SOME ASPECTS OF HOMOLYTIC ARYLATION AND SILYLATION ~~REACTIONS~~

A thesis presented for the degree of
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by

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To My Parents and Family

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ABSTRACT

The effects of additives such as ferric benzoate, cupric benzoate, m-dinitrobenzene and nitrobenzene on the thermal decomposition of benzoyl peroxide in toluene, anisole and t-butylbenzene have been investigated over a wide range of additive concentrations. In the reactions of anisole, the effect of air, oxygen, t-butyl hydroperoxide and nitrosopentafluorobenzene were also examined. The additives exhibited different effects on the product distribution of these substrates. Explanations have been suggested to account for these observations.

The effects of these additives on the competitive reactions of toluene, anisole and t-butylbenzene with benzene as a standard solvent have been studied over a wide range of additive concentrations. Relative rates are significantly lowered in the presence of additives, and partial rate factors are also altered. These observations have been interpreted in terms of the formation of some weak complexes between phenyl radicals or their precursors with the substrate molecules in the absence of additives, but such complications are removed in the presence of additives. The mean values of the relative rate and the partial rate factors which are determined in this work in the presence of additives are considered to be the best definitive set now available. The competitive reactions containing various molar concentrations of anisole and benzene, toluene and benzene with or without the presence of additives were also studied. Finally, the cross-checked experiments involving the direct competitive reactions between toluene/anisole, toluene/t-butylbenzene and anisole/t-butylbenzene were carried out. The results substantiated the order of reactivity determined for toluene, anisole and t-butylbenzene towards the phenylation reactions by benzoyl peroxide.

To study the silylation reaction on aromatic substrates, attempts were made to generate dimethylphenylsilyl radicals, thermally or photolytically, from dimethylphenylsilane in the presence of radical initiators such as t-butyl peroxide, azo-bisisobutyronitrile and benzoyl peroxide. The formation of dimethyldiphenylsilane and diphenyltetramethyldisilane in the reaction of the dimethylphenylsilane in benzene indicated the formation of silyl radicals. Benzoyl peroxide was found to be the most efficient initiator in this reaction. Investigation was extended to the study of the reactions of dimethylphenylsilane with toluene, naphthalene and halobenzenes (chlorobenzene, bromobenzene, p-dichlorobenzene and iodobenzene) and anisole. In the reactions with toluene, naphthalene and anisole, nuclear silylated products were detected. However, in the reaction with halobenzene, the main reaction was the displacement or the abstraction of the halogen from the aromatic nucleus by silyl radicals. Mechanisms have been suggested to account for these observations. These results indicated the nucleophilic character of the dimethylphenylsilyl radical.

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1 INTRODUCTION

1. Homolytic Aromatic Substitution Reactions

In 1934, Hey and Grieve[1] showed that in a number of biaryl-forming reactions, in which the hydrogen atom on the aromatic nucleus is replaced by an aryl group, the isomer distribution in the attack of mono-substituted benzenes could not be explained by the normal laws governing aromatic substitution reactions proposed by Ingold[2]. In these reactions, the substituent group on the substrate did not exhibit the well-documented polar effects shown in aromatic electrophilic substitution. Hey suggested a non-ionic type of mechanism, in which a neutral species participated in the reaction, to account for such observations. After this, a wealth of information was rapidly accumulated and was reviewed in detail by Hey and Waters in 1937[3].

The subject of homolytic aromatic substitution has been reviewed subsequently by Dermer and Edmison[4]. Augood and Williams[5], Williams [6a,b], and more recently by Hey[7], Williams[8] and Perkins[9].

(A) Homolytic Aromatic Substitution by Benzoyl Peroxide.

The thermal decomposition of benzoyl peroxide is one of the most widely studied sources of phenyl and benzoyloxy radicals. It provides the 'cleanest', most convenient source of the phenyl radical and often higher yield of products than other sources. However, the reaction is more complex than was at one time thought.

Some of the earlier work on the reaction of benzoyl peroxide with various solvents was done by Gelissen and Hermans (1925)[10a] and Boeseken and Hermans(1935)[10b]. They found that in aromatic substrates, unsymmetrical biaryls (Ar-R where Ar and R were provided by the peroxide and solvent respectively), and carbon dioxide were obtained. They proposed the so-called 'RH' scheme to explain the products but did not specify any mechanism for the reaction.

The homolytic nature of this reaction was recognised later by Hey[1]. In 1937, Hey and Waters[3] proposed the participation of short-lived aryl radicals in this reaction and suggested the following scheme to account for the observed products.

$$(\mathrm{ArCO{\cdot}O})_2 \longrightarrow \mathrm{ArCO{\cdot}O{\cdot}} + \mathrm{Ar{\cdot}} + \mathrm{CO_2} \qquad \text{......} \ (1)$$

$$\mathrm{Ar{\cdot}} + \mathrm{RH} \longrightarrow \mathrm{Ar{\cdot}R} + \mathrm{H{\cdot}} \qquad \text{......} \ (2)$$

$$\mathrm{ArCO{\cdot}O{\cdot}} + \mathrm{H{\cdot}} \longrightarrow \mathrm{ArCO{\cdot}OH} \qquad \text{......} \ (3)$$

$$\mathrm{Ar{\cdot}} + \mathrm{RC_6H_5} \longrightarrow \mathrm{ArC_6H_4R} + \mathrm{H{\cdot}} \qquad \text{......} \ (4)$$

$$\mathrm{ArCO{\cdot}O{\cdot}} + \mathrm{RH} \longrightarrow \mathrm{ArCO{\cdot}OR} + \mathrm{H{\cdot}} \qquad \text{......} \ (5)$$

Equations (4) and (5) were included to account for the minor products, polyphenyls and phenolic esters.

(I) Kinetics and mechanism of benzoyl peroxide decomposition

From present day knowledge, the basic scheme outlined above needs some modifications. These modifications are of degree rather than of kind, for the concept of intervention by aryl and aroyloxy radicals remains.

Kinetic studies of the decomposition of benzoyl peroxide in aliphatic and aromatic solvents have been reported by a number of workers[11a-e]. The results show that the decomposition can be represented by the sum of a first order reaction and one of another order, i.e. concurrent unimolecular homolysis and an induced homolysis the extent of which varies with the solvent and the initial peroxide concentration. A kinetic form of first order unimolecular decomposition and an n^{th} order induced decomposition was demonstrated by Nozaki and Bartlett[11b] for the decomposition in benzene.

$$-\frac{d[P]}{dt} = k_1[P] + k_2[P]^n \qquad \text{......} \ (6)$$

$[P]$ = Peroxide concentration at time t, k_1 and k_2 are rate constants. By the application of the steadystate approximation, it can be shown than n can have values of three-half or one depending on the modes of termination[12].

It has a value of three-half for termination involving reaction between two like radicals and one if termination is between unlike radicals.

By kinetic analysis or by employing radical traps[13a,b] to eliminate the induced decomposition, it was found that the rate constant for unimolecular decomposition also varies slightly with the solvent. Hammond and Soffer[14], using iodine in moist carbon tetrachloride, demonstrated that the spontaneous decomposition is in fact the homolysis of the oxygen to oxygen bond of the peroxide to form two moles of benzoyloxy radicals. They were able to isolate two moles of benzoic acid per mole of peroxide.

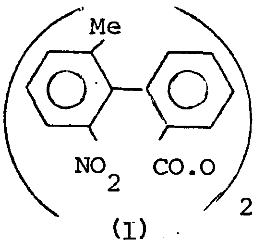
$$
\begin{aligned}
(\mathrm{PhCO{\cdot}O})_2 &\longrightarrow 2\mathrm{PhCO{\cdot}O{\cdot}} \\
\mathrm{PhCO{\cdot}O{\cdot}} + \mathrm{I}_2 &\longrightarrow \mathrm{PhCO{\cdot}OI} + \mathrm{I{\cdot}} \\
\mathrm{PhCO{\cdot}OI} + \mathrm{H_2O} &\longrightarrow \mathrm{PhCO_2{\cdot}H} + \mathrm{IOH} \\
2\mathrm{I{\cdot}} &\longrightarrow \mathrm{I_2} \\
5\mathrm{HOI} &\longrightarrow 2\mathrm{H_2O} + 2\mathrm{I_2} + \mathrm{HIO_3}
\end{aligned}
$$

This confirms that the benzoyloxy radicals have a sufficient life-time to escape from the solvent cage under these conditions. If the decomposition of benzoyl peroxide in benzene and in this reaction are of the same nature, it is necessary to modify equation (1) to read.

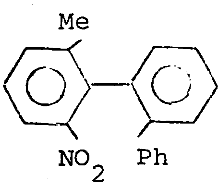
$$\mathrm{ArCO{\cdot}O{-}O{\cdot}CO{\cdot}Ar} \longrightarrow 2\mathrm{ArCO{\cdot}O{\cdot}} \qquad \ldots\ldots \ (7)$$

$$\mathrm{ArCO{\cdot}O{\cdot}} \longrightarrow \mathrm{Ar{\cdot}} + \mathrm{CO_2} \qquad \ldots\ldots \ (8)$$

The most direct evidence of aryl radical participation comes from the work of De Tar and Howard[15] on the decomposition of the optically active peroxide (1) in benzene. The o-terphenyl derivative (2) was isolated, only 25-50% of the optical activity being retained.



(I)



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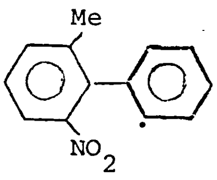


(3)

This partial racemization demonstrated the independent existence of the short-lived intermediate radical (31) in which free rotation about the inter-nuclear bond is possible.

Furthermore, it is necessary to include a reaction to represent the induced decomposition.

$$\mathrm{R\cdot + ArCO\cdot O - O\cdot CO\cdot Ar \longrightarrow ArCO\cdot O\cdot R + ArCO\cdot O\cdot} \qquad \ldots\ldots (9)$$

The work of Williams and co-workers[16b] on the decomposition of benzoyl peroxide in benzene and alkylbenzenes has provided kinetic and other evidence to show that the σ-complex is responsible for the induced decomposition of the peroxide. In some cases the induced decomposition is more complex and eqn. (6) is an over-simplification. The following complex scheme (benzene as substrate at 80°C) was proposed to account for the observations, those steps marked with an asterisk being of minor importance.

$$\mathrm{P \longrightarrow 2Ph\cdot CO\cdot O\cdot} \qquad \ldots\ldots (10)$$

$$\mathrm{PhCO\cdot O\cdot \longrightarrow Ph\cdot + CO_2} \qquad \ldots\ldots (11)$$

$$\mathrm{Ph\cdot + PhH \longrightarrow \sigma\cdot} \qquad \ldots\ldots (12)$$

$$\mathrm{PhCO\cdot O\cdot + PhH \longrightarrow \sigma\cdot'} \qquad \ldots\ldots (13)^*$$

$$\mathrm{\sigma\cdot + P \longrightarrow Ph\text{-}Ph + PhCO_2H + PhCO\cdot O\cdot} \qquad \ldots\ldots (14)$$

$$\mathrm{\sigma\cdot' + P \longrightarrow PhCO\cdot O\cdot Ph + PhCO_2H + PhCO\cdot O\cdot} \qquad \ldots\ldots (15)^*$$

$$\mathrm{\sigma\cdot + PhCO\cdot O\cdot \longrightarrow Ph\text{-}Ph + PhCO_2H} \qquad \ldots\ldots (16)^*$$

$$\mathrm{\sigma\cdot' + PhCO\cdot O\cdot \longrightarrow PhCO\cdot OPh + PhCO_2H} \qquad \ldots\ldots (17)^*$$

$$\mathrm{2\sigma\cdot \longrightarrow Ph\text{-}Ph + Ph\text{-}C_6H_6} \qquad \ldots\ldots (18)$$

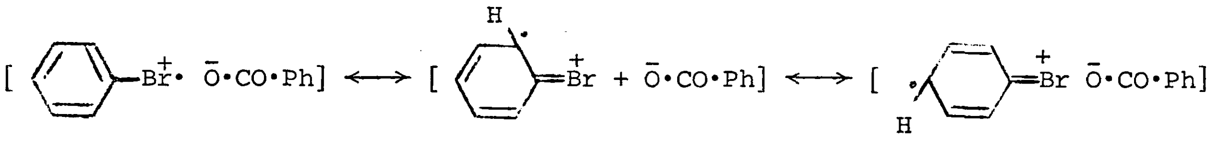
$$\mathrm{2\sigma\cdot \longrightarrow (PhC_6H_6)_2} \qquad \ldots\ldots (19)$$

$$\mathrm{2\sigma\cdot' \longrightarrow} \text{Oxygen containing dimerization and disproportionation products} \qquad \ldots\ldots (20)^*$$

For the reaction in benzene, alkylbenzene, fluorbenzene and chlorobenzene at low initial peroxide concentration, the rate obeys equation (6) with

$n = \frac{3}{2}$, so that the chain termination reactions involve dimerization and disproportionation of the σ-complex. It is also observed that in high dilution, where secondary radical reactions of the dihydroaromatic products are minimized, the best yields of quaterphenyls are obtained. When results from this and related experiments are extrapolated to infinitely low concentration of peroxide, almost all of the peroxide could be accounted for as carbon dioxide and the products of dimerization and disproportionation of σ-complex, with dimerization accounting for as much as 75% of the reaction[16a,17,18].

However, the reaction in bromobenzene shows a kinetic form with first order induced decomposition. In this case the termination involves the direct oxidation of the σ-radicals by benzoyloxy radicals, the importance of the termination by dimerization and disproportionation being much reduced. This is thought to be due to the stabilization of benzoyloxy radicals by the formation of a one electron charge transfer complex.



The reaction in nitrobenzene is more complicated. At very low concentration of peroxide, the rate law (21) is obeyed indicating both modes of termination are important.

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

At higher concentration, the rate law becomes (22)

$$-\frac{d[P]}{dt} = k_1[P] + k_2[P] \qquad \ldots\ldots \ (22)$$

In summary, in solvents showing the three-halves order term e.g. benzene, biaryls are formed in reactions (14) and (18), and the chain is terminated by reactions (18) and (19). Since reaction (16) does not occur, yields of biaryl and acid are low and those of residue are high. In solvents showing the first order induced decomposition terms such as bromobenzene, and in solvents of the former group in the presence of additives such as iron(III) benzoate, chains are terminated by reaction (16) or its equivalent, (14) and (18) occur to a much smaller extent, and consequently yields of biaryl and aroic acid are high, and those of the residue are low.

(II) Further mechanistic features

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

The finding that the isomer ratio in the arylation of substituted benzenes appears to be nearly independent of the nature of the radical source suggests that the step (23) is common to all homolytic phenylation reactions. There are three possible pathways to achieve this

$$\mathrm{Ph{\cdot}} + \mathrm{ArH} \longrightarrow \mathrm{PhAr} + [\mathrm{H{\cdot}}] \qquad \ldots\ldots \ (23)$$

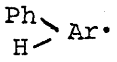
(a) The abstraction and addition mechanism.

$\mathrm{Ph{\cdot}} + \mathrm{ArH} \longrightarrow \mathrm{PhH} + \mathrm{Ar{\cdot}}$

$\mathrm{Ph{\cdot}} + \mathrm{Ar{\cdot}} \longrightarrow \mathrm{Ph{-}Ar}$

$\mathrm{Ar{\cdot}} + \mathrm{Ar{\cdot}} \longrightarrow \mathrm{Ar{-}Ar}$

(b) The addition-abstraction mechanism.

$\mathrm{Ph{\cdot}} + \mathrm{ArH} \longrightarrow$ 

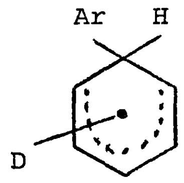
$$\mathrm{Ph{\cdot}} + \mathrm{ArH} \longrightarrow {}^{\mathrm{Ph}}_{\mathrm{H}}{>}\mathrm{Ar{\cdot}}$$

$\mathrm{PhArH{\cdot}} + \mathrm{R{\cdot}} \longrightarrow \mathrm{PhAr} + \mathrm{RH}$

(c) The synchronous mechanism.

$$\text{Ph}\cdot + \text{Ar-H} \longrightarrow \text{Ph----Ar----H} \longrightarrow \text{Ph-Ar} + \text{H}\cdot$$

Mechanism (a) is considered unlikely by energy considerations and the absence of symmetrical biaryls in the reaction products. The absence of a significant change in the hydrogen isotope distribution in the recovered substrates from reaction in deuterated and tritiated benzene[19a-c] also argues against mechanisms (a), (c) and freely reversible addition in (b). Hey and his colleagues [19c] suggested that the acceptable mechanism consistent with this observation is the addition-abstraction mechanism with an irreversible addition step to form the σ-complex. More recently Saltiel and Curtis[20] also reported the absence of a hydrogen isotope effect in the phenylation of deuterated benzene and supported the irreversible addition of phenyl radicals to benzene to form the σ-complex. Based on thermochemical data, Jackson[21] constructed a table to predict the feasibility of the addition reaction to olefins and benzene by free radicals. It was suggested that the formation of the phenylcyclohexadienyl radical is irreversible at temperatures below 200°C. Eliel and co-workers[22] also reported the absence of an isotope effect in the recovered substrate in the deuterated benzene, but an isotope effect was observed in the products of certain arylation reaction, this isotope effect is attributed to the isotopic discrimination in the competition between dimerization and disproportionation of the two types of arylcyclohexadienyl radicals.



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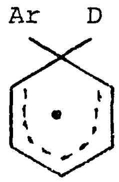
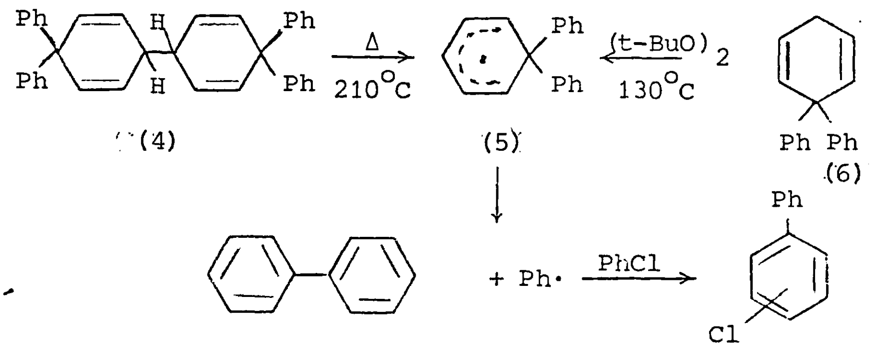


Within the mechanism proposed, the addition step is held to be rate-determining[22,19c] and the hydrogen atom in the σ-radical is never free but lost in a bimolecular hydrogen transfer to another radical in solution. The isolation of dimerization and disproportionation products of σ radicals also gives strong support to this mechanism[23].

However, results from recent studies by Perkins[24] indicate that in some cases the formation of the arylcyclohexadienyl radicals, at least at high temperature, could be reversible. The σ-radicals (5) and (8) were formed by pyrolysis of (4) and (7) respectively at 210°C, (5) was also formed by hydrogen abstraction of (6), in chlorobenzene. The three isomeric chlorobiphenyls were detected and formed in proportions characteristic of homolytic phenylation of chlorobenzene.



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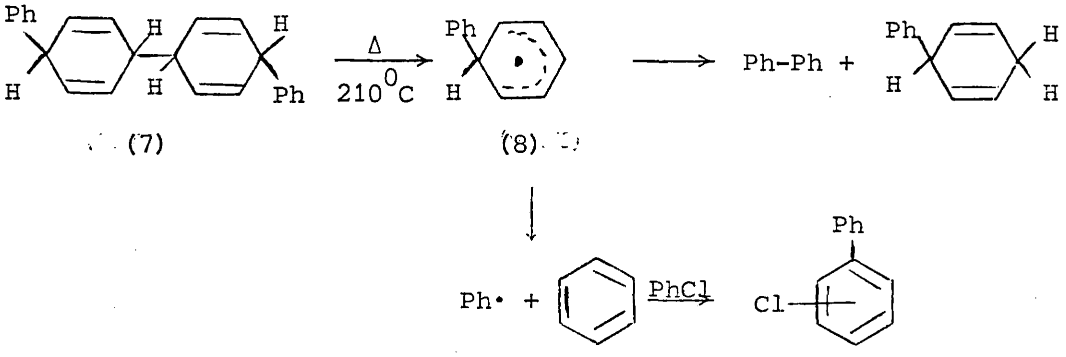

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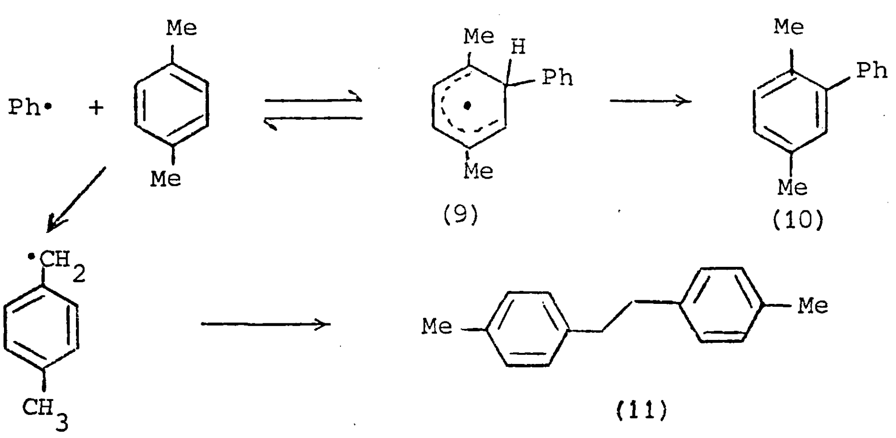
The pyrolysis of 2-chloro-1,4-dihydrotritylbiphenyl in chlorobenzene afforded 2-chlorobiphenyl and triphenylmethane as the sole detectable products. This was interpreted as the non-occurrence of the fragmentation of 2-chlorophenylcyclohexadienyl radical to give phenyl radicals. Kobayashi et al[25a] reported the observation of an isotope effect in the phenylation of chlorobenzene, nitrobenzene and m-dinitrobenzene in dimethyl sulphoxide at 20°C. The isotope effect was found to be greatest for the formation of ortho substituted biaryls. This observation was explained in terms of reversible addition of phenyl radicals to the substituted benzenes to form arylcyclohexadienyl radicals. However, it was suggested that the reversibility of phenyl radicals addition to aromatic substrates in dimethylsulphoxide could arise from the solvent effect of dimethylsulphoxide on free radical behaviour[23]. More recently Nonhebel and co-workers[26a,b,c] claimed to have obtained evidence in favour of the reversible addition of phenyl radicals to disubstituted benzenes, e.g. xylene and dichlorobenzenes at moderate temperatures. In the phenylation of p-xylene with benzoyl peroxide at different temperatures (80-120°C) or in the presence of additives, the ratio of the yield of (11) to (10) increases with increase in temperature.



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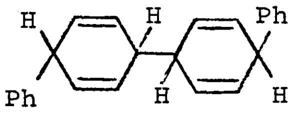
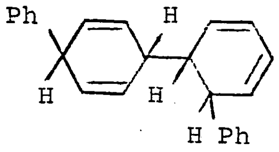
...... (27)

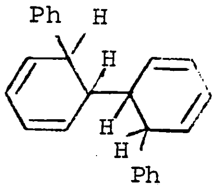
In *o*-dichlorobenzene the ratio of the yield of 2,3-dichlorobiphenyl to 3,4-dichlorobiphenyl decreases with increase in temperature, although inclusion of copper benzoate increases the ratio. It was also found that partial rate factors for phenylation of *p*-dichlorobenzene vary with temperature and additives. These observations were attributed to the reversible addition of phenyl radicals to the disubstituted benzenes. It was also reported that in the vapour phase (500°C) the addition of phenyl radical to chlorobenzene is reversible[27].

It should be noted that if the reversibility of phenyl radicals addition is substantiated, the yield of biaryl in reversible addition of phenyl radicals depends on the standing concentration of the σ-radicals at equilibrium. This kinetic stability is distinct from the thermodynamic stability where the yield of biaryl is determined by the rate of irreversible formation of the σ-radicals. As yet, there is no unequivocal evidence for reversibility of phenylation in systems involving aroyl peroxides.

In phenylation reactions with benzoyl peroxide, as much as 40-50% of the products can be involatile residue. In 1957, Pausacker and Lynch[28] and Walling[29] independently reported that the σ-radical is a resonance-stabilized arylcyclohexadienyl radical and is capable of dimerization and disproportionation to give three of the positional isomers of tetrahydroquaterphenyls.







It was suggested that the residue could consist of these compounds and their further phenylated products, and also of some terphenyl arising from further phenylation of the biaryl. Some polyaryls were later isolated by Pausacker[28], and Hey, Perkins and Williams[30] by dehydrogenation of the involatile residue from the reaction in benzene, confirming the nature of the residue in this reaction. Pausacker also demonstrated that the quaterphenyls are not derived from the further phenylation of biphenyl or terphenyl, for if this were the case, we should expect the yield of terphenyls to exceed those of the quaterphenyls. In fact the contrary is true. Pausacker[31] also observed that the decomposition of symmetrically di-substituted benzoyl peroxides e.g. p-chlorobenzoylperoxide in benzene resulted in the formation of symmtrically di-substituted p-quaterphenyls which are presumably formed by the dimerization of the p-disubstituted phenylcyclohexadienyl radical and subsequent dehydrogenation.

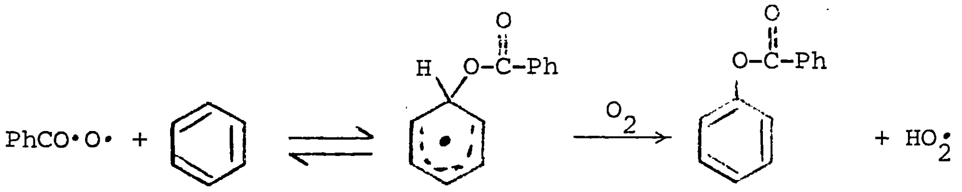
By isotope labelling (1-^{13}C in benzene)[32], it was shown that the residue contains a small amount of p-terphenyl (formed from further phenylation of biphenyl) labelled in one nucleus, and a much greater amount of p-quaterphenyl labelled in two benzene rings.

The above evidence firmly established the participation of the phenylcyclohexadienyl radical in the phenylation reaction, and the nature of residue.

(b) Benzoyloxylation

Esters always accompany biaryls in the phenylation of aromatic substrates. Combination of phenyl and benzoyloxy radicals within the solvent cage to give esters does not occur widely, particularly in thermolysis, when loss of carbon dioxide occurs readily. The direct homolytic benzoyloxylation of the aromatic nucleus by benzoyloxy-radicals must compete with their decarboxylation to give phenyl radicals which subsequently react with the aromatic system. Under conditions where the decarboxylation is slow, e.g. photolysis, the combination of phenyl and benzoyloxy radicals does occur as shown by the isolation of 10% of phenyl benzoate from the photolysis of benzoyl peroxide in chlorobenzene[33]. Under thermal conditions benzoyloxylation occurs only to reactive aromatic substrates which are most susceptible to homolytic attack, e.g. polycyclic compounds (naphthalene[34a], anthracene[34b] and anisole[35a,b]). Thus reaction of benzoyl peroxide with naphthalene gives α and β-benzoyloxynaphthalene in addition to α and β-phenylnaphthalene.

The aryloxycyclohexadienyl radicals are believed to be formed in a reversible manner. The yields of the phenolic ester are increased in the presence of oxidising agents, e.g. oxygen[33], copper salts[36a] and iodine[36b]

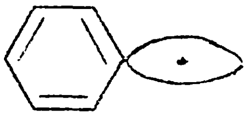


.... (28)

In the benzoyloxylation of benzene, Saltiel and Curtis[20] have provided evidence to show that the benzoate is formed at the expense of biphenyl, in contrast to the report of Simamura, Tokumaru and Nakata[33] who suggested that the benzoate is formed at the expense of benzoic acid. Recently physical evidence on the reversibility of aryloxylation has been obtained by carbon-13 CIDNP studies, which indicate that the addition of pentafluorobenzoyloxy radical to chlorobenzene is reversible[37].

