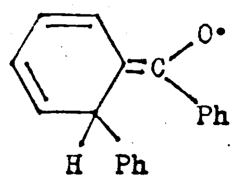
The benzoyl-group attached to the benzene ring is seen to strongly activated the nucleus for homolytic substitution, and to result in high values of relative rate in both catalysed and uncatalysed reactions in this system.

The yield of phenylbenzophenone in the competitive reaction containing metal benzoates increased (7.8% with cupric and 10.8% with ferric), but the yield of biphenyl is increased to a much greater extent (15% with cupric- and 22.4% with ferric benzoate), consequently lowering of the relative rate in the presence of metal benzoate is observed here.

The high values of the partial rate factors in the *o*- and *p*-positions compared with *m*-position can be explained by stablisation of σ-complexes for *o*- and *p*-substitution arising from conjugation between the unsaturated benzoyl-group and nucleus (XVIII) and (XIX).



(XVIII)



(XIX)

The extent of the stablisation of these σ-complexes through delocalisation should be of a similar order, and should result in similar values of partial rate factors. However in this system the value of F*o* is found to be considerably lower than F*p*. This is unusual because all the results from previous systems indicated that the *o*-position, if any, was the one which gave the higher value. This anomalous observation possibly arises from the effect of the bulky benzoyl-group in benzophenone in hindering *o*-attack. This steric effect therefore depresses the reactivity of this position.

Also the high value of Fo (1.39) in uncatalysed reaction is anomalous, probably for the same reasons described earlier (p. 146) This position is expected to have a partial rate factor of unity if the selecting process between the two competing solvents involves the same species. Therefore the large partial rate factors of m- and p-positions (both of which are reduced considerably in the presence of metal benzoates) indicates that the initial complexation also occurs between phenyl radicals or their precursors and benzophenone molecules, resulting in the increased reactivity of the whole molecule, including the m-positions. In this system, the complexation is likely to occur between benzoyl peroxide or benzoyloxy-radicals and benzophenone molecules through some week Van der Waals forces prior to decarboxylation. The phenyl radicals generated, in this situation would be closely associated with benzophenone molecules and their attack on benzophenone woul be favoured, thus leading to an enhanced reactivity of benzophenone molecules relatively to the competing solvent, benzene.

This complexation is lifted in the presence of metal benzoates. Therefore the phenyl radicals generated were free within the solution to show a selection between the competing substrate molecules, hence leading to a decrease in the reactivity of the sites which otherwise would be favourable for the attack of phenyl radicals.

D.12 The Decomposition of Benzoyl Peroxide in Benzonitrile in the Presence and Absence of Metal Benzoates.

Table (46)

Summary of the decomposition of benzoyl peroxide in benzonitrile in the presence and absence of metal benzoates.

experiment number	additives	PhC_6H_4CN (m/m)	Ph-Ph (m/m)	isomer ratios		
				o	m	p
I. average	none	0.7233	0.087	52.3	17.4	30.3
Cu. $_I$. ave.	cupric benzoate	0.7832	—	57.0	15.2	27.8
Fe. $_I$. ave.	ferric benzoate	0.8337	0.028	57.6	15.7	26.7

The above Table shows the summary of the results from catalysed and uncatalysed phenylation reactions of benzonitrile.

The yield of benzoic acid in these reactions were not determined in the present work.

The effects of ferric benzoate or cupric benzoate on the decomposition of benzoyl peroxide in this solvent are less apectacular here because of the alresdy relatively high yields of the uncatalysed reaction. However the fairly small increases necessary to give the very high yields of cyanobiphenyls obtained when the metal benzoates were present in the reactions were accompanied by the usual alternations of isomer ratios. Traces of biphenyl detected in the uncatalysed reaction may be formed by the union of two phenyl radicals or by the attak of a phenyl radical on the 1-position of nucleus of the solvent (p.156); the effect of catalyst however caused a marked decrease in the formation of biphenyl, and the g.l.c. analysis of the reaction mixtures containing cupric benzoate as catalyst gave no indication of biphenyl being formed in this reaction.