(c) Nature of phenyl and benzoyloxy radicals

E.s.r. studies of phenyl radicals trapped in a solid matrix at 77°C revealed that the unpaired electron remains localized in the sp^2 orbital of the carbon atom at which bond breaking has occurred[7]. The phenyl radical is therefore represented as a sigma radical. This lack of resonance stabilization is reflected in the highly reactive nature of the phenyl radical



The near zero ρ values of the Hammett's slope[38] (0.09 for meta, 0.31 for meta and para together) indicate the almost neutral nature of phenyl radical. This is because phenyl radical is of the σ type and has a 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[39].

(III) Quantitative studies of phenylation and criticism thereof.

(a) Competitive reactions

In 1951, Hey and his co-workers embarked upon a quantitative study of homolytic arylation using the competitive method which has been used extensively by Ingold and others to study electrophilic substitution. From the relative amounts of each products formed, the ratio of the total reaction rates of the two compounds may be calculated e.g. total rate factor:

${}^{PhX}_{PhY}K$ = the ratio of the total rate of phenylation of PhX to that of PhY.

Using the relationship (29) it is possible to make an indirect determination

$${}^{PhX}_{PhY}K = {}^{PhX}_{PhZ}K \cdot {}^{PhZ}_{PhY}K \qquad \ldots\ldots \ (29)$$

of ${}^{PhZ}_{PhY}K$. Its identity with the value determined directly may provide a check of the method, and may furthermore demonstrate that solvent-solvent complexing may be disregarded[40]. Combination of this total rate factor with the isomer ratio of substituted biaryls, determined spectroscopically or gas chromatographically or by isotope dilution techniques, gives a new set of reactivity indices called partial rate factors. This is an expression of the reactivity of any specific nuclear position in PhX with reference to that of any one position in benzene. Expressions leading to the partial rate factors for mono-substituted benzene are given below:

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

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

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

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

The partial rate factors of a large number of compounds were determined chiefly by Hey, Williams and co-workers in England, De Tar[41], Dannley[40,41] and Rondestvedt[43], and their co-workers in America, Huisgen and his school in Germany[44] and Simamura in Japan[45]. Some of the results are summarized in Table 1 for phenylation with benzoyl peroxide at 80°C [6a].

Table 1

Substrates	Relative Rate	Isomer Ratio (%)			Partial Rate Factors		
	(PhH = 1)	o-	m-	p-	Fo	Fm	Fp
$PhNO_2$	2.94	62.5	9.8	27.7	5.5	0.86	4.9
PhF	1.03	55.2	29.8	15.0	1.7	0.92	0.93
PhCl	1.06	56.9	25.6	17.5	1.8	0.81	1.1
PhBr	1.29	55.7	28.8	15.5	2.2	1.1	1.2
PhI	1.32	51.7	31.6	16.7	2.0	1.3	1.3
PhMe	1.23	65.4	20.0	14.6	2.4	0.74	1.1
PhEt	0.90	51	28	21	1.4	0.76	1.1
$PhPr^i$	0.64	30	42	28	0.58	0.81	1.1
$PhBu^t$	0.64	24	49	27	0.46	0.94	1.0
Ph-Ph	2.94	48.5	23.0	28.5	2.1	1.0	2.5
PhCN	3.7	60	10	30	6.5	1.1	6.1
$PhCO_2Me$	1.77	57.0	17.5	25.5	3.0	0.93	2.7
PhOMe	2.01	69.8	14.5	15.8	4.2	0.87	1.9
Pyridine	1.04	54	32	14	1.7	1.0	0.87

(b) Validity of partial rate factors

In the formulation of partial rate factors, one tacit assumption has been made, i.e. the rate of formation of binuclear products is directly related to the rate of formation of the various σ-complexes. If the phenylation reaction proceeds in one step, the validity of this assumption could not be contested, but as shown before the reaction proceeds in two steps. Thus if the σ-radicals are not all oxidised to biaryl and are selectively diverted from direct oxidation e.g. by dimerization or disproportionation of σ-complexes to other non-biaryl products, this will render the derived partial rate factors invalid. On these grounds, Pausacker and Lynch[28], Walling[29] and Cade and Pilbeam[46] criticised the validity of such partial rate factors as a true measure of the reactivity of the various positions in the aromatic nucleus. The observations: (1) of a non-statistical hydrogen isotope distribution in the binuclear products (though not in the unconsumed substrate) in the phenylation of deuterated benzene indicates that the oxidation of the σ - complex to biphenyl must compete with other side-reactions leading to non-biaryl formation, and (2) that side reaction was greatly suppressed and the yields of biaryls greatly enhanced by conducting the decomposition of benzoyl peroxide in benzene in a stream of oxygen, raise further uncertainty about the basic assumptions concerned with the partial rate factors[47].

However, the work of Morrison, Cazes, Samkoff and Howe[48] provided evidence that the diversionary reaction of the σ - complexes are non-selective, and Cazes[49] also showed that neither variation in peroxide concentration, nor the inclusion of benzene as a co-reactant influenced the relative rates and isomer distributions of the mono-substituted benzenes. In the presence of oxygen the yields of biaryls are trebled, but the rate factors and the isomer ratios are unaffected. Consequently it can be concluded at least tentatively, that the rate factors determined based on products analysis in the absence of oxygen do provide reliable information about the reactivity of the various positions towards phenyl radicals. This conclusion is reinforced by subsequent investigations in which various additives have been used to increase the yields of biaryls (Table 2).

Recently, the question of the validity of partial rate factors has been raised again by Norman[50] and by Bonnier[51]. Norman noted that the isomer ratio and total rate factors in the decomposition of benzoyl peroxide in anisole are not the same in the presence and the absence of cupric benzoate.

Bonnier *et al* [51a] also showed that the conclusion drawn by Morrison and co-workers might not be valid in all cases. They found that the isomer ratio of phenylated 4-methylpyridine depends on the concentration of the peroxide. Such variation in isomer ratio is not observed when catalysts, e.g. oxygen and nitrobenzene are included in the reaction. An isotope effect was also reported in the phenylation of the deuterated 4-methylpyridine[51b]. The above observations were attributed to the fact that the side reaction of the various σ – complexes leading to the formation of the biaryls could be selective. They also reported that[52] the isomer ratio and partial rate factors in the phenylation of pyridinium chloride changed drastically in the presence of catalytic amounts of nitrobenzene. Don *et al* [53] also reported the variation of isomer ratio

Table 2[48]

Reaction of Aromatic Substrates with Benzoyl Peroxide at 80°C

Substrate	Oxygen	Yield of biaryl (mole/mole of peroxide)	Isomer Ratio (%) ortho-	meta-	para-	Total Rate Factor (C_6H_6 = 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
$PhBu^t$	-	0.72	21.1	49.9	29.0	0.63
$PhBu^t$	+	1.40	21.1	50.0	28.8	0.61
$PhNO_2$	-	0.19	63.2	9.7	27.1	2.95
$PhNO_2$	+	0.68	62.8	9.7	25.7	2.85

with oxidising agent in the phenylation of 4-methylpyridine.

Competitive reactions have often been determined with nitrobenzene as the standard solvent. Recently, Ohta and Tokumaru[54] have pointed out that nitrobenzene is not a suitable standard solvent for competitive studies with substrates having abstractable hydrogen, because the intermediate nitrophenylcyclohexadienyl radical is diverted to products other than nitrobiphenyls. This observation necessitates the re-determination of rate factors for alkylbenzenes with other suitable standards, e.g. p-di-chlorobenzene as used recently by Hey, Davies and Summers[55].

(IV) The effect of oxidising agents on arylation by aroyl peroxides.

(a) Oxygen

The effect of oxygen in increasing the yield of biaryl was first reported by Eberhadt and Eliel[47]. The results were substantiated by subsequent work[48]. It is known that phenyl radicals are not very reactive towards oxygen[56]. Therefore oxygen is thought to abstract hydrogen from the σ-intermediate, presumably by the formation of a hydroperoxide radical, which could bring about the oxidation of another σ-radical.

$$[PhC_6H_6]\cdot + O_2 \longrightarrow PhC_6H_5 + HO_2\cdot \qquad \ldots\ldots \quad (30)$$

$$[PhC_6H_6]\cdot + HO_2\cdot \longrightarrow H_2O_2 + Ph\cdot C_6H_5 \qquad \ldots\ldots \quad (31)$$

Hydrogen peroxide has been detected in these reactions[57]. Theoretically two moles of biphenyl per mole of peroxide could be formed in the presence of oxygen. The benzoic acid formed in this reaction is unaffected by oxygen, in fact the yield of benzoic acid is lower in the presence of oxygen than in its absence and much less than in the presence of other additives. Some phenol is also formed in this reaction, with higher yields at lower temperature[57].

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

$$\text{Ph}\cdot + \text{O}_2 \longrightarrow \text{Ph-O-O}\cdot \longrightarrow \text{PhOH}$$

It was also reported[58] that oxygen shows no effect upon the isomer ratio and the yields of biaryl in the attack by o-tolyl radical on pyridine and in fact a slight reduction in the yield of biaryl was observed in phenylation.

(b) Nitro-compounds and other electron acceptors.

Augood and Williams[5] were the first to point out that the presence of a nitro-compound would increase the yield of biaryls, though the mechanism was not clear at that time. It was Hey, Perkins and Williams[59] who showed that the inclusion of a small quantity of nitrobenzene in the phenylation of benzene with benzoyl peroxide, was sufficient to enhance the yield of biphenyl and benzoic acid to above 0.8 mole per mole of peroxide, while the formation of residue was greatly suppressed, with no change in the yield of phenylbenzoate. Also, the nitro-compounds could be recovered almost quantitatively after the reaction. This phenomenon has been referred to as the 'nitro-group' effect.

Hall[60] investigated a number of electron-acceptors and showed that all (with the exception of nitromethane) manifest the same effect. However, there appears to be no simple relationship between the effectiveness of the additive and its reduction potential.

It is now known that the nitroso-compound, from the reduction of the nitro-compounds, is in fact the effective catalyst[61]. The conclusion was based on (a) the greater efficiency of nitrobenzene and phenylhydroxylamine (which is converted into nitrobenzene) than that of nitrobenzene, (b) the amount of nitro-compound unrecovered, which is sufficient to produce the oberved effect, (c) a signal characteristic of diphenylnitroxide (a_N = 10.5 gauss), detected by e.s.r. spectroscopy in such decomposition of benzoyl peroxide in benzene catalysed by nitrobenzene. The following scheme was proposed to account the catalytic effect of the nitroso compounds.

$$\mathrm{PhNO_2} \xrightarrow{-[O]} \mathrm{PhNO} \qquad \ldots\ldots \ (32)$$

$$\mathrm{Ph}\cdot + \mathrm{PhNO} \longrightarrow \mathrm{Ph_2NO}\cdot \qquad \ldots\ldots \ (33)$$

$$\mathrm{Ph_2NO}\cdot + [\mathrm{PhC_6H_6}]\cdot \longrightarrow \mathrm{Ph{-}Ph} + \mathrm{Ph_2NOH} \qquad \ldots\ldots \ (34)$$

$$\mathrm{Ph_2NOH} + (\mathrm{PhCO{\cdot}O})_2 \longrightarrow \mathrm{Ph_2NO}\cdot + \mathrm{PhCO_2H} + \mathrm{PhCO{\cdot}O}\cdot \qquad \ldots\ldots \ (35)$$

$$\mathrm{Ph_2NOH} + \mathrm{PhCO{\cdot}O}\cdot \longrightarrow \mathrm{PhCO_2H} + \mathrm{Ph_2NO}\cdot \qquad \ldots\ldots \ (36)$$

(c) The effect of transition metal ions

Perusal of the literature gives abundant examples of the effect of metal ions on free radical reactions, notably the Sandmeyer, Gatterman, Pschorr and Meerwein reactions and the reactions of Fenton's reagent.

In 1959, Kharasch[62a,b] observed that catalytic amounts of copper salts could drastically alter the course of many homolytic reactions. It was also found that the course of the reaction is sensitive to the nature of the salts. In the reaction of benzoyl peroxide with olefins, he showed that, in the presence of cuprous salts, the tarry residue is greatly decreased. The yield 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[62a] 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.

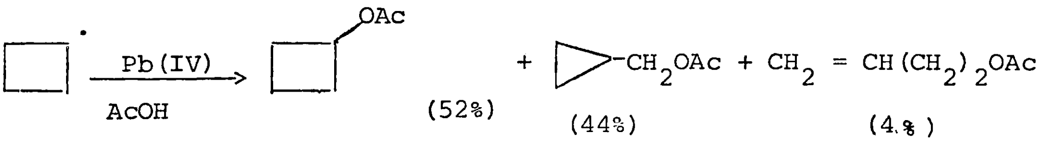
$R\cdot + R'H + Cu^{+} \longrightarrow [CuRR'H]^{+\cdot}$ .... (37)

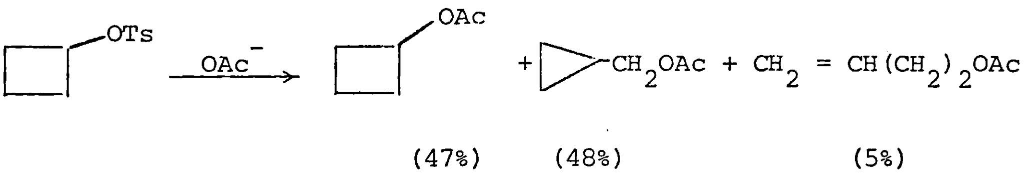
Recently, Kochi[63] has classified the oxidation effected by metal salt into ligand-transfer (a) and electron transfer (b) by analogy with the inner sphere and outer sphere mechanism developed by Taube[69] to describe redox reaction in inorganic systems.

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

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

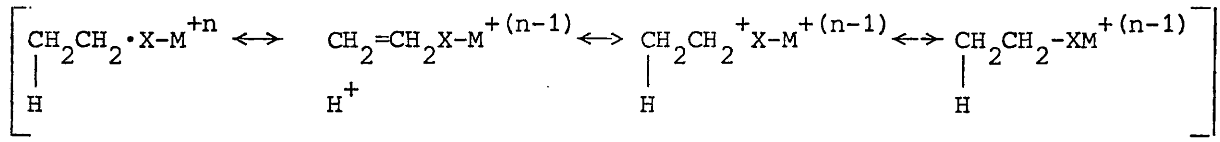
Ligand transfer mechanisms involve transfer of a group or an atom (eg. chlorine in (a)) from the metal complex to the radical through a bridge transition state, to form halide, the metal ion being reduced to its lower valent state. Halides and pseudohalides are good transfer agents, sulphate and perchlorate are not good bridging ligands, while carboxylate, alkoxide and hydroxide are of intermediate activity[65]. The metal ions Fe(III), Cr(VI), Pt(IV) and Pb(IV) have been used in the preliminary studies[63]. 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 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 that obtained in solvolysis proceeding via the carbonium ion[66].





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 groups attached to the tervalent carbon to stabilise the developing positive charge. In accordance with this, *p*-methoxybenzyl radicals are much more readily oxidized by Pb(IV) than benzyl radicals[67], 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[63] pointed out that such classification of oxidation mechanisms was arbitrary and argued that the two mechanisms may have a related transition state, the importance of the resonance contribution depending on the structure of the radicals, the metal ion, and the ligands. He proposed the following generalised transition state for these oxidation reactions.



$$\left[\underset{\mathrm{H}}{\mathrm{CH_2}}\mathrm{CH_2}\cdot\mathrm{X{-}M}^{+n} \longleftrightarrow \underset{\mathrm{H^+}}{\mathrm{CH_2}}\mathrm{{=}CH_2X{-}M}^{+(n-1)} \longleftrightarrow \underset{\mathrm{H}}{\mathrm{CH_2}}\mathrm{CH_2}^{+}\mathrm{X{-}M}^{+(n-1)} \longleftrightarrow \underset{\mathrm{H}}{\mathrm{CH_2}}\mathrm{CH_2{-}XM}^{+(n-1)}\right]$$

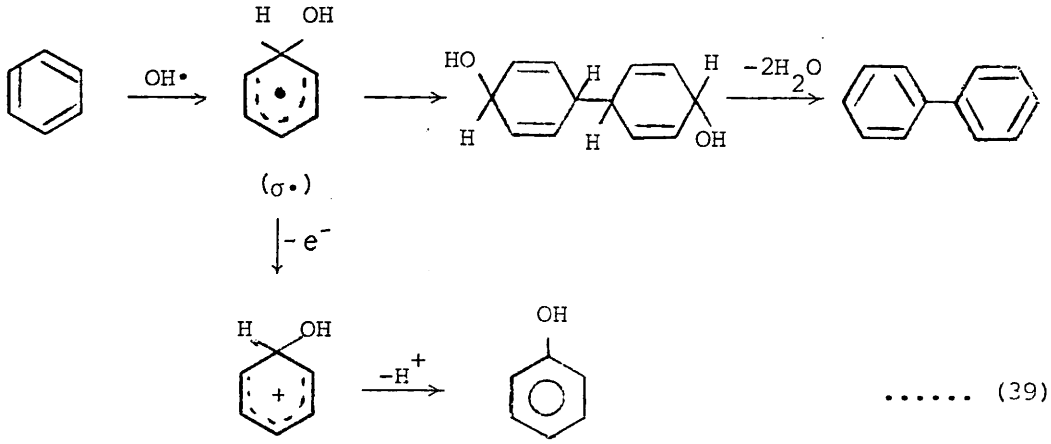
...... (38)

After this brief consideration of the mechanisms of such oxidation, the reaction mentioned at the beginning of this section will be re-examined in terms of the redox properties of the transition metal.

The Fenton reagent, which is a solution of hydrogen peroxide and ferrous sulphate, is generally used to generate hydroxyl radicals.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO\cdot + OH^-$$

Using this reagent, the hydroxylation of some aromatic compounds has been achieved[68a,b]. However, benzene and toluene give biphenyl and bibenzyl respectively in addition to the respective phenols. In a re-investigation of this reaction, the following mechanism was proposed, with benzene as the example[69].



...... (39)

The σ-complex in this reaction has been detected by the e.s.r. technique by Dixon and Norman[70].

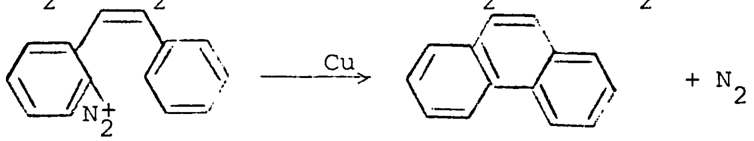
In the Sandmeyer, Gatterman, Meerwein and Pschorr reactions the copper or copper salts are functioning as redox catalysts. In these reactions the diazonium salts are reduced by electron transfer, with the resultant generation of aryl radicals.

Sandmeyer reaction: $\text{Ar-N}_2\text{Cl} \xrightarrow{\text{CuCl}} \text{ArCl} + \text{N}_2$

Gattermann reaction: $\text{ArN}_2\text{Cl} \xrightarrow{\text{Cu}} \text{ArCl} + \text{N}_2$

Meerwein reaction: $\text{ArN}_2\text{Cl} + \text{CH}_2 = \text{CHX} \longrightarrow \text{ArCH}_2\text{CHClX} + \text{N}_2$

Pschorr reaction:



The key step in these reactions is the electron transfer reduction of the diazonium salt to generate the aryl radicals, e.g.

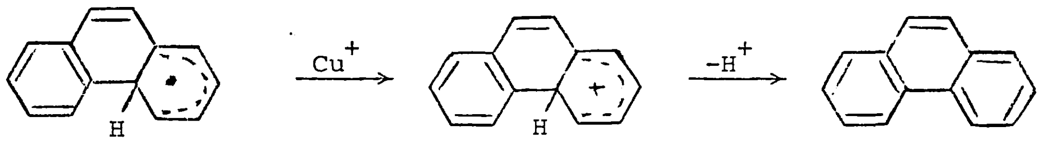
$$\text{ArN}_2^{+} + \text{CuCl}_2^{-} \longrightarrow \text{Ar}\cdot + \text{N}_2 + \text{CuCl}_2 \qquad \text{......} \ (40)$$

$$\text{ArN}_2{+} + \text{Cu} \longrightarrow \text{Ar}\cdot + \text{N}_2 + \text{Cu}^{+} \qquad \text{......} \ (41)$$

In the Sandmeyer and Meerwein reactions, the final stage of the reaction involves a chlorine atom transfer from the cupric chloride to the aryl radical to form the arylhalide and regenerate the cuprous species[71].

$$\text{Ar}\cdot + \text{CuCl}_2 \longrightarrow \text{ArCl} + \text{CuCl} \qquad \text{......} \ (42)$$

In the Pschorr reaction the intermediate radical may be oxidised to a carbonium ion followed by loss of a proton[72].



....(43)

In the decomposition of benzoyl peroxide in the presence of copper salts, Kharasch[73] found that, in the absence of hydrogen donating substrates, the catalytic effect of copper salts upon the reaction is inoperative. This is because there are no carbon radicals formed (with the exception of the fragmentation products of the oxy-radical) and hence no way of regenerating the cuprous species.

Dailly and Williams[8,74] have found that the yields of biaryl and benzoic acid are increased greatly by the addition of Fe(III) benzoate in the decomposition of benzoyl peroxide in benzene, chlorobenzene, fluorobenzene and toluene. It was suggested that Fe(III) ions catalysed the oxidation of σ-complex by benzoyloxy radicals, hence preventing their dimerization. The following mechanism was proposed to explain the observed catalytic effect of Fe(III) ion.

$$\mathrm{PhArH\cdot + Fe(III) \longrightarrow Ph\text{-}Ar + H^{+} + Fe^{2+}} \quad \ldots\ldots (44)$$

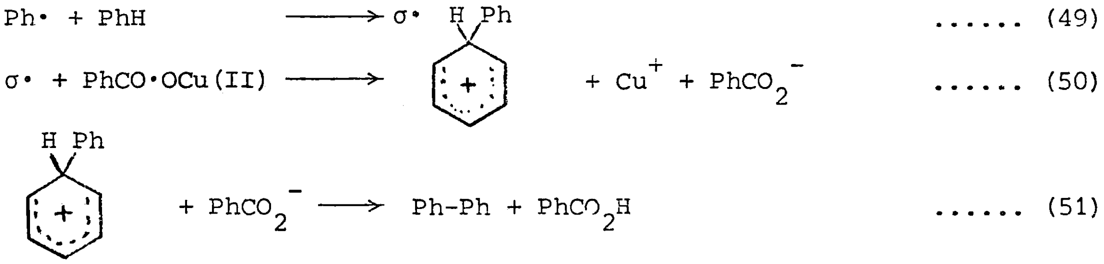
$$\mathrm{PhCO\cdot O\cdot + Fe^{2+} \longrightarrow PhCO\cdot O^{-} + Fe^{3+}} \quad \ldots\ldots (45)$$

$$\mathrm{PhCO\cdot O^{-} + H^{+} \longrightarrow PhCO_2H} \quad \ldots\ldots (46)$$

The main feature of this catalytic reaction is the equimolar production of biaryl and benzoic acid in agreements with the above schemes. Similar catalytic effects were observed by Hey, Perkins and Liang[75], who used cupric benzoate, cobalt naphthenate and copper bronze. The following reaction sequence, by analogy with the Kochi scheme was proposed.

$$\mathrm{(PhCO\cdot O)_2 + Cu^{+} \longrightarrow PhCO\cdot OCu^{+} + PhCO\cdot O\cdot} \quad \ldots\ldots (47)$$

$$\mathrm{PhCO\cdot O\cdot \longrightarrow Ph\cdot + CO_2} \quad \ldots\ldots (48)$$



The steps (50) and (51) could be a concerted process as indicated by the work of Kochi[63,76] on electron transfer oxidation of radicals. The Cu(I) thus generated would catalyse the induced decomposition of benzoyl peroxide.

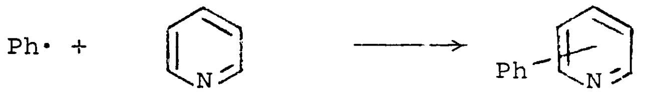
Krienes[77] found that there seems to be no apparent relationship between the ability of metal salts to trap radicals and the metal's reduction potential on the reaction of 2-cyano-2-propyl radical in benzene solution in the presence of transition metal chlorides.

(V) Other sources of phenyl radicals

(a) Other sources of benzoyloxy radicals

(i) Electrolysis of benzoic acid (Kolbe reaction). This method is of little synthetic use[78].

$$PhCO_2^- \xrightarrow{-e^-} PhCO{\cdot}O{\cdot} \longrightarrow Ph{\cdot} + CO_2 \qquad \ldots\ldots (52)$$



(ii) Decomposition of lead tetrabenzoate[79a] and silver halide dibenzoates.

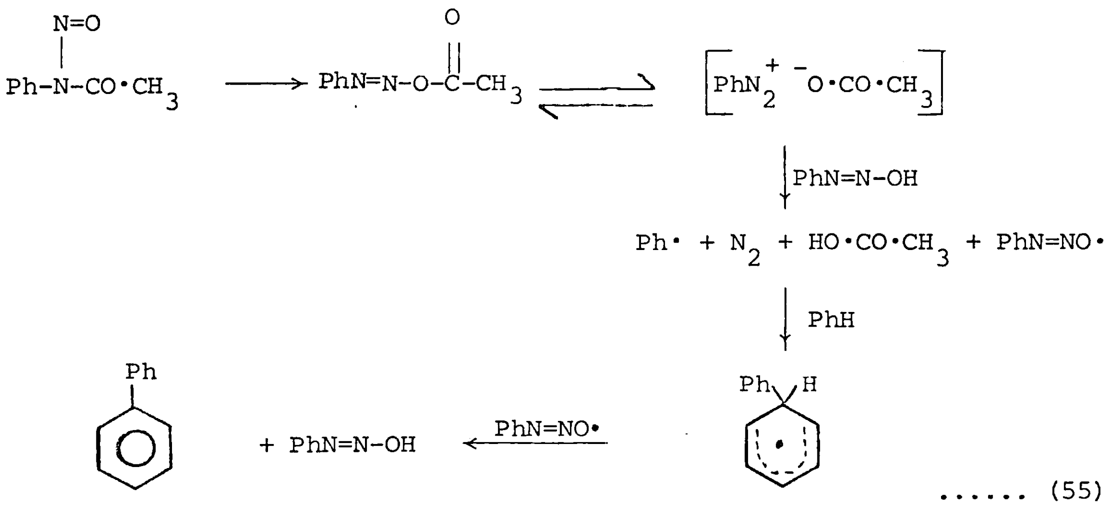
$$Pb(O{\cdot}CO{\cdot}Ph)_4 \xrightarrow{125^\circ C} Pb(O{\cdot}CO{\cdot}Ph)_2 + 2Ph{\cdot}CO{\cdot}O{\cdot} \qquad \ldots\ldots (53)$$

$$AgX(O{\cdot}CO{\cdot}Ph)_2 \longrightarrow 2PhCO{\cdot}O{\cdot} + AgX \qquad \ldots\ldots (54)$$

(b) From diazo, azo and related compounds

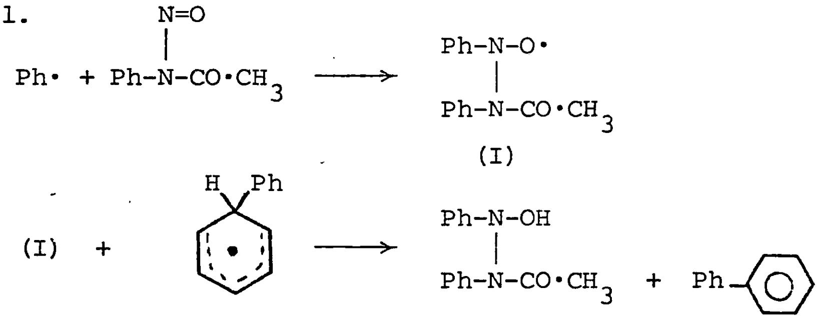
(c) N-Nitrosoacetanilide

The mechanism of the decomposition of this compound has been the subject of much controversy[80a,b] because the proposed mechanism fails to take account of the absence of any evidence for the existence of acetoxy radical and the absence of hydroaromatic products derived from dimerization and disproportionation of cyclohexadienyl intermediates. The mechanism generally accepted was that proposed by Ruchardt[81].



...... (55)

The detection of N-(phenylacetamido)phenyl nitroxide radical (I) by e.s.r. led Perkins and Chalfont[82] to suggest a new mechanism similar to the above scheme, but differing in that the N-(phenylacetamido)phenyl nitroxide radical, formed by addition of phenyl radical to N-nitrosoacetanilide (eqn. 56) was the key chain carrying radical rather than (phenylazo)oxy radical.

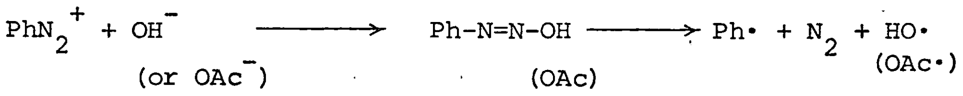


...... (56)

However, the observation of (phenylazo)oxy radical by e.s.r. together with other evidence, led Cadogan, Paton and Thomson[83] to suggest that the (phenylazo)oxy radical is the more significant chain carrying radical in the decomposition of acylarylnitrosolamine in such solvent.

(d) <u>Aryl diazonium ionic derivatives</u>

(i) The heterogeneous Gomberg and Gomberg-Hey reaction had been used to provide phenyl radicals.



$$\underset{}{PhN_2^+} + \underset{(or\ OAc^-)}{OH^-} \longrightarrow \underset{(OAc)}{Ph{-}N{=}N{-}OH} \longrightarrow Ph\cdot + N_2 + \underset{(OAc\cdot)}{HO\cdot}$$

......(57)

These reactions have been modified to provide a cleaner homogeneous system involving reaction of an aromatic amine in situ in an organic solvent with amyl nitrite at 60-80°C[82].

(ii) Electrolytic reduction of diazonium salts has recently been developed as a source of phenyl radicals[85].

$$ArN_2^+ + e^- \longrightarrow Ar\cdot + N_2$$

Thermolysis of phenylazotriphenylmethane at 80°C is also a convenient source of phenyl and triphenylmethyl radicals, the driving force for the reaction being the stability of triphenylmethyl radical and the formation of molecular nitrogen[86].

(iii) Photolysis of haloarenes and of organometallic compounds.

Bryce-Smith[87a] and Kharasch[87b] have shown that photolysis of aryl iodides and also aryl bromides in aromatic solvents generates aryl radicals.

$$ArI \xrightarrow{h\nu} Ar\cdot + I\cdot$$

Photolysis of diphenylmercury, tetraphenyllead and triphenylbismuth and phenylmercuric iodide have all been employed as sources of phenyl radicals[87a].

(iv) Miscellaneous methods.

Phenyl iodobenzoate, on heating to 125°C, breaks down to give phenyl radicals, which comes from the phenyl group of the iodosobenzene moiety rather than from the benzoate group as was believed at one time[88].

Phenyl radicals are also generated in reaction between arylhalides and Grignard reagent in the presence of catalytic amount of cobalt(II) salt[89].

The pyrolysis of nitrobenzene at 600°C was also shown to afford phenyl radical in vapour phase. A review on the subject has appeared very recently[90].

(B) Homolytic Silylation Reactions

(I) Some General Considerations and Comparisons of the Properties of Carbon and Silicon Free Radicals

The evidence for the production of silyl radicals in the primary process in the thermal decomposition of silane, alkylsilanes and alkyldisilanes in the gas phase was inconclusive[91-94]. However, in solution, the rapid accumulation of results interpretable by the participation of silyl radicals have fully established the intermediacy of silyl radicals in such chemical reactions. The subject of silicon free-radical chemistry has been reviewed by Friswell and Gowenlock[95] and more recently by Jackson[96a,b,c,d] and Sakurai[97].

It is relevant to consider the bond dissociation energy of the Me_3Si-Y bond. A comparison of these values with the corresponding carbon-Y bonds provides some insight into the differences in chemical behaviour of these two classes of free radicals. Although many studies on the bond dissociation energy of the Me_3Si-Y bond have been carried out, and many values of the bond dissociation energy of Me_3Si-Y have been published, there is poor agreement over the range. This is due to experimental difficulties in carrying out these determinations. The bond dissociation energy $D(Me_3Si-Y)$ could be determined in two ways, i.e. (1) kinetic method[99] and (2) electron impact method[100]. In the kinetic method unreliable bond energies will result if the mechanism of the decomposition has been misinterpreted. This has occurred frequently in silicon chemistry owing to the complex nature of the reactions. In electron impact method, the appearance potential of the silyl cation Me_3Si^+ is determined, combining these data from tetramethylsilane (Me_4Si) and hexamethyldisilane ($Me_3Si-SiMe_3$), and their heats of formation, the bond dissociation energy of (Me_3Si-Y) could be calculated. However, the unreliability of the values of the heats of formation of the silicon compounds[101a,b] casts uncertainty on the values calculated. Recently, a table of bond dissociation energy for group IVB elements was compiled by Jackson[96]. Though these values should be treated with reserve some general trend can be seen. The values for silicon and carbon have been reproduced in Table 3.

Table 3

Bond dissociation energy D(Me_3M-Y) kcal $mole^{-1}$

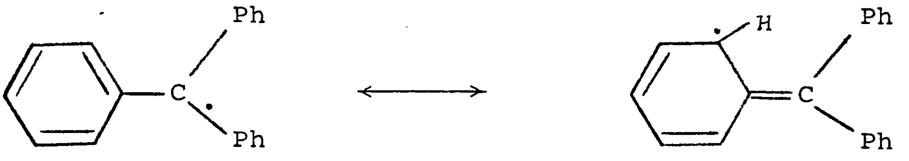
	Y = H	Me	MMe_3	OH	F	Cl	Br	I
M = C	104	88	80	91	118	82	69	56
M = Si	81	76	67	119	(143)	104	87	78

These differences in bond energy account for several differences in carbon and the silicon radical chemistry. Carbon will form stronger bonds to hydrogen or alkyl groups than silicon and also the silicon-silicon bond is weaker than the carbon-carbon bond. Moreover, silicon forms a stronger bond to halogen, oxygen and nitrogen atoms than does carbon. The basic differences in the bond energies are reflected in the differences in chemical behaviour exhibited by carbon and silicon radicals in chemical reactions. As a result of these differences, silyl radicals prefer to abstract halogen[102] (an exothermic process) rather than to abstract hydrogen (energetically unfavourable); the reverse is true for carbon radicals which tend to abstract hydrogen and are less reactive towards halogen abstraction.

Recently a kinetic reinvestigation of the pyrolysis of hexamethyldisilane[103] (Me_3Si-$SiMe_3$) has given a new bond dissociation energy of 80.5 kcal $mole^{-1}$ for the Si-Si bond. The appearance potential of tetramethylsilane and hexamethyldisilane were determined[104]. Combining these with data from the heat of formation[105] the values of 88 and 80 kcal mole^{-1} for D(Me$_3$Si-CH$_3$) and D(Me$_3$Si-SiMe$_3$) respectively were obtained. The latter value was in good agreement with the value from the kinetic measurement referred to above[103].

Silyl radicals, like organic radicals undergo dimerization, addition to alkynes and alkenes[106a-c], rearrangement[107] and cyclisation[112]. But unlike organic radicals, silyl radicals add to the oxygen atom of the carbonyl group[108] and they do not disproportionate. The reason for the inability of silyl radicals to disproportionate is that silyl radicals can not form Pπ-Pπ bonds.

Although the stability of triphenylmethyl radicals is well established, hexaphenyldisilane is a stable solid (m.p. 352°) and does not appear to dissociate even on prolonged heating in xylene[109]. This observation seems to contradict the idea that the silicon-silicon bond is weaker than the carbon-carbon bond. The thermal stability of hexaphenyldisilane could be explained by the following two reasons. (1) The triphenylmethyl radical is resonance stabilised, the free electron being delocalised over ten carbons.



(12)

Silicon does not form a double bond to carbon and hence the contribution from structures analogous to (12) is much less important.

Thus the dissociation towards the formation of triphenylsilyl radicals is unfavourable. (2) The second reason is of steric origin. The longer silicon-silicon and silicon-carbon bonds (owing to the larger size of silicon) make it possible for six phenyl groups to surround two silicon atoms with virtually no steric hindrance, and a recent report of the quinonoid structure of the dimer of triphenylmethyl radicals provides further support of the importance of bond length in the structure of the bulky dimer[110].

The relative electron density (atomic number/atomic radius) for silicon is the minimum, so that the electropositivity of silicon is at a maximum within group IVB. The greater electropositivity of silicon than carbon is reflected in the greater polar effect in the transition state of a particular reaction. The organosilyl radical ($R_3Si\cdot$) should be able to supply more electrons in the transition state of chemical reactions, and more easily than the corresponding carbon radicals.

Table 4

Element	Covalent Radius	Electronegativity Pauling Scale	Stable double bond	Maximum number of electron pair bonds formed
C	0.77	2.55	Yes	4
Si	1.18	1.90	No	6

(II) Methods of Production of Organosilyl Radicals

(a) Pyrolysis

There are some reports on the pyrolysis of silane and alkylsilanes at high temperature, where it seemed that silyl radicals were produced[91-4]. However, an interpretation involving formation in the primary process should be made with care, as it has been argued, mainly on thermodynamic grounds, that a silene intermediate (13) is in fact more possibly involved in the primary process.

$R_2Si:$

(13)

The heating of bis(trimethylsilyl)mercury[111-4] and bis(triphenylsilyl)mercury[115] in solution gave products interpretable by the intermediacy of silyl radicals. These mercury compounds may decompose in a stepwise manner (58) or in a simultaneous process (59).

$$R_3Si{-}Hg{-}SiR_3 \xrightarrow{\Delta} R_3Si\cdot + HgSiR_3 \longrightarrow Hg + \cdot SiR_3 \qquad \ldots\ldots (58)$$

$$R_3SiHgSiR_3 \longrightarrow 2R_3Si\cdot + Hg \qquad \ldots\ldots (59)$$

R = Me, Ph.

As a result, it appears that these mercury compounds are promising sources of silyl radicals. However, it was realised later that[116a,b,c] the major pathway by which these mercurials react with most organic compounds is a molecular reaction, rather than by a free radical mechanism, under thermal conditions. The stereospecific cis-elimination of two bromine atoms leading to the formation of alkenes in reactions of bis(triphenylsilyl)-mercury and 1,2-dibromo-compounds provide evidence for such a molecular reaction, and suggest that a one stage molecular mechanism is operating in this reaction[117]. As a result, application of free radical mechanisms to the thermal reaction of these mercury compounds should be exercised with care.

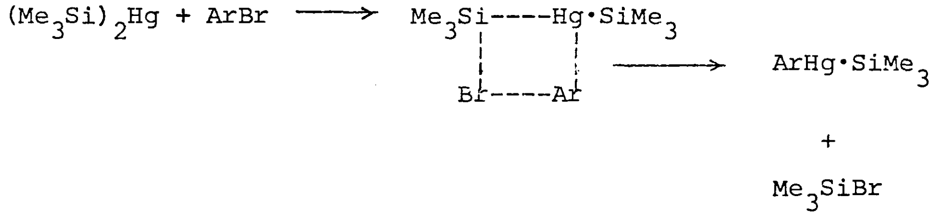
(b) Photolysis

Silane and alkylsilanes do not have a convenient absorption band in the ultra-violet region and so direct photochemical production of silyl radicals is not possible. The production of silyl radicals may be achieved by mercury photosensitization[107,118]. However, this method is of relatively little use as a source of silyl radicals in spite of the attractiveness of this method in terms of lack of contamination from radical initiators.

The presence of a chromophore like the phenyl group in the molecules makes the silicon compounds susceptible to photolysis[119]. The photolysis of trichlorosilane has also been shown to produce trichlorosilyl radicals[120].

It has been demonstrated that the photolysis of organisilyl mercury compounds is a useful method of production of silyl radical[121a,b,c,d]. However, even in photolysis, reactive molecules like anisole and bromobenzene gave products similar to those produced in the pyrolytic (molecular) reaction.

e.g.



$$(Me_3Si)_2Hg + ArBr \longrightarrow \begin{array}{ccc} Me_3Si & \text{----} & Hg\cdot SiMe_3 \\ | & & | \\ Br & \text{----} & Ar \end{array} \longrightarrow ArHg\cdot SiMe_3 + Me_3SiBr$$

$$ArHg\cdot SiMe_3 + ArBr \longrightarrow Ar_2Hg + Me_3SiBr$$

(c) Production of silyl radicals by metathesis

Organosilyl radicals may be made indirectly by treating an organosilicon hydride with free radicals, usually from an organic initiator, e.g. di-t-butylperoxide or benzoyl peroxide[102].

$$R_3SiH + R\cdot' \longrightarrow R_3Si\cdot + R'\text{-}H$$

This method is widely used to produce silyl radicals. However, complications might arise from reactions between the silyl radicals produced and the initiator, or the radical from the initiator might react with the solvent. But for chain reactions where only a small amount of initiator is required, this is one of the most important methods of generating silyl radicals[106b,c].

(d) Other methods of production of silyl radicals

γ-Radiolysis has also been employed to break the Si-X bond[123a,b], but this method is relatively little used because of the high energy of the radiation. Indiscriminate breakage of the various bonds in the molecule usually results, giving rise to a wide variety of products even from simple starting materials. The radiation chemistry of silicon compounds has been reviewed by Shaw[124].

Electrochemical reduction of organosilicon halides (R_3Si-hal) can also be used as a source of organosilyl radicals ($R_3Si\cdot$)[125] for example in a controlled-potential electrolysis of triphenylsilylchloride, triphenylsilane was obtained. Intermediate triphenylsilyl radicals were postulated indicating that silyl radicals were able to abstract hydrogen from the solvent.

(III) Some Reactions of Silyl Radicals

(a) The hydrogen abstraction reactions

Silyl radicals are known to abstract hydrogen atoms though these reactions do not proceed readily. For example, some trimethylsilane is produced in the photolysis of solutions of bis(trimethylsilyl)mercury in hydrocarbon solvents[126], presumably by hydrogen abstraction from the solvent. With toluene, where a reactive α hydrogen is present, only a little hydrogen-abstraction took place even at high temperature, though small amounts of benzyltrimethylsilane and bibenzyl are formed[126].

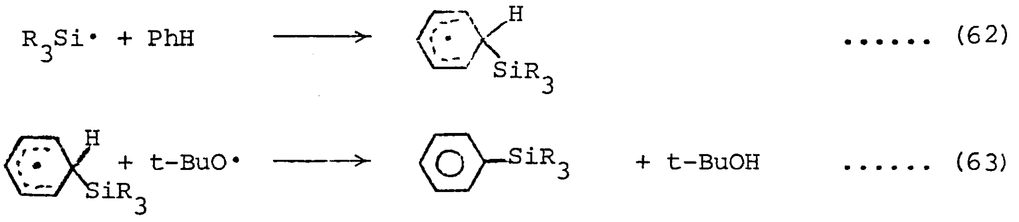
Hydrogen abstraction by organosilyl radicals has also been reported by Kumada's group[127], Davidson, Band, Lambert and Stephenson[99], and Dessy, Kitching and Chivers[125].

(b) Homolytic aromatic silylation reactions

Reports of homolytic aromatic substitution reaction by silyl radicals are rather limited. In 1967, Eaborn, Jackson and co-workers were the first to recognise the occurrence of aromatic silylation via trimethylsilyl radicals generated by photolysis of bis(trimethylsilyl)-mercury in benzene to give phenyltrimethylsilane in low yield[131a,b]. Subsequently Sakurai, Hosomi and Kumada[128] also reported the formation of silyl substituted benzene in the thermolysis reaction of di-t-butylperoxide in solutions of hydrosilanes in benzene. In their studies a number of hydrosilanes had been tested. The following reaction sequence was proposed.

$$(\text{t-BuO})_2 \longrightarrow 2\ \text{t-BuO}\cdot \qquad \ldots\ldots (60)$$

$$\text{t-BuO}\cdot + R_3\text{SiH} \longrightarrow \text{t-BuOH} + R_3\text{Si}\cdot \qquad \ldots\ldots (61)$$



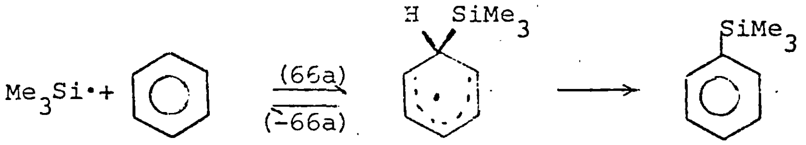
...... (62)

...... (63)

$$2\ R_3\text{Si}\cdot \longrightarrow R_3\text{Si-Si}R_3 \qquad \ldots\ldots (64)$$

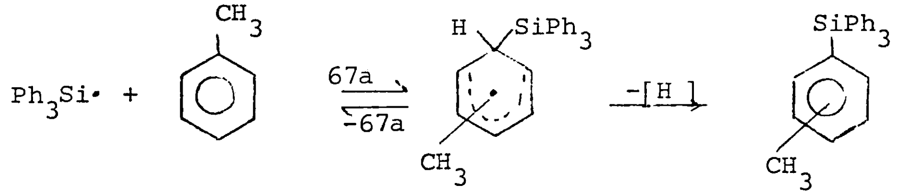
Subsequently they extended their investigation to substituted benzenes to study the orientation effect of the substituents and the relative reactivities of silyl radicals, by competitive reactions[129]. Some interesting results were obtained. Firstly, it was found that the pentamethyldisilanyl and n-propyldimethylsilyl radicals used in their studies appeared to be nucleophilic in character giving a Hammett reaction constant (ρ) of 1.4 and 1.6 respectively. Secondly, in the competitive silylation of hexadeuteriobenzene and benzene by n-propyldimethylsilyl and pentamethyldisilanyl radicals, kinetic isotope effects with k_H/k_D values of 1.50 and 1.45 respectively were observed. They suggested that this isotope effect could have come from the irreversible addition to form the cyclohexadienyl radicals and included a secondary isotope effect arising from the inductive effect of deuterium atoms in the change of hybridization at a reaction centre of the deuteriobenzene system. However, Eaborn, Jackson and their co-workers[115b,121b] favoured the idea of reversible addition based on the observation that the yield of trimethylsilylbenzene falls with increasing temperature. This may indicate that reaction (-66a) becomes relatively more favourable at high temperature. When toluene was employed as the substrate the yields of substitution products were also observed to decrease, and that of bibenzyl to increase with increase in temperature.

$$(Me_3Si)_2Hg \longrightarrow 2\,Me_3Si\cdot + Hg \qquad ...... (65)$$



...... (66)

More recently similar observation was also noted by Eaborn, Jackson and Rahman in the reaction of triphenylsilyl radicals with toluene[115b]. They argued in favour of the reversible addition of the silyl radicals by considering the entropy change of the addition. The aromatic substitution reaction (67a) though exothermic and presumably having a moderate activation energy, proceeds with loss of entropy. At high temperature, this will make the reverse reaction more favourable,



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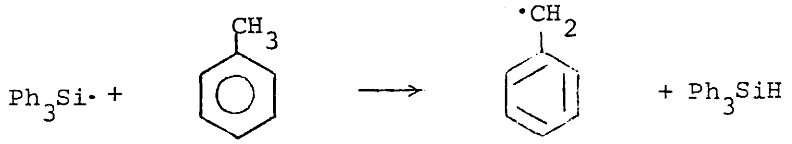


...... (68)

and in fact no aromatic substitution was observed at 220°C. Attack of triphenylsilyl radicals at the methyl group in toluene is possibly slightly endothermic, but there is no loss of entropy in this reaction which will therefore be more favoured at higher temperature. The triphenylsilyl radicals were produced by photolysing or heating a solution of bis(tri-phenylsilyl)mercury in the aromatic solvent. Using thermochemical data, Jackson showed that the addition of organosilyl radical to benzene is reversible[121].

Recently, it has been reported that the radicals pentamethyldisilanyl ($Me_3Si-SiMe_2$), 1,1,2,2,3,3,3-heptamethyltrisilanyl ($Me_3Si-Si(Me)_2SiMe_2$) and 2,2,2-trimethyl-1,1-diphenyldisilanyl ($Me_3Si-SiPh_2$) radicals gave significant quantities of aromatic substitution products with benzene at 130°C, but branched chain radicals such as 1,1,1,2,3,3,3-heptamethyltrisilan-2-yl $[(Me_3Si)_2SiMe]$, and tris(trimethylsilyl)silyl $[(Me_3Si)_3Si\cdot]$ radicals gave the dimers in good yield, indicating that these branched chain radicals may be somewhat stabilized[130,131].

The results of investigations on aromatic homolytic silylation reaction on substituted benzenes are summarised in Table 5.

Table 5

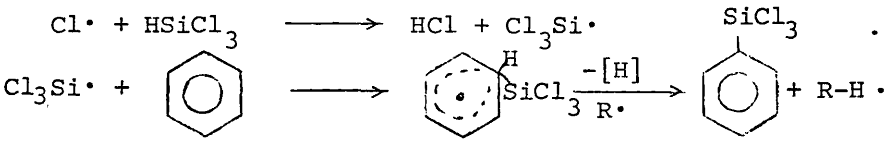
	Substrate										
	$PhCH_3$			PhOMe			$PhCF_3$				Reference
Radicals	o-	m-	p-	o-	m-	p-	o-	m-	p-	ρ Hammett's Reaction Constant	
$Me_3Si\cdot$	39	42	19	62	31	7	-	-	-	-	113
$Ph_3Si\cdot$	16	59	25	-	-	-	-	-	-		115(b)
$n\text{-}PrMe_2Si\cdot$	16	64	20	-	-	-	-	-	-	+1.6	129
$Me_5Si_2\cdot$	21	52	27	58	34	8	0	48	52	+1.4	129

The positive values of Hammett's ρ constant is indicative of the nucleophilic nature of organosilyl radicals.

In 1964, it was reported[132] that the illumination of a mixture of chlorine, trichlorosilane and benzene by an incandescent lamp gave 35% of phenyltrichlorosilane and 43% of tetrachlorosilane in accordance with the following reaction scheme.

$$Cl_2 \xrightarrow{h\nu} 2\,Cl\cdot \qquad \ldots\ldots\ldots (69)$$

$$Cl\cdot + HSiCl_3 \longrightarrow HCl + Cl_3Si\cdot \qquad \ldots\ldots (70)$$

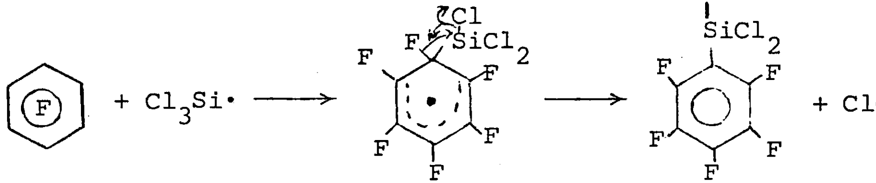


...... (71)

$$Cl_3Si\cdot + Cl_2 \longrightarrow SiCl_4 + Cl\cdot \qquad \ldots\ldots\ldots (72)$$

Subsequently, in 1965 Birchall, Daniewski, Haszeldine and Holden reported that the photolysis of trimethylsilane and trichlorosilane could also afford nuclear silylated products in hexafluorobenzene, and a novel reaction was observed with trichlorosilane[133]. Approximately equal amounts of trimethylpentafluorobenzene and fluorotrimethylsilane were obtained with trimethylsilyl radicals. In reaction with trichlorosilyl radicals, the major product was (fluorodichlorosilyl) pentafluorobenzene suggesting the following novel rearrangement being taking place.

$$Cl_3SiH \xrightarrow{h\nu} H\cdot + Cl_3Si\cdot$$ ...... (73)

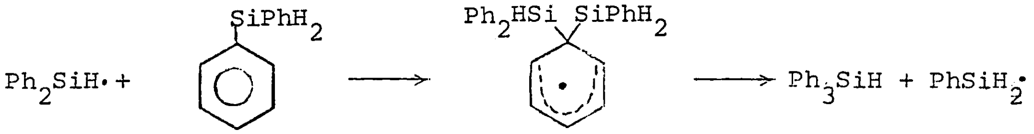


...... (74)

Cooper in 1967 showed that on u.v. irradiation (chlorophenyl) trimethylsilane was formed from a mixture of chlorobenzene and excess trimethylsilane[134].

In polyphenylated silanes, a redistribution reaction in which silicon-containing groups are displaced can occur, e.g. diphenylsilane irradiated with ultra-violet light or in the presence of free radicals give a mixture of tetra-, tri-, di- and monophenylsilanes and silane. The following reaction scheme was postulated[75-77].

$$R\cdot + Ph_2SiH_2 \longrightarrow RH + Ph_2SiH\cdot$$ ...... (75)



...... (76)

$$PhSiH_2\cdot + Ph_2SiH_2 \longrightarrow PhSiH_3 + Ph_2SiH\cdot$$ ...... (77)

Similar redistribution reactions have also been reported by other workers[113,115a,135-6] and it has been shown that this type of reaction has a substantial activation energy and will only be important at high temperatures[135,136].

(c) Reactions of silyl radicals with halogeno-compounds

Halogen abstraction by silyl radicals is a thermodynamically favourable process. In 1957, Curtice, Gilman and Hammond were the first to postulate chlorine abstraction reaction from chlorobenzene by silyl radicals in the reaction with triphenylsilane catalysed by t-butylperoxide[102].

$Ph_3SiH + t\text{-}BuO\cdot \longrightarrow Ph_3Si\cdot + t\text{-}BuOH$ ......(78)

$Ph_3Si\cdot + PhCl \longrightarrow Ph_3SiCl + Ph\cdot$ ...... (79)

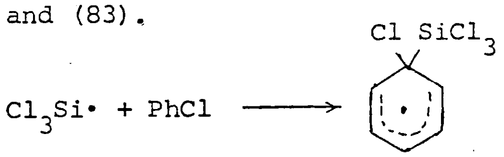
The isolation of triphenylchlorosilane and chlorobiphenyls supported the above mechanism. This observation seemed to contradict the reaction of phenyl radicals with chlorobenzene, where a homolytic phenylation reaction takes place to produce 2-, 3- and 4-chlorobiphenyl. These workers argued that the production of the resulting phenyl radicals (a reactive species with low heat of formation and no resonance stabilization energy arising from delocalization of the unpaired electron) was compensated for by the formation of the strong silicon-halogen bonds. In high temperature gas phase reaction[137], the reaction between trichloro silane and chlorobenzene, where the main products were benzene, phenyltrichlorosilane, tetrachlorosilane and hydrogen chloride, was also believed to involve trichlorosilyl radicals. In these reactions two simultaneous processes were thought to occur, namely a condensation reaction (80) and a reduction reaction (81).