D.13 The Competitive Reactions of Benzoyl Peroxide in Equimolar Benzene-Benzonitrile System in the Presence and Absence of Metal Benzoates.

The results of the individual yields of cyanobiphenyls and biphenyl are given in Table (26). The relative rate and partial rate factors for phenylation obtained in the present work from reactions in the presence and absence of additives together with the values obtained by Dannley and Gregg[50] are shown in the following Table (47).

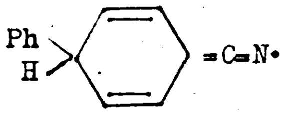
Table (47)

Relative rates and partial rate factors of benzonitrile in the presence and absence of metal benzoates.

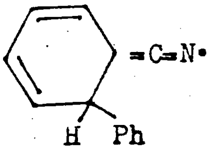
additives	relative rate	partial rate factors Fo	 Fm	 Fp	reference numbers
none	3.7	6.5	1.1	6.1	50
none	1.92	3.01	1.00	3.49	T.average
cupric benzoate	1.73	2.82	0.86	3.02	Cu. T. ave.
ferric benzoate	1.82	3.12	0.85	2.98	Fe. T. ave.

The relative rate (1.92) obtained in uncatalysed reactions in the present work is very much lower than the value of 3.7 reported by Dannley and Gregg[50], who used pyridine as the reference solvent. This is probably due to the reasons given earlier in Section D.2 (p.144) (i.e. the use of conversion equations in the reactions in the absence of additives can give rise to erroneous results, and more accurate analytical method was employed in the present studies.

The high values of partial rate factors for the o- and p-positions, as compared to that for the m-position, which is unity, is attributed to the possibility, which exists in benzonitrile, for the delocalisation of the unpaired electron in the σ-complex to the extended into the substituent group as represented in (XX) and (XXI), thus giving rise to selective activation of ortho and para-positions.



(XX)



(XXI)

Since the yields of uncatalysed reactions are high in this solvent, the presence of ferric benzoate or cupric benzoate in the reaction mixture had no significant effect on the relative rate or partial rate factors, although partial rate factors in the presence of additives are preferred because possible removal of o-substituted σ-complexes by dimerisation is reduced.

IV. CONCLUSION

The results of phenylation reactions of benzene, fluorobenzene, chlorobenzene, bromobenzene, p-dichlorobenzene, 1,3,5-trichlorobenzene, methyl benzoate, benzophenone and benzonitrile suggest the following conclusions :-

(1) In the absence of additives side reactions of σ-radicals can be selective, this is especially true, when the yields of biaryls in the uncatalysed reaction are low.

(2) In some solvents (e.g bromobenzene and benzophenone) complexation between a precursor of phenyl-radicals and solvent molecules may occur.

The presence of additives in the reactions suppress the side reactions of various σ-radicals and remove some of the initial complexation reactions of solvent molecules with a precursor of phenyl radicals.

Therefore the results obtained in the presence of additives, which are also independent of benzene/substituted benzene ratio (p.152) reflect the true intra-molecular and inter-molecular reactivity of substrates in the phenylation reactions.

The best set of reactivity indices for fluorobenzene, chlorobenzene, bromobenzene, p-dichlorobenzene, 1,3,5-trichlorobenzene, methyl benzoate, benzophenone and benzonitrile in the phenylation reaction with benzoyl peroxide are given in Table (48).

The values obtained under the influence of different additives agreed reasonably well with each other. Consequently the best sets of relative and partial rate factors obtained by taking the mean values in the presence of additives, e.g ferric benzoate and cupric benzoate are considered to be the best definitive set.

Table (48)

Summary of relative rates and partial rate factors for the systems being studied in the presence of additives.

solvents	relative rates	Fo	Fm	Fp
fluorobenzene	1.26	2.0	1.1	1.2
chlorobenzene	1.48	2.5	1.1	1.5
bromobenzene	1.49	2.5	1.3	1.4
benzonitrile	1.78	3.0	0.9	3.0
methyl benzoate	2.05	3.4	1.0	3.5
p-dichlorobenzene	2.06		—	
benzophenone	4.05	3.0	1.1	4.0
1,3,5-trichlorobenzene	4.86		—	

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