$PhCl + HSiCl_3 \longrightarrow PhSiCl_3 + HCl$ ...... (80)

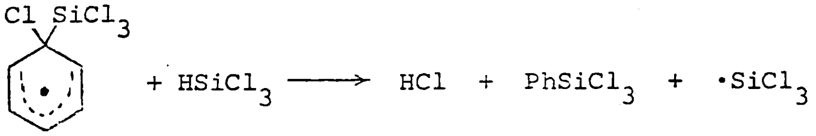
$PhCl + HSiCl_3 \longrightarrow PhH + SiCl_4$ ...... (81)

The mechanism was believed to involve initial homolytic dissociation of trichlorosilane, followed by two simultaneous reactions.

The condensation reaction (80) involves an addition-displacement process as in (82) and (83).



...... (82)



...... (83)

The reduction reaction (81) involves direct chlorine abstraction by the trichlorosilyl radicals (84 and 85).

$$Cl_3Si\cdot + PhCl \longrightarrow Ph\cdot + SiCl_4 \quad ...... (84)$$

$$Ph\cdot + HSiCl_3 \longrightarrow PhH + \cdot SiCl_3 \quad ...... (85)$$

Evidence for the condensation and reduction reactions at low temperature and on photolysis was also available[113,234].

The halogen abstraction reactions from halogeno-alkanes and alkenes have received great attention[138-142]. Kerr, Smith, Trotman-Dickenson and Young, in 1966, studied the photochemically initiated gas-phase reduction of alkyl halides with trichlorosilane. They proposed the following mechanism for the chain reaction[139a].

$$SiCl_3\cdot + RCl \longrightarrow SiCl_4 + R\cdot \quad ...... (86)$$

$$R\cdot + HSiCl_3 \longrightarrow RH + Cl_3Si\cdot \quad ...... (87)$$

They have also evaluated the activation energies for (86), R represents a variety of alkyl groups. They found that the activation energy falls in the series R = ethyl > isopropyl > t-butyl consistently with the increasing stability of the incipient alkyl radicals. The relative ease of chlorine abstraction from the trichloromethyl group of X-CCl_3 with chloroform as standard by triethylsilyl and phenyldimethylsilyl radicals has also been determined. The data correlated fairly well with Taft's σ^* constants with a ρ^* value of +0.26 and +0.29 for phenyldimethylsilyl and triethylsilyl radicals respectively, the positive sign of the reaction constants indicating some nucleophilic nature of the silyl radicals[142].

The relative ease of chlorine abstraction from benzyl chloride by pentamethyldisilanyl radicals had also been studied and fairly satisfactory Hammett correlations were obtained with $\rho = +0.29$[143].

Recently the halogen abstraction property of silyl radicals has been used to generate specific alkyl radicals for structural studies from the corresponding bromides or chlorides[144].

2 EXPERIMENTAL

A. Instruments and Apparatus

(a) Infrared spectra were measured by a Perkin-Elmer 457 Grating Infrared Spectrophotometer.

(b) N.m.r. spectra were measured by Perkin-Elmer R12B 60 MHz N.m.r. Spectrometer.

(c) Gas chromatographic analysis was done by using a Pye 104 and Perkin-Elmer F21D model gas chromatograph with a flame ionisation detector.

(d) Photolysis: The photolytic experiments were carried out by a Hanovia IL Photochemical Reactor, with a medium pressure straight arc tube emitting predominantly u.v. light at 254 mμ, 265 mμ, 297 mμ, 313 mμ and 366 mμ.

B. Preparation and Purification of Compounds

I. Purification of solvents

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

(1)	Benzene	b.p. 79.5°-80.5°C.	760 mm	(Lit.b.p. 80.5°)	760 mm
(2)	Toluene	b.p. 109°-110°C	760 mm	(Lit.b.p. 110.5°)	760 mm
(3)	Chlorobenzene	b.p. 132°C	760 mm	(Lit.b.p. 132°)	760 mm
(4)	Bromobenzene	b.p. 150-1°C	758 mm	(Lit.b.p. 156°	760 mm
(5)	Anisole	b.p. 152-3°C	758 mm	(Lit.b.p. 155°)	760 mm
(6)	t-Butylbenzene	b.p. 168°	760 mm	(Lit.b.p. 168°)	760 mm

II. Purification of compounds

The solid compounds were recrystallised at least once in ethanol.

(a) Bibenzyl (B.D.H.) m.p. 52° (Lit. m.p. 52°)

(b) Biphenyl (B.D.H.) m.p. 70° (Lit. m.p. 70°)

(c) Pentamethylbenzene (Aldrich) m.p. 53° (Lit. m.p. 53°)

(d) p-Dichlorobenzene (B.D.H.) m.p. 52° (Lit. m.p. 53°)

(e) Naphthalene (B.D.H.) m.p. 80° (Lit. m.p. 80.3°)

(f) m-Dinitrobenzene m.p. 88-9° (Lit. m.p. 89.6°)

(g) Purification of benzoyl peroxide (B.D.H.)

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 benzoyl peroxide as fine white crystals. The solution was decanted from 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°)

III. Preparation of compounds

(a) 2-Methylbiphenyl[84a,b]

2-Methylaniline (6.7 g) and amyl nitrite (B.D.H.) (10 ml) were dissolved in benzene (250 ml) and allowed to mix thoroughly at room temperature for 10 minutes. A further quantity of amyl nitrite (10 ml) was then added and the mixture was gently warmed until a steady reaction set in. After boiling the mixture steadily under reflux for six hours, the bulk of solvent was removed by distillation at atmospheric pressure, and the residue was transferred to a Claisen flask (50 ml) to complete the removal of the solvent over an oil bath heated to 140°.

The crude biaryl fraction distilled at 50 - 120/0.1 mm Hg. The orange coloured product was chromatographed on a neutral alumina column, eluated with light petroleum (b.p. 60 - 80°). After removal of the solvent by an efficient rotary evaporator, the residue was distilled under reduced pressure from a 25 ml Claisen flask to yield 2-methylbiphenyl

(80 - 84°/0.1 mm) as a pale yellow oil (6.8 g, 65%). Gas chromatographic analysis revealed no impurities [Lit. b.p. 130-6°/27 mm]. Its infrared spectrum was recorded and it had bands at 730 cm^{-1}, 750 cm^{-1} and 780cm^{-1} which are characteristic of a 2-substituted biphenyl and at 1380 cm^{-1} and 1450 cm^{-1} which are characteristic of a methyl group.

The following compounds are prepared by the analogous methods.

(b) 3-Methylbiphenyl b.p. 124-5°/0.1 mm, Lit.b.p. 148-50/20 mm,Yield 60%

(c) 2-Chlorobiphenyl b.p. 82-4°/0.1 mm, m.p. = 32-3°, Lit m.p. = 32°,Yield 55%

(d) 3-Chlorobiphenyl b.p. 85-8°/0.1 mm, Lit.b.p. 79°/0.05 mm[16a],Yield 50%

(e) 4-Chlorobiphenyl b.p. 76° -7°,Lit. m.p. 77°, Yield 73%

(f) 2-Bromobiphenyl b.p. 158-160°/10 mm,Lit. b.p. 160°/11 mm, Yield 35%

(g) 3-Bromobiphenyl b.p. 170-5°/18 mm,Lit.b.p. 169-173°/17 mm,Yield 16%

(h) 4-Bromobiphenyl b.p. 169-172°/17 mm, m.p.=90-1° Lit.m.p.=91-2°, Yield 60%

(i) 3-Methoxybiphenyl b.p. 130-4°/0.1 mm, Yield 65%

Infrared absorption bands: 704 cm^{-1}, 755 cm^{-1}, 789 cm^{-1}, 870 cm^{-1}, 1040 cm^{-1}, 1180 cm^{-1}, 1270 cm^{-1}, 1420 cm^{-1}, 1480 cm^{-1}.

4-Methylbiphenyl and 2-methoxybiphenyl were kindly donated by Dr. R. Bolton.

(j) 4-Methoxybiphenyl

This compound was prepared by the methylation of p-hydroxybiphenyl with dimethylsulphate.

4-Hydroxybiphenyl (42 g, 0.25 mole) was dissolved with vigorous stirring in aqueous sodium hydroxide solution (150 ml, containing 10.5 g of sodium hydroxide), dimethyl sulphate (315 g, 0.25 mole) was added whilst the mixture was cooled in ice. The solution was warmed for one hour at 70 - 80° and allowed to cool, 4-methoxybiphenyl was filtered under suction and washed thoroughly with 10% sodium hydroxide solution. The crude 4-methoxybiphenyl (39.1 g, 0.21 mole, 85%) was recrystallised from methylated spirit, m.p. 84°. (Lit. m.p. 85°).

(k) o-Methoxyphenylbenzoate

This compound was prepared according to Vogel's method[160].

Guaicol (6 g 0.05 mole) was dissolved in 10% sodium hydroxide (75 ml), redistilled benzoyl chloride (12 g, 0.09 mole) was added, and the mixture was stoppered securely and shaken vigorously for 20 minutes. The solid product was filtered under suction, and washed thoroughly with water and drained well. The crude ester was recrystallised twice from methylated spirit to give 6.5 g of ester (61%). M.p. 57-8°. (Lit. m.p. 58°).

(l) p-Methoxyphenylbenzoate was similarly prepared. Yield 80.5%

m.p. = 73-4° Lit. m.p. 74° [161]

(m) 4-t-Butylbiphenyl[162]

The Friedel-Crafts reaction between t-butyl chloride (14.8 g, 0.16 mole) and biphenyl (25 g, 0.16 mole) was carried out in carbon disulphide (125 ml) at 25° with ferric chloride (0.045 mole) as catalyst. The 4-t-butylbiphenyl was distilled at 105-115°/0.1 mm and recrystallised from ethanol twice. The colourless plates (11 g, 0.05 mole, 30%) had m.p. 51 - 52° (Lit. m.p. 52.2°).

(n) 2,4',5-Trichlorobiphenyl

p-Chlorobenzoyl peroxide (4.0 g, 0.013 mole) was allowed to decompose in p-dichlorobenzene (50 g) in the presence of ferric benzoate (1.5 g) as catalyst at 80°C for 72 hours. When the reaction was complete, the reaction mixture was dissolved in benzene and the ferric salt was filtered off. The benzoic acid formed and the ferric salt dissolved in the reaction mixture were removed according to the method described in section 4Aa. The neutral organic solution was dried and concentrated to 10 ml, and charged on to a silica gel column, and eluated with petroleum ether (60 - 80°) 300 ml of eluant was collected and the petroleum ether was removed in a rotary evaporator. The residue was recrystallised from ethanol to constant m.p. 66° (Lit. m.p. 67°) yield 2.5 g (75%).

(o) Phenyldimethylchlorosilane

Commercial reagent (Aldrich) was redistilled under nitrogen, the fraction boiling 189° to 194°C was collected and stored in a vacuum dessicator. This compound is air sensitive and deteriorates in air. The freshly distilled reagent is colourless but turns pink initially and eventually becomes a dark brown colour.

This compound was also prepared by the reaction of a Grignard reagent (phenyl magnesium bromide) with dimethyldichlorosilane[163]. The fraction boiling 189 - 194°C was collected. Yield: 32%.

(p) Phenyldimethylsilane[164]

To lithium aluminium hydride (15 g) suspended in sodium dried ether (800 ml), phenyldimethylchlorosilane (99 g) dissolved in sodium dried ether (250 ml) was added over a period of 3 hours. The solution was refluxed for 3 hours before the excess of lithium aluminium hydride was destroyed by ethyl acetate. The reaction mixture was poured over ice, the ethereal layer was separated and the aqueous solution was extracted twice with ether. The ethereal extracts were combined, dried over anhydrous sodium sulphate and distilled. The fraction boiling 155° -160° was collected. This fraction was redistilled, the fraction boiling at 156 - 7° was collected. G.l.c. analysis showed the presence of some bromobenzene and little biphenyl. The bromobenzene was removed by refluxing the hydrosilane in a suspension of lithium aluminium hydride in ether. The excess lithium aluminium hydride was hydrolysed. Phenyldimethylsilane was distilled as described above and was purified on a silica gel column with petroleum ether (40 - 60°) as eluant. The fraction boiling at 156 - 7° was collected. G.l.c. analysis showed that it contained a trace of impurity ($\sim$ 0.1%). Yield: 3.4 g (45%).

An n.m.r. spectrum was recorded (Table (A)). The infrared spectrum showed the following characteristic absorption. 790 cm^{-1} (Si-CH$_3$), 820 cm^{-1} (Si(CH$_3$)$_2$); 850 cm^{-1} (Si-H); 1020 cm^{-1} (Si-Ph); 1120 cm^{-1} (Si-Ph) 1445 (Si-Ph); 2100 cm^{-1} (Si-H).

(q) Diphenyldimethylsilane[165]

This compound was prepared by the Grignard reaction with phenyldimethylchlorosilane. The fraction boiling 170-180° /45 mm was collected and redistilled to give the silane boiling at 175-8/45 mm (Lit. b.p. 176-8°/45 mm). G.l.c. analysis showed that it contained little diphenyltetramethyldisilane (1 - 2%). An n.m.r. spectrum was recorded (Table (A)). The infrared spectrum showed the following strong absorption 800 cm^{-1}, 825 cm^{-1}, 1015 cm^{-1}, 1140 cm^{-1}, 1440 cm^{-1}.

The following compounds were similarly prepared by the Grignard reagent route by employing the appropriate aryl bromides. G.l.c. analysis showed that the product contained little diphenyltetramethyldisilane (1-3%). The n.m.r. data of these compounds are given in table (A). The infrared spectra of these compounds showed the characteristic strong absorptions of Si-CH$_3$ and Si-Ph bonds in addition to those absorptions arising from the disubstitution of the benzene ring.

(r) o-(Phenyldimethylsilyl)anisole: b.p. 141-2°/15 mm. Yield: 15%

(s) m-(Phenyldimethylsilyl)anisole: b.p. 158-162°/25 mm Yield: 20%

(t) p-(Phenyldimethylsilyl)anisole: b.p. 170-5°/25 mm Yield: 32%.

(u) o-(Phenyldimethylsilyl)toluene: b.p. 173-8°/50 mm Yield: 20%

(v) m-(Phenyldimethylsilyl)toluene: b.p. 164-8°/45 mm Yield: 68%

(w) p-(Phenyldimethylsilyl)toluene: b.p. 152-4°/24 mm Yield: 75%

(x) α-(Phenyldimethylsilyl)naphthalene: m.p. 52.5-53.5°. Yield: 58%

(y) β-(Phenyldimethylsilyl)naphthalene: This compound was prepared in low yield (< 5%) as shown by g.l.c. analysis. The reaction mixture contained mainly unreacted β-bromonaphthalene. The formation of this compound was inferred from the presence of a peak with a similar retention time as that in the reaction mixture of t-butyl peroxide/phenyldimethylsilane/ naphthalene system.

(z) Diphenyltetramethyldisilane[166]

This compound was prepared by the Wurtz coupling reaction. Yield: 38% m.p. = 32.5 - 34°C. Lit. m.p. = 34-5°C.

Table (A)

N.M.R. Data of Organosilanes

Compounds	Chemical shift Peak centre		δ (in p.p.m.)	
	a	b	c	d
a b c PhMe$_2$SiH	7.10 (5H)	0.30 (6H)	4.40 (1H)	
a b Ph$_2$SiMe$_2$	7.50 (10H)	0.75 (12H)		
a b (PhMe$_2$Si)$_2$	7.20 (10H)	0.30 (12H)		
a b c d o-CH$_3$-C$_6$H$_4$-Si-Me$_2$Ph	2.25 (3H)	b + d 7.35 (peak (9H) centre)	0.55 (6H)	
a b c d m-CH$_3$-C$_6$H$_4$SiMe$_2$Ph	2.2 (3H)	b + d 7.3 (peak (9H) centre)	0.50 (6H)	
a b c d p-CH$_3$-C$_6$H$_4$SiMe$_2$Ph	2.2 (3H)	7.0–7.50 (9H)	0.45 (6H)	
a b c d o-CH$_3$O-C$_6$H$_4$SiMe$_2$Ph	3.70 (3H)	6.95 (4H)	0.55 (6H)	7.45 (5H)
a b c d m-CH$_3$O-C$_6$H$_4$SiMe$_2$Ph	3.80 (3H)	7.10 (4H)	0.50 (6H)	7.50 (5H)
a b c d p-CH$_3$O-C$_6$H$_4$SiMe$_2$Ph	3.70 (3H)	6.80 (4H)	0.50 (6H)	7.30 (5H)
a b c α-C$_{10}$H$_7$SiMe$_2$Ph	8.9 (7H)	0.72 (6H)	7.3 (5H)	

a,b,c,d refer to types of protons

C. Quantitative and Qualitative Analysis of Reaction Products

Throughout this work the following g.l.c. columns were employed for qualitative and quantitative analysis of reaction products, for easy reference they were designated with code numbers preceding the description of the columns.

Code Number	Description
Ap. 15C	8-ft x 1/8 inch outer diameter (O.D.) column
1	Packed with 15% Apiezon L. grease on 100-120 mesh Celite (Embacel)
Ap.20C	8-ft x 3/8 inch O.D. packed with 20% Apiezon L grease on 100-120 mesh Celite (Embacel)
C20C	8-ft x 3/8 inch O.D. column packed with 20% carbowax on 100-120 mesh Celite
OV1	8-ft x 1/8 inch O.D. column packed with 1% methyl silicon gum.
S20C	8-ft x 1/8 inch O.D. column packed with 20% silicon Elastomer E301 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. The comparison was carried out using at least two columns of different polarities. After the identification of the different components of the reaction mixture, the detector was calibrated for quantitative analyses by the method of "internal standardization".

To calibrate the detector, standard solutions of a suitable internal standard and a product of the reaction were made. The internal standard chosen must not be a product of the reaction and had a non-overlapping g.l.c. retention time to the products being studied. The general practice was to make at least 5 such standard solutions containing varying relative concentrations of internal standard to the products to be calibrated. 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 with relative peak height versus relative mole ratio. In some reactions, calibration graphs were also constructed by plotting relative peak area against relative mole ratio. The peak area was determined by multiplying the peak height by the peak width at half-height.

From the calibration curve of relative peak height versus relative mole ratio it was found that the detector response only remained linear so long as the peak heights of the standard and compounds were approximately of equal magnitude. The detector response fell off from linearity when one peak was small relative to the other. Consquently, in a system where the biaryl isomers varied considerably in concentration as well as in relative time, if the concentration of the standard was arranged so that the peak obtained was of 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 construction of calibration curves over a wide range of relative concentrations of compounds to standard.

When the detector responses of all the compounds to be determined quantitatively have been calibrated, the unknown composition of the reaction mixture containing the same compound was determined by adding a known amount of the internal standard to the reaction mixture to be analysed. A sample was injected into the column under the same experimental conditions where the authentic species were calibrated.

From the chromatograph the relative peak height or relative peak area of the products to the standard were determined. Then from the calibration graph, the molar ratio corresponding to this peak height or peak area ratio was read, and the molar yield of the products calculated therefrom. In reactions where g.l.c. peaks overlapped, special correction factors had to be calculated and these would be dealt with in the appropriate system.

The accuracy of this method was checked by analysing a mixture of known composition, It was found that the method was accurate to within 2%.

It has been shown by Hey, Perkins and Williams[157] that the yields of biaryls and aroic acid depend to a large extent on the initial concentration of aroyl peroxide, therefore for the effect of 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. Throughout these studies, a concentration of 0.083 M (1.5 g/75 ml) of benzoyl peroxide is used.

D. The Phenylation Reactions

I. The phenylation reactions of toluene

(a) The decomposition of benzoyl peroxide in toluene

	No additives	m-Dinitrobenzene (0.09 g - 0.20 g)	Ferric benzoate (0.08 g - 0.40 g)	Cupric benzoate (0.40 g)
Volume of toluene: (ml)	75	75	75	75
Benzoyl peroxide: (g) (mole)	1.5 g 6.2×10^{-3}	1.5 g	1.5 g	1.5 g
Temperature: (^{o}C)	80 ± 0.1^{o}	80 ± 0.1^{o}	80 ± 0.1^{o}	80 ± 0.1^{o}
Time: (hours)	72	72	72	72

After the reactions had been carried out under a flow of nitrogen,pentamethylbenzene (ca. 100 mg) was added as an internal standard for the g.l.c. analysis, and benzoic acid was extracted by saturated aqueous sodium bicarbonate (1 x 100 ml, 3 x 25 ml), from which it was recovered by the dropwise addition of concentrated hydrochloric acid followed by ether extraction (1 x 70 ml; 3 x 50 nl). Removal of solvent from the dried (sodium sulphate) extract, finally in a vacuum desiccator, gave the benzoic acid which was weighed.

In reaction containing metal benzoates as additive, the metal benzoate was filtered and the weight of which was recorded to give an allowance of benzoic acid formed from the subsequent hydrolysis of the metal benzoates dissolved in the reaction mixture. (The formula weight of ferric benzoate trimers and cupric benzoate dimer were taken as 1086 and 612 respectively). To the filtrate, 50% o-phosphoric acid (20 ml) was added to hydrolyse the dissolved metallic benzoate. The reaction mixture was washed with water (5 x 25 ml) until the washing is neutral to blue litmus paper. After the above pre-treatment of the reaction mixture, the benzoic acid was extracted as described above.

The original organic layer was concentrated, using a rotary evaporator, and checking (g.l.c.) the absence of detectable amounts of biaryl in the distillate, and the concentrated solution was analysed (g.l.c.). Ap.15C separated o-methylbiphenyl from its isomers; m-methylbiphenyl was partly resolved from p-methylbiphenyl, but bibenzyl could not be. SE15C separated bibenzyl and o-methylbiphenyl completely, but presented the m- and p-isomers as an irresolvable peak.

Calibration using both these columns, with the isomeric methylbiphenyls, bibenzyl and known mixture of m- and p-methylbiphenyls against pentamethylbenzene allowed the amounts of these compounds to be measured to within 2% (*o*-methylbiphenyl and bibenzyl) or 3% (*m*- and *p*-methylbiphenyls).

Analysis of mixture of known composition

	Methylbiphenyls			Bibenzyl
	o-	*m*-	*p*-	
Found (mole x 10^{-3})	5.952 (45.49%)	3.800 (29.04%)	2.120 (16.02%)	1.212 (9.27%)
Known (mole x 10^{-3})	5.898 (45.24%)	3.887 (29.82%)	2.060 (15.80%)	1.191 (9.14%)

The results obtained are tabulated in Tables 6 and 7. The following experimental conditions were adopted for the g.l.c. analysis.

Column Ap.15C
Gas liquid chromatograph, Perkin Elmer F21D
Colume temperature: 150°
Carrier gas : nitrogen
Pressure 1Kp/cm^2
Attenuation: x 128

Compounds	Relative retention times
Pentamethylbenzene	1.0
Biphenyl	1.67
Diphenylmethane	2.56
o-Methylbiphenyl	2.07
m-Methylbiphenyl	3.07
p-Methylbiphenyl	3.37
Bibenzyl	3.37

Column: SE.15C

Column temperature: 130°

Carrier gas: nitrogen

Pressure: 1 Kp/cm^2

Attenuation: x 128

Compounds	Relative retention data
Pentamethylbenzene	1.0
Biphenyl	1.67
Diphenylmethane	2.13
2-Methylbiphenyl	1.80
3-Methylbiphenyl	2.80
4-Methylbiphenyl	2.80
Bibenzyl	3.33

Table 6

The decomposition of benzoyl peroxide in toluene (75 ml) in the presence of additives at 80°

Concentration of benzoyl peroxide: 0.083 M (1.5 g/75 ml)

Experiment No.	Additive g(mole/mole)	Methylbiphenyls (mole/mole)	Bibenzyl (mole/mole)	Benzoic acid (mole/mole)	Isomer Ratio		
					o	m	p
1	Nil	0.3850	0.1175	0.401	61.11	24.85	14.03
2	Nil	0.3796	0.1206	0.416	62.05	24.25	13.70
Mean of 1 + 2		0.3823	0.1191	0.4085	61.58	24.55	13.87
	m-Dinitrobenzene						
3	0.0095 (0.014)	0.3500	0.1134	0.460	65.40	20.20	14.31
4	0.0095 (0.014)	0.3896	0.1241	0.469	64.82	23.70	11.48
Mean of 3 + 4	0.095 (0.014)	0.3698	0.1188	0.4645	65.11	22.00	12.90
5	0.248 (0.0357)	0.3620	0.0825	0.543	62.02	23.21	14.77
6	0.0248 (0.0357)	0.4043	0.0874	0.509	62.92	23.73	13.35
Mean of 5 + 6	0.0248 (0.036)	0.3832	0.850	0.526	62.47	23.47	14.06
7	0.2015 (0.290)	0.5063	0.0379	0.787	62.36	24.09	13.56

Table 6 (continued)

Experiment No.	Additive g (mole/mole)	Methylbiphenyls (mole/mole)	Bibenzyl (mole/mole)	Benzoic acid (mole/mole)	Isomer Ratio		
					o	m	p
8	0.2015 (0.2901)	0.5264	0.0378	0.768	62.57	23.86	13.57
Mean of 7 + 8	0.2015 (0.290)	0.5164	0.0379	0.775	62.47	23.98	13.57
9	0.0814 (0.0181)	0.540	0.177	not determined	63.30	21.09	15.61
10	0.0814 (0.0181)	0.528	0.185	not determined	64.51	20.73	15.12
Mean of 9 + 10	0.081 (0.018)	2.534	0.181		63.91	20.91	15.37
11	0.2072 (0.0462)	0.473	0.163	0.738	65.31	18.18	16.52
12	0.2072 (0.0462)	0.587	0.197	0.723	63.70	20.77	15.51
Mean of 11+12	0.2072 (0.046)	0.580	0.180	0.731	64.51	19.48	16.02
13	0.4050 (0.080)	0.572	0.175	0.710	63.57	20.32	16.11
14	0.4040 (0.080)	0.580	0.164	0.698	64.32	19.88	15.88
Mean of 13+14	0.4050 (0.080)	0.576	0.170	0.704	63.95	20.10	15.96

Table 6 (continued)

Experiment No.	Additive g (mole/mole)	Methylbiphenyls (mole/mole)	Bibenzyl (mole/mole)	Benzoic acid (mole/mole)	Isomer Ratio		
					o	m	p
	Cupric benzoate						
15	0.4003	0.587	0.178	0.724	65.91	20.57	13.52
16	0.4010 (0.156)	0.576	0.182	0.694	64.87	19.84	15.29
Mean of 15+16	0.4007 (0.156)	9.582	0.180	0.709	65.39	20.21	14.41

Table 7

The ratio of side-chain attack to nuclear attack on toluene in phenylation reaction by benzoyl peroxide

Peroxide concentration: 0.083 M (1.5 g/75 ml)

Experiment No	Additive g (mole/mole)	% of side chain attack	% of nuclear attack
1	Nil	23.4	76.6
2	Nil	24.1	75.9
Mean of 1 + 2		23.8	76.2
	m-Dinitrobenzene		
3	0.0095 (0.0137)	24.5	75.5
4	0.0095 (0.0137)	23.3	76.7
Mean of 3 + 4	0.0095 (0.0137)	23.9	76.1
5	0.0248 (0.0357)	18.6	81.4
6	0.0248 (0.0357)	17.8	82.2
Mean of 5 + 6	0.0248 (0.0357)	18.2	81.8
7	0.2015 (0.2902)	7.0	93.0
8	0.2015 (0.2902)	6.7	93.3
Mean of 7 + 8	0.2015 (0.2902)	6.8	93.2
	Ferric benzoate		
9	0.0814 (0.0181)	24.6	75.4
10	0.0814 (0.0181)	25.9	74.1
Mean of 9 + 10	0.081 (0.0181)	25.3	74.7

Table 7 (continued)

Experiment No	Additive g (mole/mole)	% of side chain attack	% of nuclear attack
11	0.2072 (0.0462)	25.1	74.9
12	0.2972 (0.0462)	22.2	77.8
Mean of 11 + 12	0.2072 (0.0462)	23.7	76.4
13	0.4050 (0.080)	23.4	76.6
14	0.4050 (0.080)	22.0	78.0
Mean of 13 + 14	0.4050 (0.080)	22.7	77.3
	Cupric benzoate		
15	0.4007 (0.156)	23.4	76.6
16	0.4007 (0.156)	19.1	80.9
Mean of 15 + 16	0.4007 (0.156)	21.2	78.8

II. The Competitive Reactions

(a) The decomposition of benzoyl peroxide in an equimolar mixture of benzene and toluene with or without additives

	No additive	m-Dinitro benzene (0.007 g - 0.85 g)	Nitro- benzene (0.15 g -0.85 g)	Ferric benzoate (0.25 g - 1.30 g)	Cupric benzoate (0.50 g - 1.50 g)
Volume of toluene: (ml)	40.3	40.3	40.3	40.3	40.3
Volume of benzene: (ml)	34.7	34.7	34.7	34.7	34.7
Benzoyl peroxide: (g)	1.50	1.50	1.50	1.50	1.50
(mole)	6.2×10^{-3}	6.2×10^{-3}	6.2×10^{-3}	6.2×10^{-3}	6.2×10^{-3}
Temperature: (^{o}C)	80 ± 0.1^{o}	80 ± 0.1^{o}	80 ± 0.1^{o}	80 ± 0.1^{o}	80 ± 0.1^{o}
Time: (hours)	72	72	72	72	72

A series of experiments were carried out according to the method described in the previous section. At the completion of the reaction, pentamethylbenzene (ca. 100 mg) was added as internal standard for g.l.c. analysis. White crystals precipitated from the mixtures where no additive was added. These were filtered. The reaction mixture was treated by the same work-up procedure described in the previous section.

In these competitive reactions, Carbowax column was also used to analyse the yield of biphenyl and 2-methylbiphenyl which could not be separated either by Ap.15C or SE.15C when the concentration of biphenyl is about the same as that of 2-methylbiphenyl. The experimental conditions for the determination of 2-methylbiphenyl and biphenyl are as follows.

F21 model, column: Carbowax 20%

Column temperature : 200°C

Carrier gas : Nitrogen

Attenuation : x 128

Pressure : 1.5 Kp/cm^2

Compound	Relative retention time
Pentamethylbenzene	1.00
2-Methylbiphenyl	2.13
Biphenyl	2.73

The analytical conditions described in pages 67 and 70 were used for the determination of 3- and 4-methylbiphenyl and bibenzyl.

The results are summarised in Tables 8 and 9.

Table 8

The decomposition of benzoyl peroxide in an equimolar mixture (75 ml) of benzene and toluene in the presence of additive at 80°C

Peroxide concentration = 0.083 M

Experiment No.	Additive g(mole/mole)	Biphenyl (mole/mole)	Methylbiphenyls (mole/mole)	Bibenzyl (mole/mole)	Total yield of biaryl (mole/mole)	Benzoic acid (mole/mole)
17	Nil	0.161	0.388	0.062	0.510	0.421
18	Nil	0.168	0.301	0.062	0.532	0.358
Mean of 17&18		0.165	0.294	0.062	0.521	0.390
	Nitrobenzene					
19	0.1598 (0.2095)	0.272	0.369	0.027	0.669	0.521
20	0.1605 (0.2104)	0.252	0.328	0.039	0.618	0.543
Mean of 19&20		0.262	0.349	0.033	0.643	0.532
21	0.4532 (0.5940)	0.292	0.398	0.006	0.696	not determined
22	0.85619 (1.1121)	0.331	0.442	0.009	0.782	0.603
23	0.8578 (1.1244)	0.329	0.447	0.010	0.786	0.687

Table 8 (continued)

Experiment No.	Additive g (mole/mole)	Biphenyl (mole/mole)	Methylbiphenyls (mole/mole)	Bibenzyl (mole/mole)	Total yield of biaryl (mole/mole)	Benzoic acid (mole/mole)
31	0.2999 (0.2879)	0.303	0.450	< 0.006	0.759	
Mean of 30&31		0.325	0.467		0.795	0.763
	Cupric benzoate					
32	0.5001 (0.1319)	0.298	0.396	0.021	0.715	not determined
33	0.4999	0.286	0.396	0.026	0.708	not determined
Mean of 32&33		0.292	0.396	0.024	0.712	
34	0.9998 (0.2637)	0.281	0.393	0.038	0.711	not determined
35	0.9998	0.291	0.391	0.028	0.711	not determined
Mean of 34&35	0.286	0.392	0.033	0.711		
36	1.5002 (0.3957)	0.289	0.397	0.011	0.696	not determined

Table 8 (continued)

Experiment No	Additive g (mole/mole)	Biphenyl (mole/mole)	Methylbiphenyls (mole/mole)	Bibenzyl (mole/mole)	Total yield of biaryl (mole/mole)	Benzoic acid (mole/mole)
Mean of 22&23		0.330	0.445	0.010	0.784	0.645
	m-Dinitrobenzene					
24	0.007 (0.0067)	0.180	0.305	0.034	0.519	0.384
25	0.0152 (0.0146)	0.210	0.304	0.033	0.547	0.460
26	0.0154 (0.0147)	0.231	0.351	0.034	0.616	0.435
Mean of 25&26		0.221	0.328	0.033	0.582	0.448
27	0.1039 (0.0997)	0.318	0.445	0.016	0.779	0.583
28	0.1031 (0.0989)	0.299	0.432	0.003	0.734	0.648
Mean of 27&28		0.309	0.439	0.009	0.757	0.616
29	0.2004 (0.1024)	0.269	0.399	0.013	0.679	0.653
	m-Dinitrobenzene					
30	0.2999 (0.2879)	0.347	0.484	< 0.006	0.830	0.773

Table 8 (continued)

Experiment No.	Additive g (mole/mole)	Biphenyl (mole/mole)	Methylbiphenyls (mole/mole)	Bibenzyl (mole/mole)	Totel yield of biaryl (mole/mole)	Benzoic acid (mole/mole)
	Ferric benzoate					
37	0.2547 (0.0379)	0.234	0.393	0.038	0.666	0.641
38	0.3496 (0.520)	0.239	0.408	0.070	0.717	0.696
39	0.3497	0.264	0.412	0.050	0.752	0.665
Mean of 38&39		0.252	0.410	0.060	0.721	0.681
40	0.4489 (0.0667)	0.279	0.413	0.028	0.720	0.718
41	0.4429 (0.0658)	0.262	0.441	0.032	0.735	not determined
Mean of 40&41		0.271	0.427	0.030	0.728	
42	0.5504 (0.0818)	0.270	0.420	0.042	0.731	0.606
43	0.8474 (0.1259)	0.277	0.430	0.034	0.741	0.683
44	1.3032 (0.1937)	0.272	0.445	0.055	0.772	0.767

Table 9

The rate factors of toluene

Experiment No.	Additive g (mole/mole)	Relative Rate	Isomer ratio			Partial rate factors		
		$K^{CH_3}_{H}$	o-	m-	p-	Fo	Fm	Fp
17	Nil	1.79	62.93	23.60	12.45	3.38	1.27	1.34
18	Nil	1.82	61.67	24.21	14.12	3.37	1.32	1.54
Mean of 17&18		1.81	62.30	23.91	13.29	3.38	1.30	1.44
	Nitrobenzene							
19	0.1598 (0.2095)	1.36	62.71	20.61	16.68	2.55	0.84	1.36
20	0.1605	1.31	64.12	22.69	12.95	2.53	0.89	1.02
Mean of 19&20		1.34	63.42	21.65	14.93	2.54	0.87	1.19
21	0.4491 (0.5891)	1.37	57.76	24.65	17.59	2.37	1.01	1.44
22	0.4532 (0.5942)	1.34	60.20	25.18	14.62	2.42	1.01	1.17

Table 9 (continued)

Experiment No	Additive g(mole/mole)	Relative Rate $K_{H}^{CH_3}$	Isomer Ratio			Partial rate factors		
			o-	m-	p-	Fo	Fm	Fp
	Mean of 21 & 22	1.36	58.98	24.92	16.11	2.40	1.01	1.31
23	0.8578 (1.125)	1.36	60.89	25.03	14.08	2.48	1.02	1.15
	m-Dinitrobenzene							
24	0.007 (0.007)	1.69	55.18	23.90	20.92	2.80	1.21	2.12
25	0.0152 (0.015)	1.45	59.58	21.16	19.26	2.59	0.92	1.67
26	0.0154 (0.015)	1.52	56.83	22.85	20.31	2.59	1.03	1.85
	Mean of 25 & 26	1.49	58.21	2201	19.79	2.59	0.98	1.76
27	0.1039 (0.100)	1.40	62.43	24.61	13.69	2.62	1.03	1.15
28	0.1031 (0.099)	1.44	60.69	23.56	15.75	2.59	1.01	1.36
	Mean of 27 & 28	1.42	61.56	24.09	14.72	2.61	1.02	1.26
29	0.2004 (0.192)	1.48	59.00	25.64	15.36	2.62	1.14	1.36

Table 9 (continued)

Experiment No.	Additive g (mole/mole)	Relative Rate $^{CH_3}K_H$	Isomer Ratio o-	m-	p-	Partial rate factors Fo	Fm	Fp
	m-Dinitrobenzene							
30	0.2999 (0.288)	1,40	61.10	23.15	15.75	2.56	0.97	1.32
31	0.2999 (0.288)	1.48	58.04	25.11	16.85	2.58	1.12	1.50
Mean of 30&31		1.45	59.38	24.63	15.99	2.59	1.08	1.39
	Cupric benzoate							
32	0.5001 (0.132)	1.33	65.57	22.31	12.12	2.62	0.89	0.97
33	0.4999 (0.132)	1.39	64.79	22.84	12.37	2.70	0.95	1.03
Mean of 32&33		1.36	65.18	22.58	12.25	2.66	0.92	1.00
34	0.9998	1.40	65.60	21.46	12.93	2.76	0.90	1.09
35	0.9998 (0.264)	1.35	65.10	21.42	13.48	2.63	0.86	1.09
Mean of 34&35		1.36	65.40	21.44	13.21	2.70	0.88	1.09
36	1,5002 (0.396)	1.37	64.69	21.65	13.66	2.66	0.89	1.13
	Ferric benzoate							
37	0.2547 (0.038)	1.68	64.03	21.49	14.48	3.23	1.08	1.46

Table 9 (continued)

Experiment No.	Additive g(mole/mole)	Relative Rate $\frac{CH_3}{H}$ K	Isomer Ratio			Partial rate factors		
			o-	m-	p-	Fo	Fm	Fp
38	0.3496 (0.052)	1.71	65.16	21.78	13.07	3.34	1.12	1.34
39	0.3497 (0.052)	1.56	64.51	22.78	12.73	3.02	1.07	1.19
Mean of 38&39		1.64	64.84	22.28	12.88	3.18	1.10	1.27
40	0.4489 (0.067)	1.48	66.41	21.51	12.33	2.92	0.96	1.10
41	0.4429 (0.060)	1.68	63.41	19.94	16.66	3.20	1.01	1.68
Mean of 40&41		1.58	64.91	20.73	14.50	3.06	0.99	1.39
	Ferric benzoate							
42	0.5504 (0.082)	1.56	62.49	22.18	15.33	2.92	1.04	1.43
43	0.8474 (0.126)	1.55	61.71	22.93	15.36	2.87	1.07	1.43
44	1.3032 (0.194)	1.64	60.87	21.64	17.48	2.98	1.06	1.72

Table 10

Competitive reactions containing varying molar ratios of benzene and toluene

Experiment No.	Additives g (mole/mole)	Substrate Ratio $[\mathrm{PhCH_3}]/[\mathrm{PhH}]$	Biphenyl	Methylbiphenyls	Bibenzyl	$\mathrm{PhCH_3}$/< PhH
45	Nil	2.947	0.075	0.405	0.010	1.83
46	Nil	2.947	0.073	0.373	0.0154	1.75
Mean of 45&46						1.79
47	Nil	0.328	0.686	0.282	0.0007	1.25
48	Nil	0.328	0.465	0.211	0.002	1.38
Mean of 47&48						1.32
	m-Dinitrobenzene					
49	0.3004 (0.288)	2.947	0.101	0.463	1.3×10^{-3}	0.156
50	0.2013 (0.193)	2.919	0.155	0.605	5.4×10^{-3}	1.43
Mean of 49&50						1.50
51	0.3054 (0.293)	0.3282	0.687	0.289	$<1\times10^{-3}$	1.28
52	0.2009 (0.193)	0.3250	0.613	0.296	~ 0	1.49
Mean of 51&52						1.39

Table 10 (continued)

Experiment No.	Additives g (mole/mole)	Substrate Ratio $[PhCh_3]/[PhH]$	Biphenyl	Methylbiphenyls	Bibenzyl	$PhCH_3/PhH$ /<
	Cupric benzoate					
53	0.0998 (0.026)	2.947	0.120	0.506	0.043	1.43
54	0.101 (0.027)	0.3282	0.593	0.245	0.037	1.26
	Ferric benzoate					
55	0.8033 (0.119)	2.947	1.200	0.510	0.227	1.44
56	0.802 (0.119)	0.3282	0.495	0.249	0.027	1.54

Table 11

The decomposition of benzoyl peroxide in anisole at 80° for 72 hours. Peroxide concentration: 0.083 M (1 g/50 ml)

Experiment No.	Additive (mole/mole)	Methoxy-biphenyls (mole/mole)	Methoxyphenyl-benzoates (mole/mole)	Benzoic acid (mole/mole)
57	Nil	0.407	0.032	1.164
58	Nil	0.414	0.033	1.180
59	Nil	0.414	0.047	1.184
	Mean of 57,58&59	0.412	0.037	1.176
	m-Dinitrobenzene			
60	($\sim$0.4) $\sim$0.5760	0.366	0.076	1.220
61		0.372	0.094	1.205
	Mean of 60&61	0.369	0.085	1.213
	Pentafluoronitroso-benzene			
62	($\sim$0.007) $\sim$0.009	0.389	0.048	n.d.
63		0.401	0.052	n.d.
	Mean of 62&63	0.395	0.050	
	Nil			
64	(under oxygen)	0.128	0.288	n.d.
65	(under oxygen)	0.159	0.226	n.d.
66	(under oxygen)	0.120	0.447	n.d.
67	(under oxygen)	0.288	0.255	1.274
68	(under oxygen)	0.144	0.212	1.304
	Mean	0.168	0.286	
	Nil			
69	(under air)	0.350	0.179	n.d.
70	(under air)	0.333	0.192	n.d.
	Mean of 69&70	0.342	0.186	

n.d. = not determined.

Table 11 (continued)

Experiment No	Additive g(mole/mole)	Methoxy-biphenyls (mole/mole)	Methoxyphenyl-benzoates (mole/mole)	Benzoic acid (mole/mole)
71	Cupric benzoate (0.2507) (0.100)	0.451	0.392	1.039
72	0.2498 (0.099)	0.454	0.348	1.047
	Mean 71&72	0.453	0.365	1.043
73	Ferric benzoate (0.4571) (0.102)	0.556	0.126	0.893
74	0.4599 (0.102)	0.480	0.126	1.006
	Mean 73&74	0.518	0.126	0.949
75	t-Butylhydroperoxide 0.1044 (0.281)	0.487	0.052	1.141
76	0.1000 (0.269)	0.502	0.044	1.133
	Mean 75&76	0.495	0.048	1.137

Table 12

The isomer distribution of methoxybiphenyls and methoxyphenylbenzoates

Experiment No.	Additive	Isomer ratio (%) Methoxybiphenyls			Isomer ratio (%) Methoxyphenylbenzoates	
		o-	*m*-	*p*-	*o*-	*p*-
57	Nil	73.3	12.6	14.1	69.0	31.0
58	Nil	74.6	11.4	14.0	82.5	17.5
59	Nil	73.2	11.5	15.3	62.9	37.1
	Mean value	73.7	11.8	14.5	71.5	28.5
	m-Dinitrobenzene					
60	0.3988 (0.573)	66.9	21.2	11.9	61.0	39.0
61	0.3982 (0.573)	67.9	20.2	11.9	54.6	45.4
	Man value	67.4	20.7	11.9	57.8	42.2
62	Pentafluoronitrosobenzene (0.0120) (0.013)	73.3	15.8	10.9	60	40
63	(0.0102) (0.013)	74.4	14.7	11.0	-	-
	Mean value	73.8	15.2	11.0		
	Nil					
64	(under oxygen)	65.8	22.4	11.8	36.7	63.3
65	(under oxygen)	65.8	22.6	11.6	37.6	62.4
66	(under oxygen)	64.5	22.9	12.6	33.8	66.2
67	(under oxygen)	66.1	21.5	12.4	33.5	66.5
68	(under oxygen)	66.4	21.7	11.9	38.7	60.3
	Mean value	65.7	22.2	12.1	36.1	63.7
69	Nil (under air)	67.3	19.4	13.3	40.3	59.7
70	(under air)	67.0	20.10	12.9	37.4	62.6
	Mean value	67.15	19.75	13.1	38.9	61.2

Table 12 (continued)

Experiment No.	Additive	Isomer ratio (%) Methoxybiphenyls			Isomer ratio (%) Methoxyphenylbenzoates	
		o-	m-	p-	o-	p-
	Cupric benzoate					
71	0.2507 (0.100)	70.2	19.4	10.4	66.0	34.0
72	02498 (0.099)	70.2	19.2	10.6	72.1	27.9
	Mean value	70.2	19.3	10.5	69.0	31.0
	Ferric benzoate					
73	0.4571 (0.102)	70.1	18.3	11.6	60.7	39.3
74	0.4599 (0.102)	70.50	17.9	11.7	60.7	39.3
	Mean value	70.3	18.1	11.6	60.7	39.3
	t-butylhydroperoxide					
75	0.1044 (0.281)	74.0	14.3	11.4	67.0	33.0
76	0.100 (0.269)	76.2	12.6	11.2	71.0	39.0
	Mean value	75.1	13.5	11.3	69.0	36.0

(b) The decomposition of benzoyl peroxide in a solution containing various molar ratios of benzene and toluene

In this series of experiments, the molar ratio of the substrates is varied while the total volume of solvent was still maintained at 75 ml. Benzoyl peroxide (1.5 g) was allowed to decompose in these mixtures with or without the presence of additives.

The same work-up procedures were adopted for the reaction mixtures, the results being summarised in Table 10.

III. The phenylation reaction of anisole

(a) The decomposition of benzoyl peroxide in anisole

To deaerated anisole (75 ml) was added benzoyl peroxide (1.5 g) which was allowed to react at 80°C for 72 hours under a steady stream of nitrogen gas in a thermostat. At the completion of the reaction, the acidic and non-acidic reaction products were separated (Section D.I.a). The non-acidic solution containing methoxylbiphenyls and methoxyphenylbenzoate was not concentrated but was directly taken for g.l.c. analysis with pentamethylbenzene as the internal standard. The Ap.15C column was found to be suitable for the quantitative analysis; with this column all the major reaction products are completely separated except 3- and 4-methoxybiphenyls which have partially overlapping peaks. Therefore an additional calibration curve was constructed by using standard solutions containing various molar ratios of 3- and 4-methoxybiphenyls with pentamethylbenzene. The correction factors for 3- and 4-methoxybiphenyls were 1.18 and 1.21 respectively.

Calibration curves for the other reaction products were also constructed with pentamethylbenzene as the internal standard. There was one unidentified peak immediately in front of the peak due to 2-methoxyphenylbenzoate in reaction without additive and in reactions in the presence of nitro-compounds as additives, and also in reaction under air or oxygen.

The analytical conditions together with the retention data are given below.

The results of these reactions are summarised in Tables 11 and 12.

Gas Chromatograph: Pye 104

Column: AP.15C

Column temperature: 200°

Carrier gas: nitrogen

Pressure: 1 Kp/cm^2

Attenuation: 50×10^{-2}

Compounds	Relative Retention Time
Pentamethylbenzene	1.00
o-Methoxybiphenyl	2.75
m-Methoxybiphenyl	4.38
p-Methoxybiphenyl	5.00
Unidentified peak	7.80
o-Methoxyphenylbenzoate	8.13
p-Methoxyphenylbenzoate	12.75

Analysis of mixture of known composition

	Methoxybiphenyls			Methoxyphenylbenzoates	
	o-	*m*-	*p*-	*o*-	*p*-
Found (mole × 10^{-3})	4.194	1.694	1.254	0.865	0.627
	(58.72%)	(23.72%)	(17.56%)	(57.98%)	(42.01%)
Known (mole × 10^{-3})	4.258	1.674)	1.278	0.887	0.645
	(59.06%)	(23.22%)	(17.73%)	(57.90%)	(42.10%)

(b) The effect of *m*-dinitrobenzene and pentafluoronitrosobenzene on the decomposition of benzoyl peroxide in anisole.

To anisole (50 ml) which has been purged with nitrogen for half an hour, was added to *m*-dinitrobenzene (0.40 g); to a duplicate set of experiments pentafluoronitrosobenzene (0.01 g) was added. This was followed by the addition of benzoyl peroxide (1.0 g). The solution was rapidly heated to 80°C in a thermostat, and allowed to react for 72 hours under a nitrogen atmosphere. At the completion of the reaction pentamethylbenzene (ca. 100 mg) was added as an internal standard. The work-up procedure and the g.l.c. analytical conditions described in the preceding section were adopted for the determination of benzoic acid, and biaryls. The products formed were similar to those repeated in page 93 .

The results are given in Tables 11 and 12.

(c) The effect of oxygen gas and air on the decomposition of benzoyl peroxide in anisole.

Benzoyl peroxide (1.0 g) was added to anisole (50 ml). The solution was bubbled with oxygen or air through a fine capillary glass tubing. The flow rate of the gas was adjusted so that one or two bubbles were formed per second. The solution was purged with the gas for 30 minutes. The mixture was then quickly brought to $80^{\circ} \pm 0.1^{\circ}$ and the reaction allowed to proceed for 72 hours while the oxygen gas or air was maintained at the same flow rate.

At the completion of the reaction, no new major products was detected, and consequently pentamethylbenzene was added as the internal standard. The reaction mixture was processed according to the procedure in page 68 . After separation of benzoic acid, the reaction mixture was dried and taken for g.l.c. analysis. Similar analytical conditions to page 93 were employed.

The results are tabulated in Tables 11 and 12.

(d) The effects of ferric benzoate and cupric benzoate on the decomposition of benzoyl peroxide in anisole.

A duplicate set of reactions containing ferric benzoate (0.45 g) or cupric benzoate (0.25 g) as additive in anisole (50 ml) containing benzoyl peroxide (1.0 g) was performed. The reaction was allowed to proceed for 72 hours under a nitrogen atmosphere. At the completion of the reaction, the same work-up procedure (page 68) was used to separate the acidic and non-acidic compounds. The biaryls and esters were analysed by the method described in the previous section.

The results are given in Tables 11 and 12.

(e) The effect of t-butylhydroperoxide on the deomposition of benzoyl peroxide in anisole.

Duplicate experiments, each containing a mixture of t-butylhydroperoxide (0.1 g) and benzoyl peroxide (1.0 g) in deaereated anisole (50 ml) were performed under the similar experimental conditions described for the above reactions. The standard work-up procedure was followed for the analysis of benzoic acid; biaryls and esters formed.

The results are summarised in Tables 11 and 12.

IV. The competitive reactions

(a) The decomposition of benzoyl peroxide in an equimolar mixture of anisole and benzene with or without the presence of additives.

The experimental conditions were as follows:

Additives	Volume of anisole	Volume of benzene	Benzoyl peroxide g	mole	Temperature	Time of reaction
Nil	41.3 ml	33.7 ml	1.5	6.2×10^{-3}	$80 \pm 0.1^{\circ}$	72 hours

In reactions where additives are included, the concentration ranges are given below.

Ferric benzoate (0.30 to 1.2 g); cupric benzoate (0.02 to 0.2 g); cupric p-toluate (0.01 g); m-dinitrobenzene (0.20 to 0.45 g); and nitrobenzene (0.21 g to 0.50 g).

At the completion of the reaction pentamethylbenzene (ca. 300 mg) was added as an internal standard. White crystal precipitated from the reaction mixture where no additive was included. This precipitate was filtered and was not investigated further. The benzoic acid was separated according to the standard methods (page 68). The organic solution was taken for g.l.c. analysis without further concentration. The analytical conditions used were similar to those used in the phenylation of anisole (page 93), with an additional calibration graph for biphenyl against pentamethylbenzene. For the reactions with m-dinitrobenzene as additive, it was found that the peak due to biphenyl overlapped with that of m-dinitrobenzene on the chromatogram. As a result the biphenyl formed in these reactions was determined separately using carbowax column in which biphenyl and m-dinitrobenzene could be separated. The results for these reactions were given in Tables 11 and 12. The results for reactions with m-dinitrobenzene and nitrobenzene as additives were summarised in Tables 13 and 14.

Table 13

The decomposition of benzoyl peroxide in an equimolar mixture of benzene and anisole (75 ml) at 80^{o}

Peroxide concentration = 0.083 M

Experiment No.	Additive g(mole/mole)	Biphenyl (mole/mole)	Methoxybiphenyls (mole/mole)	Methoxyphenyl-benzoates (mole/mole)	Total biaryl (mole/mole)	Benzoic acid (mole/mole)
77	Nil	0.111	0.374	0.05	0.485	0.975
78	Nil	0.121	0.377	0.05	0.503	0.961
	Mean of 77&78	0.116	0.376	0.05	0.494	0.968
	m-dinitrobenzene					
79	0.2026 (0.1945)	0.260	0.491	0.071	0.751	N.D.
80	0.2023 (0.1942)	0.278	0.460	0.073	0.737	N.D.
81	0.2017 (0.1936)	0.256	0.532	0.096	0.788	N.D.
	Man of 80&81	0.267	0.496	0.084	0.763	
82	0.4549	0.251	0.434	0.071	0.685	1.071
83	0.4543 (0.4361)	0.293	0.521	0.116	0.813	1.108
	Mean of 82&83	0.272	0.477	0.093	0.749	

Table 13 (continued)

Experiment No.	Additive g (mole/mole)	Biphenyl (mole/mole)	Methoxybiphenyls (mole/mole)	Methoxyphenyl-benzoates (mole/mole)	Total biaryl (mole/mole)	Benzoic acid (mole/mole)
	Nitrobenzene					
84	0.2160 (0.2831)	0.245	0.555	0.083	0.800	1.024
85	0.2177 (0.2853)	0.263	0.550	0.077	0.627	1.014
	Mean of 84&85	0.254	0.553	0.080	0.713	1.019
86	0.4938 (0.6473)	0.233	0.382	0.061	0.616	
87	0.4942 (0.6478)	0.209	0.362	0.043	0.571	
	Mean of 86&87	0.221	0.372	0.052	0.593	
	Ferric benzoate					
88	0.3055 (0.0454)	0.212	0.400	0.057	0.612	1.054
89	0.3050 (0.0454)	0.217	0.368	0.059	0.595	0.941
	Mean of 88&89	0.214	0.384	0.058	0.598	0.997
90	0.6004 (0.0892)	0.217	0.386	0.096	0.602	1.08
91	0.5953 (0.0085)	0.212	0.404	0.082	0.615	1.084

Table 13 (continued)

Experiment No	Additive g (mole/mole)	Biphenyl (mole/mole)	Methoxybiphenyls (mole/mole)	Methoxyphenyl-benzoates (mole/mole)	Total biaryl (mole/mole)	Benzoic acid (mole/mole)
	Mean of 90&91	0.214	0.395	0.089	0.609	1.083
92	1.1857 (0.1763)	0.206	0.563	0.134	0.562	1.103
	Cupric benzoate					
93	0.0208 (0.006)	0.267	0.525	0.215	0.788	0.930
94	0.0204	0.264	0.526	0.190	0.790	0.902
	Mean of 93&94	0.266	0.525	0.202	0.789	0.916
95	0.0400 (0.0106)	0.230	0.446	0.177	0.677	0.905
96	0.080 (0.021)	0.272	0.567	0.167	0.840	0.906
97	0.2000 (0.053)	0.250	0.413	0.171	0.663	not determined
98	0.2000	0.250	0.395	0.154	0.645	not determined
	Mean of 97&98	0.250	0.404	0.163	0.654	
	Cupric *p*-toluate					
99	0.0402 (0.010)	0.226	0.376	0.120	0.602	0.819
100	0.0406 (0.010)	0.260	0.476	0.124	0.635	0.815
	Mean of 99&100	0.376	0.122	0.619	0.817	

Table 14

The relative rates and partial rate factors for the anisole and benzene systems

Experiment No.	Additive g (mole/mole)	Relative rate of phenylation ${}^{\text{PhX}}K_{\text{PhH}}$	Methoxybiphenyls isomer ratio			Partial rate factors			Methoxyphenylbenzoates isomer ratio	
			o-	m-	p-	Fo	Fm	Fp	o-	p-
77	Nil	337	76.14	10.77	13.08	7.71	1.09	2.65	-	-
									52.60	40-48
78	Nil	2.99	75.50	11.28	13.21	6.77	1.01	2.37	-	-
	Mean value	3.18	75.82	11.03	13.15	7.24	1.05	2.51		
	m-Dinitrobenzene									
79	0.2026 (0.195)	1.89	67.54	20.96	11.50	3.83	1.19	1.30	60.78	39.22
80	0.2023 (0.104)	1.65	67.44	20.87	11.69	3.34	1.04	1.16	61.90	38.09
81	0.2017 (0.194)	2.08	66.88	21.09	12.03	4.17	1.32	1.50	57	43
	Mean value	1.87	67.29	20.97	11.74	3.78	1.18	1.32	59.89	40.11
82	0.4549 (0.4370)	1.73	66.97	21.34	11.69	3.47	1.10	1.21	57.43	42.57
83	0.4543 (0.436)	1.78	65.86	21.54	12.60	3.52	1.15	1.35	54.29	45.71
	Mean value	1.46	66.41	21.44	12.15	3.50	1.13	1.28	55.86	44.14

Table 14 (continued)

Experiment No.	Additive g (mole/mole)	Relative rate of phenylation ${}^{PhX}K_{PhH}$	Methoxybiphenyls isomer ratio			Partial rate factors			Methoxyphenylbenzoates isomer ratio	
			o-	m-	p-	Fo	Fm	Fp	o-	p-
91	0.5953 (0.089)	1.84	71.20	16.41	12.39	3.92	0.90	1.37	77.53	22.47
	Mean value	1.81	70.66	16.50	12.84	3.83	0.90	1.36	74.97	25.03
92	1.1857 (0.176)	1.72	70.72	17.15	12.13	3.66	0.89	1.25	79.70	20.30
	Cupric benzoate									
93	0.0208 (0.006)	1.99	68.23	20.14	11.63	4.07	1.20	1.39	89.06	10.94
94	0.02049	1.99	68.66	19.70	11.64	4.08	1.18	1.39	94.21	5.79
	Mean value	1.99	68.45	19.92	11.63	4.08	1.19	1.39	91.64	8.36
95	0.0400 (0.0011)	1.94	68.44	19.86	11.70	3.98	1.15	1.36	95.70	4.3
96	0.080 (0.021)	2.08	68.78	20.15	11.07	4.30	1.26	1.38	91.58	8.42
97	0.200 (0.053)	1.65	68.43	20.14	11.43	3.39	1.00	1.13	-	-
	Mean value	1.62 ± 0.03	68.32	20.16	11.52	3.31	0.98	1.12	-	-

Table 14 (continued)

Experiment No	Additive g (mole/mole)	Relative rate of phenylation $^{PhX}K_{PhH}$	Methoxybiphenyls isomer ratio			Partial rate factors			Methoxyphenyl-benzoates isomer ratio	
			o-	m-	p-	Fo	Fm	Fp	o-	p-
	Nitrobenzene									
84	0.21604 (0.283)	2.27	67.73	20.77	11.50	4.60	1.41	1.56	54.81	45.19
85	0.2177 (0.285)	2.10	67.01	21.26	11.73	4.21	1.34	1.48	56.49	43.51
	Mean value	2.19	67.37	21.02	11.61	4.41	1.38	1.52	55.65	44.35
86	0.4938 (0.647)	1.64	67.62	20.67	11.71	3.33	1.02	1.15	53.03	46.97
87	0.4942 (0.648)	1.73	67.65	20.31	12.04	3.52	1.06	1.25	59.21	40.79
	Mean value	1.69	67.64	20.49	11.88	3.43	1.04	1.20	56.12	43.88
	Ferric benzoate									
88	0.3055 (0.045)	1.88	70.46	16.71	12.83	3.98	0.94	1.45	68.76	31.24
89	0.7050 (0.045)	1.70	72.23	15.76	12.01	3.69	0.80	1.23	64.37	35.63
	Mean value	1.79	71.35	16.24	12.41	3.84	0.87	1.34	66.57	33.43
90	0.6004 (0.089)	1.78	70.12	16.58	13.30	3.74	0.89	1.34	72.41	27.59

Table 14 (continued)

Experiment No.	Additive g (mole/mole)	Relative rate of phenylation ${}^{\mathrm{PhX}}K_{\mathrm{PhH}}$	Methoxybiphenyls isomer ratio			Partial rate factors			Methoxyphenyl-benzoates isomer ratio	
			o-	*m*-	*p*-	Fo	Fm	Fp	*o*-	*p*-
	Cupric *p*-toluate									
99	0.0402 (0.010)	1.66	68.79	19.84	11.38	3.42	0.99	1.13		
100	0.0406 (0.010)	1.45	67.92	20.90	11.17	2.95	0.91	0.97		
	Mean value	1.56	68.35	20.37	11.28	3.19	0.95	1.05		

(b) The decomposition of benzoyl peroxide in a solution containing various molar ratios of benzene and anisole

In this series of experiments, reactions with the relative concentrations of anisole and benzene vary from 3:1 (58.1 ml of anisole to 16.9 ml of benzene) to 1:3 (20.6 ml anisole to 54.4 ml benzene) were carried out using benzoyl peroxide (1.5 g) with or without additives. The analysis and work-up of the reaction mixture were similar to that used in the competitive reaction of equimolar mixture of the anisole and benzene.

The results are summarised in Table 15.

Table 15

The decomposition of benzoyl peroxide in solutions containing various molar ratios of anisole and benzene at 80°. Peroxide concentration = 0.083 M (1.5 g/75 ml)

Experiment No.	Molar ratio $[PhOMe]/[PhH]$	Additive g (mole/mole) peroxide	Biphenyl (mole/mole)	Methoxybiphenyls (mole/mole)	Total biaryl (mole/mole)	Relative rate factors K
101	2.817	Nil	0.070	0.496	0.566	2.50
102	2.817	Nil	0.075	0.491	0.566	2.32
103	0.308	Nil	0.274	0.249	0.524	2.96
104	0.308	Nil	0.268	0.274	0.542	2.88
		m-Dinitrobenzene				
105	2.817	0.3126 (0.300)	0.075	0.342	0.418	1.62
106	2.819	0.2011 (0.193)	0.078	0.370	0.448	1.69
107	0.308 (0.301)	0.3133	0.526	0.214	0.656	1.31
108	0.308 (0.300)	0.3128	0.597	0.210	0.739	1.13
		Cupric benzoate				
109	2.817	0.3005 (0.079)	0.097	0.432	6.529	1.58
110	2.819 (0.014)	0.0508	0.089	0.438	0.527	1.79

Table 15 (continued)

Experiment No.	Molar ratio $[PhOMe]/[PhH]$	Additive g (mole/mole) peroxide	Biphenyl (mole/mole)	Methoxybiphenyls (mole/mole)	Total biaryl (mole/mole)	Relative rate factors K
111	0.311	0.0510 (0.014)	0.484	0.236	0.720	1.57
112	0.308	0.2974 (0.078)	0.409	0.136	0.645	1.86
		Ferric benzoate				
113	2.819	0.5882 (0.087)	0.080	0.402	0.482	1.78
114	0.311 (0.086)	1.5778	0.379	0.197	0.576	1.67
115	0.2047	0.787 (0.117)	0.487	0.185	0.671	1.85
116	0.2047 (0.119)	0.8035	0.520	0.164	0.684	1.54

V. The phenylation reactions of t-butylbenzene

(a) The decomposition of benzoyl peroxide in t-butylbenzene

Benzoyl peroxide (1.0 g) was added to t-butylbenzene (50 ml) which was purged with oxygen-free nitrogen for 30 minutes. The reaction mixture was quickly heated to 80° and allowed to react under a nitrogen atmosphere for 72 hours. At the end of this period, the solution was allowed to cool and bibenzyl was added as an internal standard for g.l.c. analysis of the biaryls. The white crystals which precipitated were filtered and were not investigated further. The benzoic acid formed was separated by the standard method (see page 68). The neutral organic layer was taken for g.l.c. analysis. The three isomers of t-butylbiphenyls were completely separated on SE.15C column.

Six calibration solutions containing varying concentrations of bibenzyl and 4-t-butylbiphenyl were prepared. The relative peak area of 4-t-butylbiphenyl to bibenzyl is plotted against the relative molar ratio of 4-t-butylbiphenyl and bibenzyl.

2- and 3-t-Butylbiphenyls were not calibrated. Their amounts in the reaction mixture were determined from their peak area relative to that of bibenzyl, from the calibration curve of 4-t-butylbiphenyl to bibenzyl assuming that all the isomers have the same detector response.

This assumption is not unreasonable since the three isomers of t-butylbiphenyls are structurally similar. The analytical conditions and retention data are given below.

Column: SE.15C; Column temperature: 135°; Nitrogen pressure 1 Kp/cm^2

Attentuation: 50 x 10^2

Compounds:	Biphenyl,	Bibenzyl,	2-t-Butylbiphenyl,	3-t-Butylbiphenyl,	4-t-Butylbiphenyl
Retention data:	0.49	1.00	1.38	2.34	1.92

(b) The effects of additives on the decomposition of benzoyl peroxide in t-butylbenzene

The reactions containing additives were performed under similar conditions to those reactions without catalysts. The additives used were ferric benzoate, cupric benzoate and _m_-dinitrobenzene. The reaction mixture was analysed by the method described above. The results are summarised in Table 16.

Table 16

The decomposition of benzoyl peroxide in t-butylbenzene at 80°

Peroxide concentration = 0.083 M (1 g/50 ml)

Experiment No.	Additive g(mole/mole) peroxide	t-Butylbiphenyls (mole/mole)	Isomer ratio			Benzoic acid (mole/mole)	% Recovery of Phenyl group
			o-	m-	p-		
117	Nil	o.590	20.3	57.4	22.4	0.394	0.492
118	Nil	0.579	18.9	56.3	26.8	0.410	0.495
	Mean value of 117 & 118	0.585	19.6	56.9	23.5	0.402	0.494
	m-Dinitrobenzene						
119	0.2656 (0.380)	0.420	22.9	55.8	21.3	0.43	0.427
120	0.2617 (0.377)	0.446	23.8	54.7	21.5	0.460	0.453
	Mean value of 119 & 120	0.433	23.4	55.2	21.4	0.445	0.440
	Copper benzoate						
121	0.1068 (0.042)	0.476	25.0	50.5	24.5	0.625	0.551
122	0.101 (0.040)	0.489	24.4	53.0	22.6	0.645	0.567

Table 16 (continued)

Experiment No	Additive g (mole/mole) peroxide	t-Butylbiphenyls (mole/mole)	Isomer ratio *o*-	*m*-	*p*-	Benzoic acid (mole/mole)	% Recovery of Phenyl group
	Mean value of 121 & 122	0.484	24.7	51.8	23.5	0.635	0.559
	Ferric benzoate						
123	0.6063 (0.135)	0.498	21.9	50.8	27.3	0.431	0.465
124	0.6034 (0.133)	0.492	19.4	54.3	26.3	0.450	0.471
	Mean value of 123 & 124	0.495	20.7	52.6	26.8	0.4405	0.468

VI. The competitive reactions

The decompositions of benzoyl peroxide in an equimolar mixture of benzene and t-butylbenzene with and without the presence of additives

Benzoyl peroxide (1.5 g) was allowed to decompose in an equimolar mixture of t-butylbenzene (47.5 ml) and benzene (27.8 ml) with and without additives. The reactions were carried out according to the standard conditions described in section 2.D.II. At the completion of the reactions white crystals precipitated out from reactions containing cupric benzoate and also from reaction mixture containing no additive. Bibenzyl was added an an internal standard, the reaction mixture was processed by the standard method and analysed by g.l.c. using the same analytical conditions described in page 108 . An additional calibration graph of relative peak height against relative mole ratio was constructed for biphenyl with bibenzyl as internal standard to determine the yield of biphenyl in these reactions.

The results are in Tables 17 and 18.

Table 17

The decomposition of benzoyl peroxide in an equimolar mixture of benzene and t-butylbenzene (75 ml) at 80° for 72 hours. Peroxide concentration = 0.083 M (1.5 g/75 ml)

Experiment No.	Additive g (mole/mole) peroxide	Biphenyl (mole/mole)	t-Butylbiphenyls (mole/mole)	Total yield of biaryls (mole/mole)	Benzoic acid (mole/mole)
125	Nil	0.252	0.272	0.524	0.381
126	Nil	0.259	0.258	0.517	not determined
	Mean of 125 & 126	0.256	0.265	0.521	
	m-Dinitrobenzene				
127	0.4020 (0.386)	0.363	0.312	0.675	0.857
128	0.4017 (0.386)	0.376	0.323	0.699	0.835
	Mean of 127 & 128	0.340	0.318		0.846
	Nitrobenzene				
129	0.4948 (0.4750)	0.382	0.302	0.684	0.918
130	0.4981 (0.478)	0.417	0.298	0.714	0.769

Table 17 (continued)

Experiment No.	Additive g (mole/mole) peroxide	Biphenyl (mole/mole)	t-Butylbiphenyls (mole/mole)	Total yield of biaryl (mole/ mole)	Benzoic acid (mole/mole)
	Mean of 129 & 130	0.399	0.300	0.699	0.844
	Cupric benzoate				
131	0.0408 (0.011)	0.370	0.270	0.640	not determined
132	0.0406 (0.011)	0.390	0.279	0.669	0.909
	Mean of 131 & 132	0.380	0.275	0.654	0.909
	Ferric benzoate				
133	0.5946 (0.088)	0.316	0.332	0.648	0.735
134	0.5981 (0.089)	0.342	0.336	0.678	0.751
	Mean of 133 & 134	0.330	0.334	0.663	

Table 18

The rate factors and isomer ratios of the benzene/t-butylbenzene systems at 80°.

Peroxide concentration = 0.083 M (1.5 g/75 ml)

Experiment No	Additive g(mole/mole) peroxide	Relative rate ${}^{tBu}_{H}K$	Isomer ratio			Partial rate factors		
			o-	m-	p-	Fo	Fm	Fp
125	Nil	1.08	18.60	54.96	26.45	0.60	1.78	1.71
126	Nil	1.04	18.20	54.05	27.75	0.57	1.69	1.73
	Mean	1.06	18.40	54.50	27.10	0.59	1.74	1.72
	m-Dinitrobenzene							
127	0.4020 (0.386)	0.86	23.70	50.18	26.12	0.61	1.29	1.35
128	0.4017 (0.386)	0.86	22.72	50.77	26.51	0.59	1.31	1.37
	Mean	0.86	23.21	50.48	26.32	0.60	1.30	1.36
	Nitrobenzene							
129	0.4948 (0.475)	0.79	22.36	54.35	23.29	0.53	1.29	1.10
130	0.4981 (0.478)	0.72	21.92	49.32	28.77	0.47	1.07	1.24
	Mean	0.76	22.14	51.83	26.03	0.50	1.18	1.17

Table 18 (continued)

Experiment No.	Additive g(mole/mole) peroxide	Relative rate ${}^{tBu}_{H}K$	Isomer ratio o-	Isomer ratio m-	Isomer ratio p-	Partial rate factors Fo	Partial rate factors Fm	Partial rate factors Fp
	Cupric benzoate							
131	0.0408 (0.011)	0.73	23.76	50.34	25.90	0.52	1.10	1.13
132	0.0406 (0.011)	0.72	23.17	49.47	27.36	0.50	1.07	1.18
	Mean	0.73	23.47	49.91	26.62	0.51	1.09	1.16
	Ferric benzoate							
133	0.5946 (0.088)	1.05	20.52	50.79	28.68	0.65	1.60	1.81
134	0.5981 (0.089)	0.98	19.39	51.30	29.31	0.57	1.51	1.72
	Mean	1.02	19.96	51.05	28.99	0.61	1.56	1.77

VII. The competitive reactions between two mono-substituted benzenes

(a) The effects of additives on the decomposition of benzoyl peroxide in an equimolar mixture of anisole and toluene

Benzoyl peroxide (1.5 g) was allowed to decompose in an equimolar mixture of toluene (37.1 ml) and anisole (38.2 ml) with or without additive according to the methods described for competitive reactions in previous sections. At the completion of the reaction, pentamethylbenzene was added as an internal standard. The benzoic acid was separated with the appropriate methods described in page 68 . The neutral organic solution was analysed with the following analytical conditions. The yields of 2-methylbiphenyl and 3- and 4-methylbiphenyls together, and that of bibenzyl were determined according to the method described in section 2.D.I, using SE.15C column. The yields of 2-, 3- and 4-methoxybiphenyls were determined by using SE 15C column The yields of methoxyphenylbenzoates were not determined. The results are summarised in Tables 19 and 20. The analytical conditions are listed below.

Column: SE. 15C; Column temperature: 130^{o}; Carrier gas: Nitrogen

Pressure: 1 Kp/cm^{2} ; Atten uation: 50 x 10^{-2}

Compounds	Relative Retention Time
Pentamethylbenzene	1.00
2-Methylbiphenyl	1.75
3-Methylbiphenyl	2.75
4-Methylbiphenyl	2.75
Bibenzyl	3.31
2-Methoxybiphenyl	3.88
3-Methoxybiphenyl	5.69
4-Methoxybiphenyl	6.31

Table 19

The decomposition of benzoyl peroxide in an equimolar solution of anisole and toluene at 80°. Peroxide concentration = 0.083 M (1.5 g/75 ml)

Experiment No.	135	136	137	138	139	140	141	142
Additive (g) (mole/mole)	Nil	Nil	m-Dinitrobenzene (0.2011) (0.1927)	m-Dinitrobenzene 0.2010 (0.1021)	Copper benzoate 0.2566 (0.0666)	Copper benzoate 0.2549 (0.0670)	Ferric benzoate 0.5982 (0.0882)	Ferric benzoate 0.6009 (0.0892)
Methoxybiphenyls (mole/mole)	0.357	0.356	0.284	0.266	0.236	0.231	0.239	0.235
Methylbiphenyls (mole/mole)	0.215	0.227	0.207	0.208	0.182	0.195	0.175	0.179
Total yield of biaryls (mole/mole)	0.572	0.583	0.491	0.475	0.418	0.425	0.415	0.414
Total rate factor $^{\text{MeO}}K_{\text{Me}}$	1.66	1.57	1.37	1.28	1.30	1.19	1.37	1.320
Mean value	1.62		1.33		1.25		1.35	

Table 20

The total rate factors determined from the decomposition of benzoyl peroxide in an equimolar mixture of anisole and toluene at 80°, 72 hours. Peroxide concentration = 0.083 M (1.5 g/75 ml)

Experiment No.	Additive g(mole/mole)	$^{\mathrm{MeO}}_{\mathrm{CH_3}}K$	$^{\mathrm{MeO}}_{\mathrm{H}}K$ $\left[{}^{\mathrm{MeO}}_{\mathrm{CH_3}}K \cdot {}^{\mathrm{CH_3}}_{\mathrm{H}}K\right]$	$^{\mathrm{CH_3}}_{\mathrm{H}}K$ $\left[{}^{\mathrm{MeO}}_{\mathrm{H}}K / {}^{\mathrm{MeO}}_{\mathrm{CH_3}}K\right]$
135	Nil	1.66	2.99	1.92
136	Nil	1.57	2.83	2.03
Mean value of	135 & 136	1.62	2.91	1.98
137	m-Dinitrobenzene 0.2011 (0.1027)	1.37	1.98	1.32
138	m-Dinitrobenzene 0.2010 (0.1021)	1.28	1.86	1.41
Mean value of	137 & 138	1.33	1.92	1.37
139	Cupric benzoate 0.2566 (0.0666)	1.30	1.81	1.25
140	Cupric benzoate 0.2549 (0.670)	1.19	1.66	1.36
Mean value of	139 & 140	1.25	1.74	1.30
141	Ferric benzoate 0.5982 (0.0882)	1.37	2.30	1.34
142	Ferric benzoate 0.6009 (0.0892)	1.32	2.21	1.39
Mean value of	141 & 142	1.35	2.26	1.37
Best value		1.30	2.0	1.40

(b) The effects of additives on the decomposition of benzoyl peroxide in an equimolar mixture of anisole and t-butylbenzene

A number of experiments, each with benzoyl peroxide (1.5 g) and a known amount of additive (if any) in an equimolar mixture of anisole (31.5 ml) and t-butylbenzene (43.5 ml), were performed according to the standard procedure described previously. Pentamethylbenzene and bibenzyl were added as internal standards for the quantitative determination of methoxybiphenyls and t-butylbiphenyls respectively. The benzoic acid was separated by the appropriate methods described previously according to the nature of the additives present. The yields of 2- and 4-methoxyphenylbenzoates were not determined. The analytical conditions used were listed below. The results are summarised in Tables 21 and 22.

Column: SE.15C	Column temperature: 130°
Attenuation: 50×10^{-2}	Carrier gas: Nitrogen
Pressure: 1Kp/cm^2	

Compounds	Relative retention time
Pentamethylbenzene (internal standard)	1.00
Bibenzyl (internal standard)	4.14
2-Methoxybiphenyl	4.91
2-t-Butylbiphenyl	6.00
3-Methoxybiphenyl	7.64
4-Methoxybiphenyl	8.46
3-t-Butylbiphenyl	10.27
4-t-Butylbiphenyl	12.91

Table 21

The decomposition of benzoyl peroxide in an equimolar mixture of anisole and t-butylbenzene at 80°. Peroxide concentration = 0.0803 M (1.5 g/75 ml)

Experiment No.	143	144	145	146	147	148	149	150
Additive (g) (mole/mole)	Nil	Nil	m-Dinitrobenzene 0.3984 (0.3816)	m-Dinitrobenzene 0.4016 (0.3847)	Cupric benzoate 0.2564 (0.0676)	Cupric benzoate 0.2592 (0.0683)	Ferric benzoate 0.4554 (0.0675)	Ferric benzoate 0.4560 (0.0677)
Methoxybiphenyls (mole/mole)	0.436	0.445	0.394	0.386	0.397	0.383	0.386	0.383
t-Butylbiphenyls (mole/mole)	0.177	0.189	0.179	0.204	0.198	0.183	0.176	0.178
Total biaryl (mole/mole)	0.613	0.634	0.572	0.590	0.595	0.565	0.562	0.561
Relative rate								
$^{MeO}_{tBu}K$	2.46	2.36	2.20	1.89	2.00	2.10	2.20	2.15
Mean value	2.41		2.05		2.05		2.18	

Table 22

The total rate factors determined from the decomposition of benzoyl peroxide in an equimolar mixture of anisole and t-butylbenzene at 80°, 72 hours. Peroxide concentration = 0.083 M

Experiment No.	Additive g(mole/mole)	${}^{MeO}_{tBu}K$	${}^{MeO}_{H}K$ $\left[{}^{MeO}_{tBu}K \cdot {}^{tBu}_{H}K\right]$	${}^{tBu}_{H}K$ $\left[{}^{MeO}_{H}K / {}^{MeO}_{tBu}K\right]$
143	Nil	2.46	2.49	1.29
144	Nil	2.36	2.39	1.35
Mean value of 143 & 144		2.41	2.44	1.32
145	*m*-Dinitrobenzene 0.3984 (0.3816)	2.20	1.89	0.82
146	*m*-Dinitrobenzene 0.4016 (0.3847)	1.89	1.63	0.96
Mean value of 145 & 146		2.05	1.76	0.89
147	Cupric benzoate 0.2564 (0.0676)	2.00	1.46	0.81
148	Cupric benzoate 0.2592 (0.0683)			
Mean value of 147 & 148		2.05	1.50	0.79
149	Ferric benzoate 0.4554 (0.0675)	2.20	2.24	0.83
150	Ferric benzoate 0.4560 (0.0677)	2.15	2.19	0.85
Mean value of 149 & 150		2.18	2.22	0.84
Best value		2.10	1.80	0.84

(c) The effect of additives on the decomposition of benzoyl peroxide in an equimolar mixture of toluene and t-butylbenzene

A series of experiments was performed according to the standard procedure. Benzoyl peroxide (1.5 g) was allowed to decompose in an equimolar mixture of toluene (30.5 ml) and t-butylbenzene (44.5 ml) for 72 hours under a stream of nitrogen. At the end of the reaction, dibenzyl ether (0.1 - 0.15 g) was added as an internal standard for the quantitative determination of t-butylbiphenyls, methyl biphenyls and bibenzyl formed. The relative peak area of t-butylbiphenyls to dibenzyl ether was determined and their yields are determined from the relative peak area against relative mole ratio calibration curve of 4-t-butylbiphenyl against dibenzyl ether. The yields of the methylbiphenyls and bibenzyl were determined from the relative peak height against relative mole ratio calibration curves. The analytical conditions are given below. The results obtained are given in Tables 23 and 24.

Column: SE 15C   Column temperature: 130°

Attenuation: 50×10^2 Carrier gas: Nitrogen

Pressure: 1 Kp/cm^2

Compounds	Relative retention time
2-Methylbiphenyl	0.29
3-Methylbiphenyl	0.46
4-Methylbiphenyl	0.46
Bibenzyl	0.54
2-t-Butylbiphenyl	0.75
Dibenzyl ether (internal standard)	1.00
3-t-Butylbiphenyl	1.26
4-t-Butylbiphenyl	1.58

Table 23

The decomposition of benzoyl peroxide in an equimolar mixture of toluene and t-butylbenzene at 80°

Peroxide concentration = 0.083 M (1.5 g/75)

Experiment No.	151	152	153	154	155	156	157	158	159
Additive (g) (mole/mole)	Nil	Nil	m-Dinitrobenzene 0.2036 (0.1954)	m-Dinitrobenzene 0.2025 (0.1943)	Cupric benzoate 0.0456 (0.0120)	Cupric benzoate 0.0458 (0.0121)	Ferric benzoate 0.5916 (0.0878)	Ferric benzoate 0.6000 (0.0888)	Ferric benzoate 0.5958 (0.0886)
Methylbiphenyls (mole/mole)	0.2892	0.2797	0.2674	0.1945	0.2366	0.2431	0.3042	0.3403	0.3087
t-Butylbiphenyls (mole/mole)	0.1791	0.1882	0.1883	1.2367	0.1891	0.1568	0.2074	10.092	0.1948
Total biaryl (mole/mole)	0.4683	0.4679	0.4557	0.5312	0.4257	0.3999	0.5116	0.5495	0.5035
Total rate factors $K^{CH_3}_{tBu}$	1.61	1.49	1.42	1.24	1.25	1.55	1.47	1.63	1.59
Mean value	1.55		1.33		1.40		1.56		

Table 24

The total rate factors determined from the decomposition of benzoyl peroxide in an equimolar mixture of t-butylbenzene and toluene at 80°, 72 hours

Peroxide concentration = 0.083 M (1.5 g/75 ml)

Experiment	Additive g(mole/mole)	${}^{CH_3}_{tBu}K$	${}^{CH_3}_{H}K$(calc) $\left[{}^{CH_3}_{tBu}K \cdot {}^{tBu}_{H}K\right]$	${}^{tBu}_{H}K$(calc) $\left[{}^{CH_3}_{H}K / {}^{CH_3}_{tBu}K\right]$
151	Nil	1.61	1.61	1.11
152	Nil	1.49	1.49	1.21
Mean value of 151 & 152		1.55	1.55	1.16
153	m-Dinitrobenzene 0.2036 (0.1954)	1.42	1.14	1.02
154	m-Dinitrobenzene 0.2025 (0.1943)	1.24	0.992	1.17
Mean value of 153 & 154		1.33	1.07	1.10
155	Cupric benzoate 0.0456 (0.0120)	1.25	0.94	1.11
156	Cupric benzoate 0.0458 (0.0121)	1.55	1.16	0.90
Mean value of 155 & 156		1.40	1.05	1.01
157	Ferric benzoate 0.5916 (0.0878)	1.42	1.47	0.96
158	Ferric benzoate 0.6000 (0.0888)	1.63	1.63	0.87
159	Ferric benzoate 0.5958 (0.0886)	1.59	1.59	0.87
Mean value of 157 & 158 & 159		1.56	1.56	0.90
Best value		1.4	1.2	1.0

E. The Homolytic Aromatic Silylation Reactions

I. The reactions of phenyldimethylsilyl radicals with benzene

(a) The reaction of phenyldimethylsilane with benzene in the presence of azo-bis-isobutyronitrile

Phenyldimethylsilane (1.5 g) and azo-bis-isobutyronitrile (0.85 g to 4.6 g) were dissolved in deareated benzene (50 ml). The solution was heated to 80° in a thermostat under a steady stream of oxygen-free nitrogen and allowed to react at that temperature for 48 hours. At the completion of the reaction, the solid precipitate (ca. 0.49 g to 1.5 g) was filtered and was not investigated further. The reaction mixture was concentrated to about 20 ml by removing the excess of benzene in an efficient rotary evaporator after pentamethylbenzene (0.1 g) had been added as internal standard for quantitative analysis. The following compounds were identified by comparison with authentic species prepared separately: dimethyldiphenylsilane, diphenyltetramethyldisilane. A compound with identical retention time to biphenyl was detected. The yields of dimethyldiphenylsilane and diphenyltetramethyldisilane were determined by constructing calibration curves of these compounds with pentamethylbenzene.

The experimental conditions are given below. The results are shown in Table 25.

Column: OV1 Column temperature: 110°

Pressure: 1.0 Kp/cm^2 Attenuation: 20 x 10^{-2}

Compounds	Retention time (relative)
Pentamethylbenzene	1.0
Diphenyldimethylsilane	4.43
Diphenyltetramethyldisilane	10.14

The unreacted phenyldimethylsilane was determined by using p-dichlorobenzene as an internal standard with the following experimental conditions:

Column: OV1 | Column temperature: 50^{o}

Pressure: 1.0 Kp/cm^2 | Attenuation: 1×10^4

Compound	Retention time (relative)
p-Dichlorobenzene	1.0
Phenyldimethylsilane	0.65

(b) The reaction of phenyldimethylsilane and benzene in the presence of benzoyl peroxide

Phenyldimethylsilane (0.5 g to 1.5 g) and benzoyl peroxide (0.5 to 1.2 g) were dissolved in benzene (50 ml). The reaction was performed and the products analysed according to the methods described in the preceding section. The major products in these reactions were biphenyl, diphenyldimethylsilane, diphenyltetramethyldisilane and a few unidentified species. The results are given in Table 25.

(c) The photolysis of t-butyl peroxide and phenyldimethylsilane in benzene

In this experiment phenyldimethylsilane (4.0 g) and t-butyl peroxide (6.0 g) were dissolved in 500 ml of deaereated benzene in a Hanovia IL photochemical reactor. The reactor was covered with aluminium foil to minimise the loss of u.v. radiation. The solution was photolysed at room temperature for 100 hours under a steady stream of nitrogen to sweep away the ozone formed above the surface of the reaction mixture. At the end of the reaction pentamethylbenzene was added as an internal standard for g.l.c. analysis. There were at least six products formed: t-butyl alcohol, biphenyl, diphenyldimethylsilane and diphenyltetramethyldisilane were amongst them. Similar analytical conditions as employed in the previous sections were used. In another reaction a more concentrated

Table 25

The reactions of silyl radicals with benzene at 80°

Experiment No.	160	161	162	163
Benzene	50 ml	50 ml	50 ml	50 ml
Radical initiators	AIBN (5.2 x 10^{-3} mole)	AIBN (5.2 x 10^{-3} mole)	AIBN (2.8 x 10^{-2} mole)	AIBN (2.9 x 10^{-2} mole)
Time	24 hours	24 hours	24 hours	24 hours
Phenyldimethylsilane:				
Initial amount	5.02 x 10^{-3} mole	5.04 x 10^{-3} mole	1.1 x 10^{-2} mole	1.2 x 10^{-2} mole
Amount remaining unreacted	1.16 x 10^{-3} mole	1.3 x 10^{-3} mole	4.26 x 10^{-3} mole	4.03 x 10^{-3} mole
Amount consumed	3.86 x 10^{-3} mole	3.74 x 10^{-3} mole	6.74 x 10^{-3} mole	7.97 x 10^{-3} mole
Biphenyl	N.D.	N.D.	3.87 x 10^{-4} mole 0.06 mole/mole silane consumed	N.D.
Diphenyldimethylsilane	9.3 x 10^{-5} mole (2.4%)	5.24 x 10^{-5} mole (1.4%)	5.09 x 10^{-4} mole (7.6%)	1.12 x 10^{-3} mole (14%)
Diphenyltetramethyldisilane	N.D.	N.D.	9.2 x 10^{-4} mole (14%)	1.36 x 10^{-3} mole (17%)

Table 25 (continued)

Experiment No.	164	165	166	167
Benzene	50 ml	100 ml	500 ml	500 ml
Radical initiator	Benzoyl peroxide 2.0×10^{-3} mole	Benzoyl peroxide 4.96×10^{-3} mole	u.v. t-butylperoxide (3.4×10^{-2} mole)	u.v., t-butylperoxide (4.2×10^{-2} mole)
Temperature °C	80	80	Room temperature	Room temperature
Time	72 hours	72 hours	100 hours	100 hours
Phenyldimethylsilane:				
Initial amount	2.28×10^{-3} mole	4.953×10^{-3} mole	4.333×10^{-2} mole	2.93×10^{-2} mole
Amount remaining unreacted	1.09×10^{-3} mole	2.968×10^{-3} mole	1.995×10^{-2} mole	4.45×10^{-3} mole
Amount consumed	1.19×10^{-3} mole	1.985×10^{-3} mole	2.338×10^{-2} mole	2.48×10^{-2} mole
t-Butyl alcohol	Nil	Nil	N.D.	N.D.
Biphenyl	N.D.	N.D.	N.D.	4.7×10^{-4} mole 0.02 mole/mole silane cons.
Diphenyldimethylsilane	3.57×10^{-4} mole (30%)	6.95×10^{-4} mole (35%)	7.88×10^{-3} mole (33.6%)	1.87×10^{-3} mole (7.5%)
Diphenyltetramethyl-disilane	2.38×10^{-5} mole (2%)	Trace	5.47×10^{-3} mole (23.4%)	1.82×10^{-3} mole (14.5%)

Table 25 (continued)

Experiment No.	168	169
Benzene	500 ml	50 ml
Radical initiator	u.v. light	u.v. light
Temperature	Room temperature	Room temperature
Time	100 hours	100 hours
Phenyldimethylsilane:		
Initial amount	3.474×10^{-2} mole	3.72×10^{-2} mole
Amount remaining unreacted	2.03×10^{-2} mole	3.14×10^{-3} mole
Amount consumed	1.434×10^{-2} mole	3.38×10^{-2} mole
Biphenyl	Not determined	2.89×10^{-4} mole 0.01 mole/mole silane consumed
Diphenyldiemthylsilane	3.36×10^{-3} mole (23%)	7.8×10^{-4} mole (6%)
Diphenyltetramethyldisilane	Trace	2.11×10^{-3} mole (12%)

Notes:

AIBN = azo-*bis*-isobutyronitrile

N.D. = Detected, yield not determined.

solution of t-butyl peroxide (6.0 g) and phenyldimethylsilane (5.0 g) in benzene (50 ml) was performed. The results are summarised in Table 25.

(d) The photolysis of phenyldimethylsilane in benzene

Phenyldimethylsilane (4.7 g) was dissolved in deareated benzene (500 ml) in a photochemical reactor. The reaction was carried out under the conditions used for reactions in the preceding section, and at the end of the reaction the products were identified by using similar analytical conditions. In another set of experiments a more concentrated solution was used (5 g/50 ml). The results are in Table 25.

II. The Reaction of Phenyldimethylsilyl Radicals with Toluene

(a) The photolysis of the t-butyl peroxide, phenyldimethylsilane and toluene system

t-Butyl peroxide (5.2 g) and phenyldimethylsilane (5.0 g) were dissolved in toluene (500 ml). The solution was photolysed for 50 hours. At the end of this period, excess of toluene was removed by an efficient rotary evaporator. G.l.c. analysis showed that the main reaction product was bibenzyl which was formed in so large a quantity that the g.l.c. peak due to it masked the peaks of other products and rendered analysis for other products difficult. Consequently further analysis of the product was not carried out.

(b) The photolysis of phenyldimethylsilane in toluene

A solution of phenyldimethylsilane (4.6 g) in toluene (500 ml) was photolysed for 50 hours., after which period the solution was concentrated to 100 ml and the residue was taken for g.l.c. analysis. The following products, together with some unknown products were formed: bibenzyl, diphenyldimethylsilane, *o*- and *m*- and *p*-(phenyldimethylsilyl)toluene and diphenyltetramethyldisilane. The yields of these products are determined by constructing calibration graphs with pentamethylbenzene as an internal standard. The phenyldimethylsilane remained unreacted and was determined by adding p-dichlorobenzene as the internal standard as used in section 2.E.I(a). Only one experiment was performed. The experimental conditions are given below. The results are summarised in Table 26.

Column AP. 15C Column temperature: 185°C

Nitrogen pressure: 1.0 Kp/cm^2 Attenuation: 50 x 10^2

Compounds	Relative Retention time
Pentamethylbiphenyl	1.00
Diphenyldimethylsilane	1.50
Bibenzyl	1.88
m-(Phenyldimethylsilyl)toluene	2.38
o- and p-(Phenyldimethylsilyl)toluene	2.75
Diphenyltetramethyldisilane	3.88

Table 26

Reactions of silyl radicals with toluene

Experiment No.	170
Temperature	Room temperature
Radical initiator	u.v. light
Hours of irradiation	50 hours
Toluene (ml)	500 ml
Phenyldimethylsilane:	
Initial amount	0.034 mole (0.068 M)
Amount remaining unreacted	0.014 mole
Amount consumed	0.020 mole
Diphenyldimethylsilane	N.D.
o- and *p*-(Phenyldimethylsilyl)toluene	1.92×10^{-3} mole(9.6 %)
m-(Phenyldimethylsilyl)toluene	4×10^{-4} mole (2%)
Diphenyltetramethyldisilane	1.56×10^{-3} mole (7.8%)
Bibenzyl	2.28×10^{-3} mole (11.4%)
Isomer Ratio : Phenyldimethylsilyltoluene	
o- and *p*-	83%
m-	17%

III. The reaction of phenyldimethylsilane with naphthalene in the presence of t-butyl peroxide

To naphthalene (50 g) was added t-butyl peroxide (2.9 g) and phenyldimethylsilane (2.5 g). The reaction mixture was rapidly heated to 130° under a stream of nitrogen gas and maintained at that temperature for 24 hours. At the completion of the reaction, excess of naphthalene was removed by distillation. The distillate was analysed for unreacted phenyldimethylsilane using p-dichlorobenzene as an internal standard using the g.l.c. conditions employed in section 2E.I(a).

The residue (15 g) was dissolved in 20 ml of hot benzene. The solution was analysed by g.l.c. and the following products were identified by comparison of retention time with authentic compounds: α- and β-(phenyldimethylsilyl)naphthalenes, diphenyltetramethyldisilane and at least 2 other products. After the qualitative analysis, p-nitrobiphenyl was added as an internal standard for quantitative determination of α- and β-(phenyldimethylsilyl)naphthalene, and pentamethylbenzene was also added for the determination of the amount of diphenyltetramethyldisilane formed. The experimental conditions for the analysis of α-, and β-silylnaphthalene are given below. The results are shown in Table 27.

Column: OV1	Column temperature: 175°
Nitrogen pressure: 1.5 Kp/cm^2	Attenuation: 1 x 10^4

Compounds	Relative retention time
p-Nitrobiphenyl	1.00
α-(Phenyldimethylsilyl)naphthalene	0.56
β-(Phenyldimethylsilyl)naphthalene	0.68
Unidentified peak	0.30
Unidentified peak	0.14

Table 27

The reactions of silyl radicals with naphthalene at 130°

Experiment No.	173	174
Naphthalene (g)	50 g	50 g
t-Butyl peroxide (mole)	0.020 mole	0.021 mole
Phenyldimethylsilane (mole):		
Initial amount	0.0183 mole	0.0184 mole
Amount remaining unreacted	2.33×10^{-3} mole	7.4×10^{-3} mole
Amount consumed	0.016 mole	0.011 mole
α-(Phenyldimethylsilyl)naphthalene	2.21×10^{-3} mole (13.8%)	2.45×10^{-3} mole (22.3%)
β-(Phenyldimethylsilyl)napthalene	7.37×10^{-4} mole (4.6%)	1.00×10^{-3} mole (9.1%)
Diphenyltetramethyldisilane	Detected, yield not determined	Detected, yield not determined
Isomer ratio		
Phenyldimethylsilylnaphthalene		
α-	75%	72%
β-	25%	28%

IV. The reactions of phenyldimethylsilane with chlorobenzene in the presence of t-butyl peroxide

t-Butyl peroxide (1.6 g) and phenyldimethylsilane (1.5 g) were added to chlorobenzene (50 ml). The solution was allowed to react at 130° for 24 hours under a nitrogen atmosphere. At the completion of the reaction, the reaction was analysed by g.l.c. The following major products were identified o-, m-, and p-chlorobiphenyls, diphenyldimethylsilane and diphenyltetramethyldisilane. Phenyldimethylchlorosilane was also detected at lower column temperature. There were at least 4 unidentified peaks. The yields of o-, m- and p-chlorobiphenyls are determined using SE 15C stationary phase and those of diphenyldimethylsilane and diphenyltetramethyldisilane were determined with a OV1 column. The internal standard used in these determinations is pentamethylbenzene. The yields of m- and p-chlorobiphenyls were determined together as they could not be separated on the AP.15C column. With other columns these two isomers could be separated but their peaks overlapped with peaks from other reaction products. Durene was added to determine the amount of phenyldimethylsilane unreacted. The yield of phenyldimethylchlorosilane was not determined owing to the ready hydrolysis of this compound in moist air. The experimental conditions are listed below. The results are summarised in Table 28.

Column AP. 15C	Column temperature: 200°
Pressure: 1.0 Kp/cm^2	Attenuation: 20 x 10^2
Compounds	**Relative retention time**
Pentamethylbenzene	1.00
Diphenyldimethylsilane	2.80
2-Chlorobiphenyl	2.20
3-Chlorobiphenyl	3.20
4-Chlorobiphenyl	3.20
Diphenyltetramethyldisilane	5.70

Table 28

The reaction of silyl radicals with chlorobenzene at 130°

Experiment No.	171	172
Chlorobenzene	50 ml	50 ml
t-Butyl peroxide	0.011 mole (0.220 M)	0.012 mole (0.240 M)
Phenyldimethylsilane:		
Initial amount	0.11 mol (0.220 M)	0.011 mole (0.220 M)
Amount remaining unreacted	1.01×10^{-3} mole	9.28×10^{-4} mole
Amount consumed	9.9×10^{-3} mole	0.010 mole
t-Butanol	detected, yield not determined	N.D.
Phenyldimethylchlorosilane	detected, yield not determined	N.D.
Diphenyldimethylsilane	5.01×10^{-3} mole (50.6%)	5.26×10^{-3} mole (52.6%)
Diphenyltetramethyldisilane	1.05×10^{-3} mole (10.6%)	0.97×10^{-3} mole (9.7%)
o-Chlorobiphenyl	1.10×10^{-3} mole (11.1%)	1.213×10^{-3} mole (12.1%)
m- and p-Chlorobiphenyl	9.68×10^{-4} mole (9.8%)	1.107×10^{-3} mole (11.1%)
Isomer ratio: Chlorobiphenyl		
o-	53.2%	52.3%
m- and p-	46.8%	48.6%

V. The reaction of phenyldimethylsilane with p-dichlorobenzene in the presence of t-butyl peroxide

t-Butyl peroxide (1.0 g) and phenyldimethylsilane (1.0 g) were added to *p*-dichlorobenzene (34 g). The reaction was allowed to proceed for 24 hours at 130°. At the end of this period, Durene (1.1 g) was added as an internal standard for the g.l.c. determination of unreacted phenyldimethylsilane. After this determination, the reaction mixture was concentrated by distillation. The residue was dissolved in benzene and taken for g.l.c. analysis. The following major products were identified: *p*-chlorophenylsilane, 2,4',5-trichlorobiphenyl and diphenyltetramethyldisilane. Phenyldimethylchlorosilane was also detected at a column temperature of 90°C. Pentamethylbenzene was added as an internal standard for the determination of the yield of (phenyldimethyl)-*p*-chlorophenylsilane and diphenyltetramethyldisilane, while 4-bromobiphenyl was added for the determination of the amount of 2,4',5-trichlorobiphenyl formed.

The experimental conditions are shown below, the results are given in Table 29.

Column: OV1	Column temperature: 150°
Pressure: 1.0 Kp/cm^2	Attenuation: 20 x 10^2

Compounds	Relative retention time
4-Bromobiphenyl	1.00
p-Chloro-(phenyldimethylsilyl)benzene	1.39
Diphenyltetramethyldisilane	1.74
2,4',5-Trichlorobiphenyl	2.44

Table 29

The reactions of silyl radicals with p-dichlorobenzene at 130°

Experiment No.	175	176
p-Dichlorobenzene (g)	34 g	34 g
t-Butyl peroxide (mole)	7.53×10^{-3} mole	7.58×10^{-3} mole
Phenyldimethylsilane:		
Initial amount	7.4×10^{-3} mole	7.3×10^{-3} mole
Amount remaining unreacted	4.9×10^{-3} mole	4.9×10^{-3} mole
Amount consumed	2.5×10^{-3} mole	2.70×10^{-3} mole
p-Chloro-(phenyldimethylsilyl)benzene	2.4×10^{-4} mole (9.6%)	3.0×10^{-4} mole (11.1%)
Diphenyltetramethyldisilane	1.10×10^{-4} mole (4.4%)	1.04×10^{-4} mole (4%)
2,4',5-Trichlorobiphenyl	1.36×10^{-4} mole (5.5%)	1.41×10^{-4} mole (5.2%)

VI. The reaction of phenyldimethylsilane with bromobenzene in the presence of t-butyl peroxide

A solution containing t-butyl peroxide (1.5 g) phenyldimethylsilane (1.0 g) in bromobenzene (50 ml) was allowed to react for 24 hours at 130°. At the completion of the reaction, pentamethylbenzene was added as an internal standard. The major reaction products were the three isomeric bromophenyls together with a little of the dimer of the silyl radical. The bromo biphenyl peaks were calibrated with pentamethylbenzene as an internal standard, m- and p-bromobiphenyls being only partially separated under the experimental conditions employed, so that correction factors were determined for each isomer (1.0 and 0.88 for m- and p-bromobiphenyl respectively). The amount of phenyldimethylsilane remaining unreacted was not determined because the silane has the same retention time as bromobenzene and could not be separated.

A set of control experiments containing only t-butyl peroxide in bromobenzene was performed under similar experimental conditions. Only a little bromobiphenyl was formed in this reaction. The g.l.c. analytical conditions are given below, and the results are in Table 30.

Column: AP 20 Column temperature: 185°C

Nitrogen pressure: 1.0 Kp/cm^2

Attenuation: 50 x 10^2

Compounds	Relative retention time
Pentamethylbenzene	1.00
2-Bromobiphenyl	4.14
3-Bromobiphenyl	7.20
4-Bromobiphenyl	7.80

Table 30

The reactions of silyl radicals with bromobenzene at 130°

Experiment No.	177	178
Bromobenzene	50 ml	50 ml
t-Butyl peroxide (mole)	9.39×10^{-3} mole	0.0.13 mole
Phenyldimethylsilane (mole)		
Initial amount	7.354×10^{-3} mole	7.362×10^{-3} mole
o-Bromobiphenyl	2.19×10^{-3} mole	2.32×10^{-3} mole
m-Bromobiphenyl	9.16×10^{-4} mole	1.02×10^{-3} mole
p-Bromobiphenyl	4.88×10^{-4} mole	5.53×10^{-4} mole
Isomer Ratio		
o-Bromobiphenyl	60.9%	59.6%
m-Bromobiphenyl	25.5%	26½2%
p-Bromobiphenyl	13.6%	14.2%

VII. The reaction of phenyldimethylsilane with anisole in the presence of t-butyl peroxide

t-Butylperoxide (1.0 g) was allowed to decompose in anisole (50 ml) containing phenyldimethylsilane (1.0 g) at 130° for 24 hours under a nitrogen atmosphere. The following reaction products were detected using an OV 1 column: t-butyl alcohol, o-methylanisole(trace) at lower temperature (60°C), diphenyltetramethyldisilane, o- m- and p-(phenyldimethylsilyl) anisole and at least four unidentified peaks at 120 C°. Using the OV 1 column the m-isomer overlapped with one unknown compound and consequently, its peak height was boosted. However the m-(phenyldimethylsilyl) anisole was separated completely using the AP 15C column, and with the two columns it was possible to determine the yields of o-, m- and p-(phenyldimethylsilyl)anisole.

Column: OV 1

Column temperature: 120°

Nitrogen pressure: 1.0 Kp/cm^2

Attenuation: 20 x 10^2

Compounds	Relative retention time
Pentamethylbenzene	1.00
Diphenyldimethylsilane	1.75
Diphenyltetramethyldisilane	3.88
o-(Phenyldimethylsilyl)anisole	4.21
m-(Phenyldimethylsilyl)anisole	5.50
p-(Phenyldimethylsilyl)anisole	6.58

Table 31

The reaction of silyl radicals with anisole at 130°

Experiment No.	179	180
Anisole	50 ml	50 ml
t-Butyl peroxide (mole)	6.90 x 10^{-3} mole	7.3 x 10^{-3} mole
Phenyldimethylsilane (mole):		
Initial amount	7.39 x 10^{-3} mole (0.1478 M)	7.36 x 10^{-3} mole (0.1472 M)
Amount remaining unreacted	5.54 x 10^{-3} mole	5.87 x 10^{-3} mole
Amount consumed	18.5 x 10^{-4}	15.2 x 10^{-3} mole
Diphenyldimethylsilane	0.74 x 10^{-4} mole (4%)	1.22 x 10^{-4} mole (8%)
Diphenyltetramethyldisilane	1.1 x 10^{-4} mole (6%)	0.76 x 10^{-4} mole (5%)
o-(Phenyldimethylsilyl) anisole	1.57 x 10^{-4} mole (8.5%)	1.02 x 10^{-4} mole (6.7%)
m-(Phenyldimethylsilyl) anisole	1.21 x 10^{-4} mole (6.6%)	0.95 x 10^{-4} mole (6.3%)
p-(Phenyldimethylsilyl) anisole	0.69 x 10^{-4} mole (3.9%)	0.46 x 10^{-4} mole (3.0%)
Isomer ratio:		
o-(Phenyldimethylsilyl) anisole	45%	42%
m-(Phenyldimethylsilyl) anisole	35%	39%
p-(Phenyldimethylsilyl) anisole	20%	19%

3 DISCUSSION

(A) Homolytic Aromatic Substitution with Benzoyl Peroxide

(I) The effects of additives on the decomposition of benzoyl peroxide in toluene

(a) The decomposition of benzoyl peroxide in toluene

The reactions of benzoyl peroxide with alkylbenzenes with α-hydrogen in the side-chain are complicated by hydrogen abstraction as well as substitution reactions. Thus the nuclear reactions of benzoyl peroxide with toluene, ethylbenzoate and isopropylbenzene are always accompanied by the formation of bibenzyl or its analogues in proportions varying from 13% in toluene to 60% in isopropylbenzene in the "biaryl fraction"[137].

Table 32[137]

Substrate	% of side-chain attack	% of nuclear attack
Toluene	13	87
Ethylbenzene	55	45
Isopropylbenzene	60.5	39.5
t-Butylbenzene	0	100

Phenyl radicals in these substrates not only can effect phenylation of the nucleus but can also abstract an hydrogen atom from the side chain to give rise to a resonance stabilized benzyl radical which can dimerise in solution to give bibenzyls. In concentrated solution of benzoyl peroxide in toluene, phenyl radicals could also facilitate substitution reaction in the side chain to produce diphenylmethane. Benzoyloxy radicals could also effect hydrogen abstraction from the side chain to give benzyl radicals[74,138].

The amount of side chain attack giving rise to bibenzyl formation determined in the present work (24%) is higher than that reported by previous workers[138]. It is likely that the different methods of analysis employed are responsible. The gas chromatographic method, which is more accurate than the infrared method, has been adopted for analysis in this work, consequently the result is likely to be more reliable.

The formation of bibenzyl , and of diphenylmethane can be accounted for by the following mechanism.

$$(PhCO{\cdot}O)_2 \longrightarrow 2PhCO{\cdot}O{\cdot} \qquad \ldots\ldots \quad (88)$$

$$PhCO{\cdot}O{\cdot} \longrightarrow Ph{\cdot} + CO_2 \qquad \ldots\ldots \quad (89)$$

$$PhCH_3 + Ph{\cdot} \longrightarrow PhCH_2{\cdot} + PhH \qquad \ldots\ldots \quad (90)$$

$$PhCH_3 + PhCO{\cdot}O{\cdot} \longrightarrow PhCH_2{\cdot} + PhCO_2H \qquad \ldots\ldots \quad (91)$$

$$2PhCH_2{\cdot} \longrightarrow PhCH_2 - CH_2Ph \qquad \ldots\ldots \quad (92)$$

$$PhCH_2{\cdot} + Ph{\cdot} \longrightarrow PhCH_2\text{-}Ph \qquad \ldots\ldots \quad (93)$$

No attempt was made to determine the relative contribution of side-chain hydrogen abstraction by phenyl and by benzoyloxy radicals.

In a detailed investigation of the kinetics of the decomposition of benzoyl peroxide in alkylbenzenes, Foster and Williams[16b] showed that in these reactions the decomposition of benzoyl peroxide has the following rate equation:

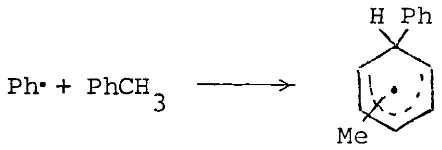
$$\frac{-d[P]}{dt} = k_1[P] + k_{3/2}[P]^{3/2} \qquad \ldots\ldots \quad (94)$$

where P = benzoyl peroxide.

k_1 = rate constant of the unimolecular homolysis of benzoyl peroxide,

$k_{3/2}$ = rate constant of the induced decomposition of benzoyl peroxide.

Though toluene was not included in the studies, the decomposition of benzoyl peroxide is expected to follow a similar rate law. Consequently, the major contribution to the formation of methylbiphenyls and benzoic acid comes from reaction (96),



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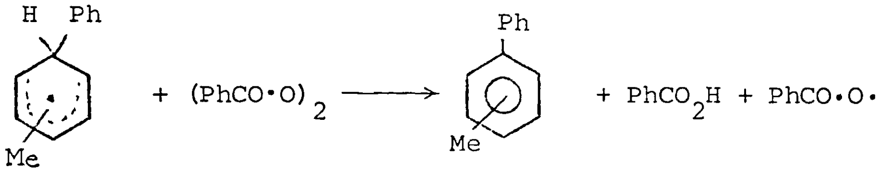

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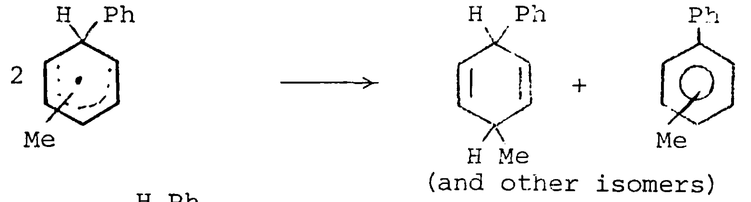

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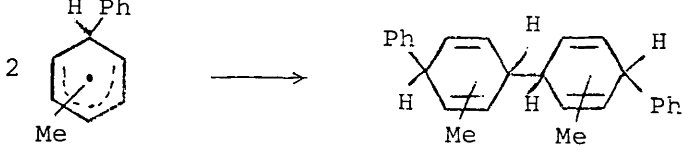


...... (98)

with reactions (97) and (98) as the termination reactions.

From table 33 it was found that the isomer ratio is slightly different from those reported by previous workers[85, 137]. The different methods of analysis could be responsible for the difference.

Table 33

The isomer ratios of methylbiphenyls from the phenylation of reactions of toluene

2-Methylbiphenyl	3-Methylbiphenyl	4-Methylbiphenyl	
65	19	16	Zaremnsky and Dannley[137]
66.5	19.2	14.3	Hey, Pengilly and Williams[138]
54	25.8	20.2	Gadallah and Elofson[85]
62	20	18	this work

The larger discrepancy in the results of Gadallah and Elofson[85] could be due to the fact that they used a different phenyl radical source, namely electrochemical reduction of benzene diazonium tetrafluoroborate in aprotic solvents.

(b) The effect of m-dinitrobenzene on the decomposition of benzoyl peroxide in toluene

After the discovery of the "nitro-group effect"[59] in the decomposition of benzoyl peroxide in benzene, Perkins[139] also reported a reduction in the extent of bibenzyl and 2,3-dimethyl-2,3-diphenylbutane formation in the decomposition of benzoylperoxide in toluene and isopropylbenzene, respectively, containing m-dinitrobenzene. This observation is further confirmed by the present results. However, unlike the reaction in benzene the inclusion of m-dinitrobenzene did not cause a great increase in the yield of benzoic acid and methylbiphenyls. The results are shown in table 34 and figure 1. The presence of m-dinitrobenzene caused only a slight increase in the yield of methylbiphenyls whereas a larger increase in the amount of benzoic acid was found. The increase in yield could be due to a similar effect to that observed in the reaction in benzene though in a much reduced way. The reduced effect of the nitro-group in these reactions could be due to some side reactions which can direct the nitroxide radicals from abstracting hydrogen atom from the σ-radicals to give methylbiphenyls. The increase in yield could also partly result from the suppression of bibenzyl formation. If the benzyl radicals in solution are being removed by interaction with m-dinitrobenzene, loss of σ-radicals resulting from their combination with benzyl radicals would be reduced.

Table 34

The products of decomposition of benzoyl peroxide in toluene in the presence of m-dinitrobenzene

Experiment	Additive g (m/m)	Methybiphenyls (m/m	Bibenzyl (m/m)	Benzoic acid (m/m)
Mean of 1+2	Nil	0.383	0.119	0.409
" 3+4	0.009_5 (0.014)	0,370	0.119	0.465
" 5+6	0.0248 (0.036)	0.383	0.085	0.526
" 7+8	0.201_5 (0.290)	0.516	0.038	0.778

With hindsight it is now clear that the efficient oxidising agents responsible for the conversion of phenylcyclohexadienyl radicals to biphenyl are the nitroxide radicals formed from the nitroso-compound, which itself arises from the reduction of the nitro-compound. In the decomposition of benzoyl peroxide in toluene, the nitro-compound is reduced by the σ-radicals to form a nitroso-compound, which then, on intercepting a phenyl or a benzoyloxy or a benzyl radical gives rise to stable nitroxide radicals. These stable radicals could then oxidise σ-intermediates to form methylbiphenyls, themselves being reduced to the hydroxylamine derivatives. The nitroxide radicals are regenerated in the induced decomposition of benzoyl peroxide by the hydroxylamine derivative, according to the following reaction.

The decomposition of benzoyl peroxide in toluene containing m-dinitrobenzene

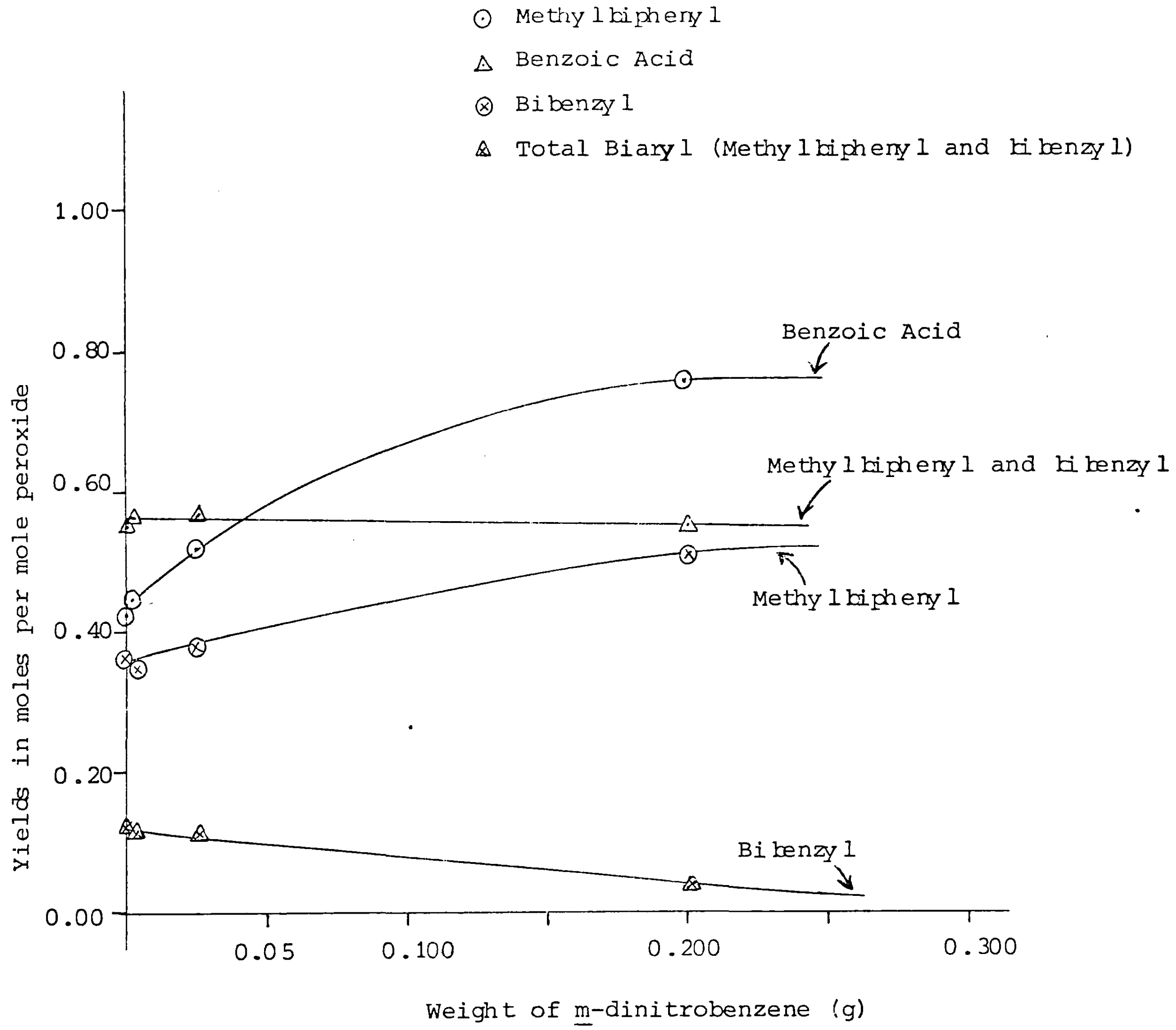
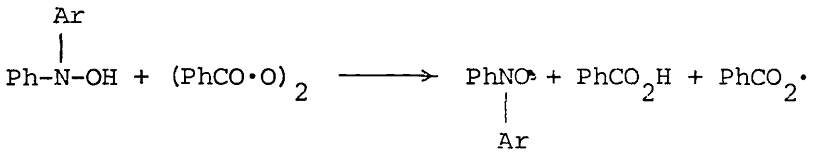


FIGURE 1

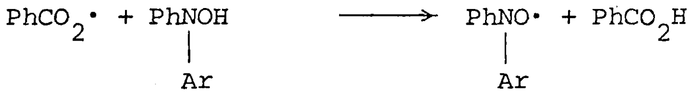
$$ArNO_2 \longrightarrow ArNO \qquad ...... \quad (99)$$

$$ArNO + Ph\cdot \longrightarrow Ar\text{-}N(Ph)\text{-}O\cdot \qquad ...... \quad (100)$$

$$Ar\text{-}N(Ph)\text{-}O\cdot + PhC_6H_5CH_3\cdot \longrightarrow PhN(Ar)OH + PhC_6H_4CH_3 \qquad ...... \quad (101)$$

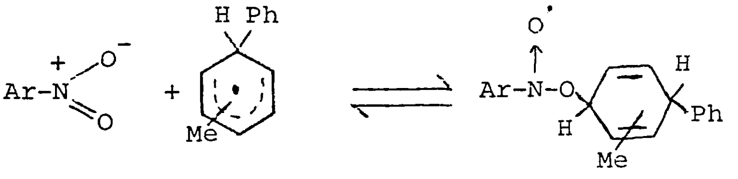


$$Ph\text{-}N(Ar)\text{-}OH + (PhCO\cdot O)_2 \longrightarrow PhN(Ar)O\cdot + PhCO_2H + PhCO_2\cdot \qquad ...... \quad (102)$$



$$PhCO_2\cdot + PhN(Ar)OH \longrightarrow PhN(Ar)O\cdot + PhCO_2H \qquad ...... \quad (103)$$

For the reaction in toluene, there are two possible ways by which m-dinitrobenzene could be reduced to the corresponding nitroso-compound. Firstly, the nitroso compound could result from the reaction of m-dinitrobenzene with the arylcyclohexadienyl radicals as shown in reactions (104) and (105). Secondly, it may be formed by the interaction of m-dinitrobenzene with benzyl radicals in a similar way to that suggested by Jackson and Waters[138a] in reactions (107) and (108).



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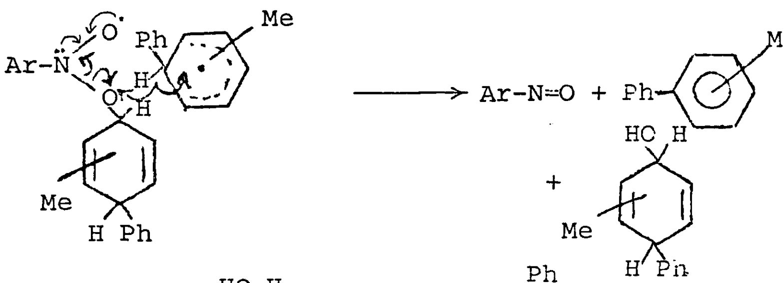

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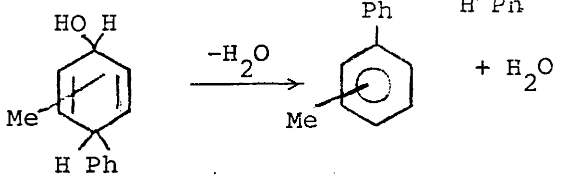

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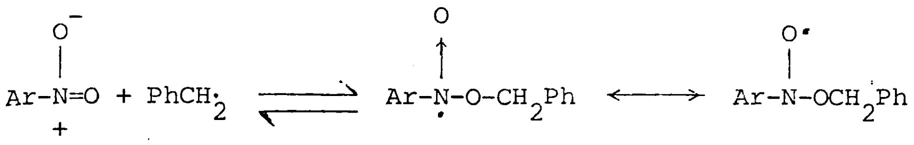
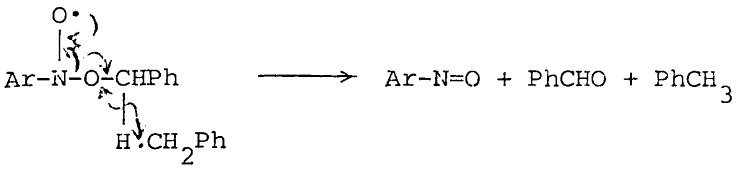


$$\mathrm{Ar\text{-}\overset{O^-}{\underset{+}{N}}{=}O + PhCH_2^{\bullet} \rightleftharpoons Ar\text{-}\overset{O}{\overset{\uparrow}{\underset{\bullet}{N}}}\text{-}O\text{-}CH_2Ph \longleftrightarrow Ar\text{-}\overset{O^{\bullet}}{N}\text{-}OCH_2Ph}$$

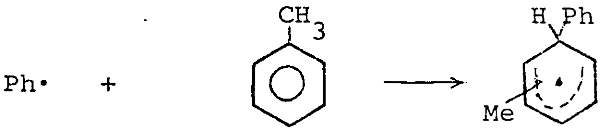
...... (107)



$$\mathrm{Ar\text{-}\overset{O^{\bullet}}{N}\text{-}O\text{-}\underset{H^{\bullet}CH_2Ph}{CHPh} \longrightarrow Ar\text{-}N{=}O + PhCHO + PhCH_3}$$

...... (108)

No attempt was made to isolate the oxidation product, benzaldehyde, in the present work. The increase in yield of methylbiphenyls observed in the present work could be due to the nitro-group effect of m-dinitrobenzene, in which the nitroxide radicals effectively intercept the σ-radicals and prevent them from dimerising.



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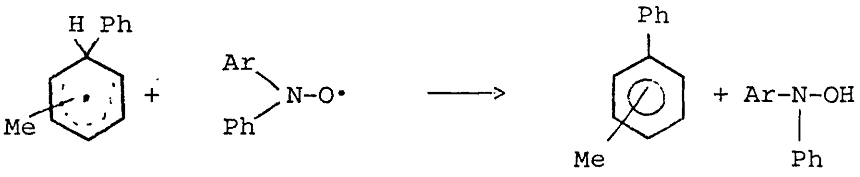

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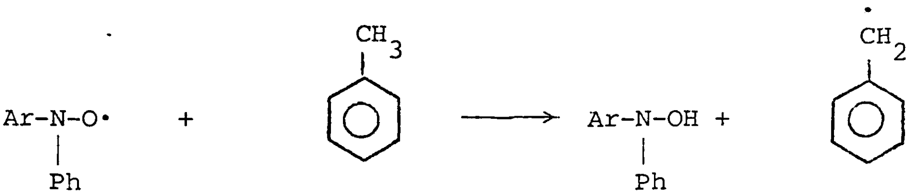

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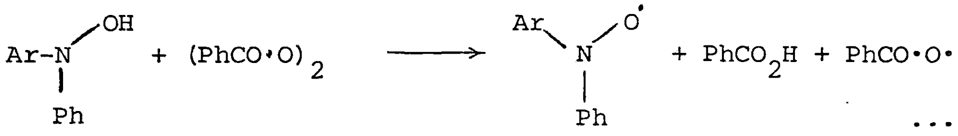


$$\mathrm{Ar\text{-}\underset{Ph}{N}\text{-}OH + (PhCO{\cdot}O)_2 \longrightarrow Ar\text{-}\underset{Ph}{N}\text{-}O^{\bullet} + PhCO_2H + PhCO{\cdot}O^{\bullet}}$$

...... (112)

The absence of a sharp increase in the yield of methylbiphenyls is probably due to the fact that there are active hydrogens in the side chain of toluene and consequently many nitroxide radicals are diverted to side chain hydrogen abstraction. The latter reaction would be a more favourable one than the hydrogen abstraction reaction from σ-radicals in view of the large concentration of toluene molecules in solution.

The lower proportion of side-chain to nuclear attack observed (table 35) in the presence of m-dinitrobenzene does not necessarily mean that fewer benzyl radicals are generated in these reactions. It is more probable that the benzyl radicals formed are diverted to form products other than bibenzyl.

Table 35

The ratio of side chain attack to nuclear attack on toluene (50 ml) in phenylation reaction by benzoyl peroxide (1.0 g) at 80^0

Peroxide concentration = 0.083 M

Additive g (m/m)	% of side chain attack	% of nuclear attack
Nil	23.8	76.2
m-Dinitrobenzene		
0.009_5 (0.014)	24.5	75.5
0.0248_9 (0.036)	18.2	81.8
0.201_5 (0.290)	7.0	93.0
Ferric benzoate		
0.081_4 (0.018)	25.3	74.7
0.207_2 (0.046)	23.7	76.3
0.405_0 (0.080)	22.7	77.3
Cupric benzoate		
0.400_7 (0.156)	21.2	78.8

There are two possible explanations for the decrease in the yield of bibenzyl. Firstly it may be due to the nitro-group effect which facilitates the nuclear phenylation reaction, hence proportionately reducing the extent of side-chain hydrogen abstraction. This explanation seems unlikely because more than a catalytic amount of *m*-dinitrobenzene had to be included to give an observable suppression of bibenzyl formation. If it is the nitro-group effect that is responsible a little *m*-dinitrobenzene should be as efficient as a larger amount. Secondly, the benzyl radicals may be oxidised by *m*-dinitrobenzene to benzaldehyde according to reactions (107) and (108) as suggested by Jackson and Waters[140a] and by Goble *et al*[140b]. This mechanism which requires a stoichiometric amount of *m*-dinitrobenzene is probably a more likely explanation.

(c) The effect of ferric benzoate and cupric benzoate on the decomposition of benzoyl peroxide in toluene

There is extensive literature on transition metal modified free radical reactions[9]. The mechanisms through which these metal salts influence the reactions depend markedly on the nature of the ligands of the salts and are classified by Kochi[63] into electron transfer and ligand transfer mechanisms. The transition metal carboxylates are generally useful as electron transfer oxidants. The reactions proceed through cationic intermediates or transition states.

The effect of ferric benzoate on the yields of the major products of the phenylation of toluene found in this work is illustrated in figure 2 and table 36. The yields of the biaryl and benzoic acid are increased while that of the residue is reduced by the presence of ferric benzoate. Almost equimolar quantities of biaryl and benzoic acid are formed.

The decomposition of benzoyl peroxide in toluene containing ferric benzoate

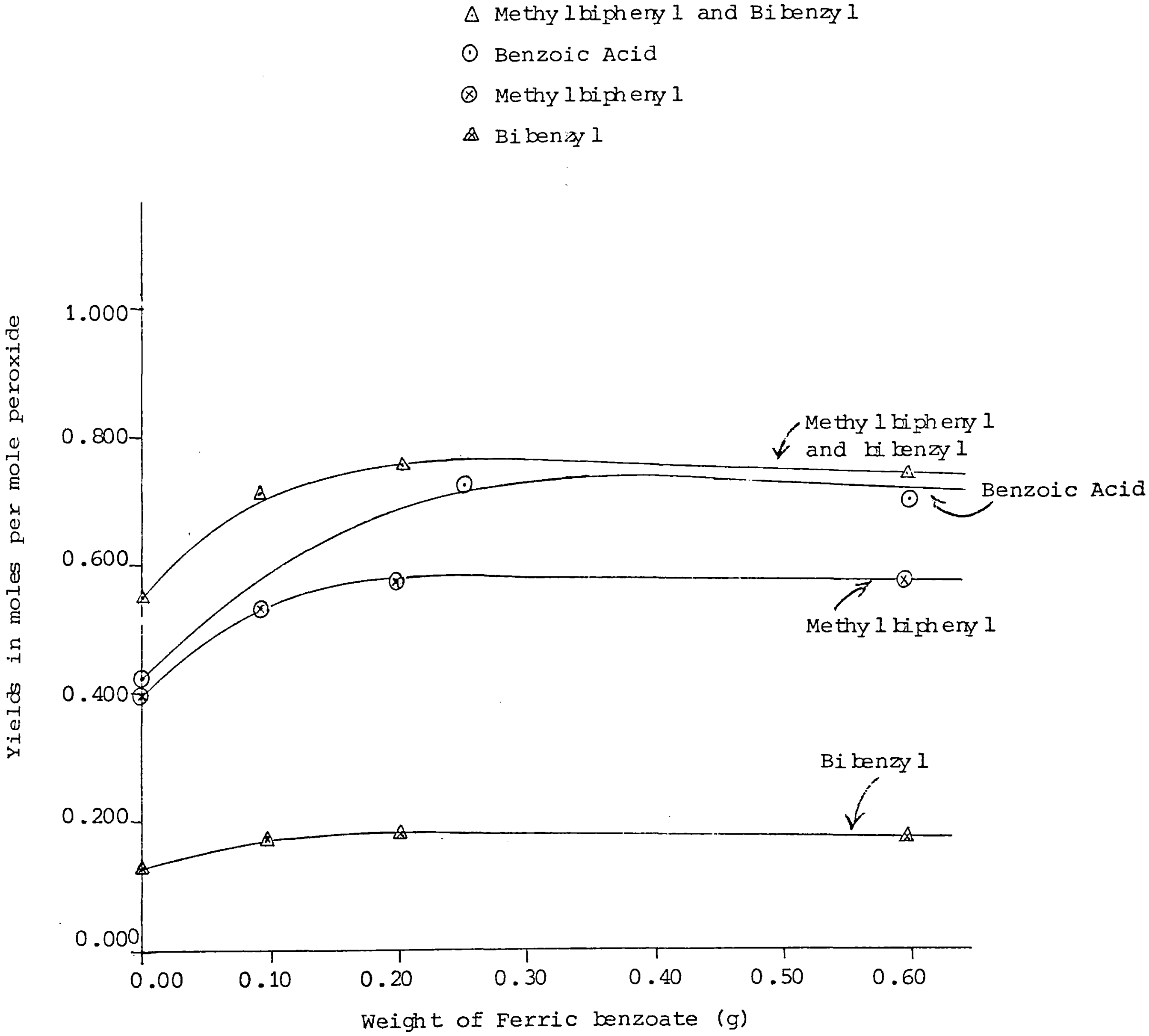


FIGURE 2

Table 36

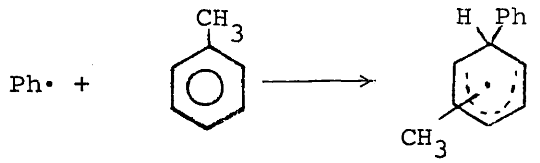
Products from the decomposition of benzoyl peroxide in toluene in the presence of ferric benzoate and cupric benzoate at 80°

Experiment Number	Additive g (m/m)	Methylbiphenyls (m/m)	Bibenzyl (m/m)	Benzoic acid (m/m)
Mean: 1+2	Nil	0.382	0.119	0.409
	Ferric benzoate			
9+10	0.081_4 (0.018)	0.534	0.181	not determined
11+12	0.207_2 (0.046)	0.580	0.180	0.731
13+14	0.402_0 (0.089)	0.576	0.170	0.704
	Cupric benzoate			
	0.400_7 (0.156)	0.582	0.180	0.709

The following mechanism, by analogy with that suggested by Dailly[74] for the decomposition of benzoyl peroxide in benzene in the presence of ferric benzoate, is proposed to account for the observation.

$$(PhCO{\cdot}O)_2 \longrightarrow 2Ph{\cdot}CO{\cdot}O{\cdot} \qquad \ldots\ldots \quad (113)$$

$$PhCO{\cdot}O{\cdot} \longrightarrow Ph{\cdot} + CO_2 \qquad \ldots\ldots \quad (114)$$



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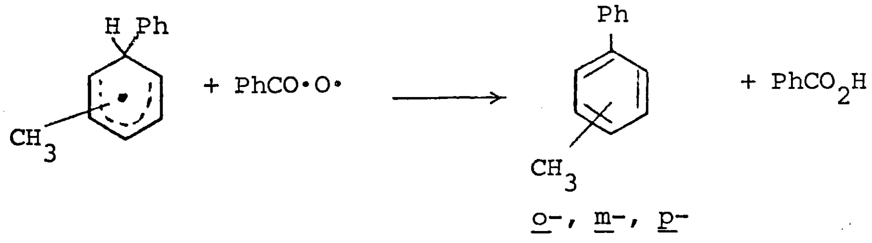
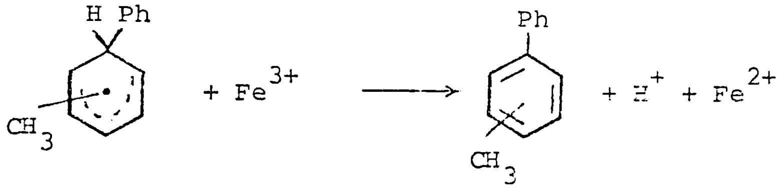


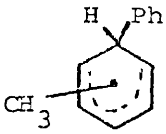
...... (116)



...... (117)

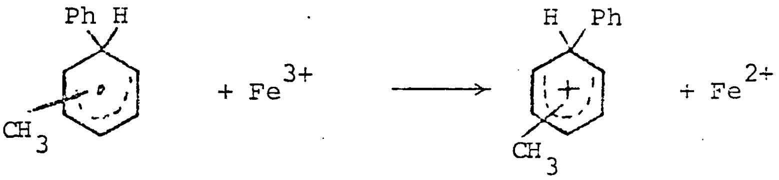
$$Fe^{2+} + PhCO{\cdot}O{\cdot} \longrightarrow Fe^{3+} + PhCO_2^- \qquad \text{......} \quad (118)$$

$$PhCO_2^- + H^+ \longrightarrow PhCO_2H \qquad \text{......} \quad (119)$$



$\longrightarrow$ dimerisation and disproportionation products ...... (120)

Reaction (117) could be split into two steps



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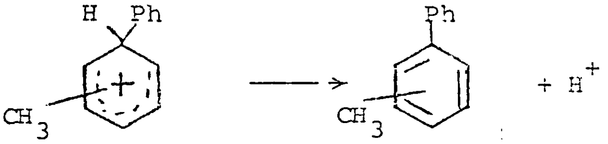


...... (122)

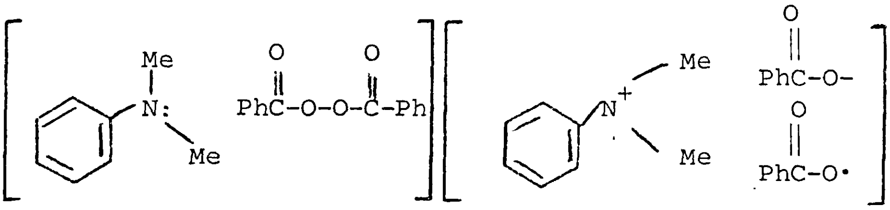
These two reactions could be a concerted process. In the above oxidation process an initial co-ordination of the σ-intermediate to the ferric ion could be a pre-requisite followed by the one electron transfer from the σ-intermediate to the ferric ion. Reactions (116) and (117) are the main steps for the formation of methylbiphenyls and benzoic acid; so that this reaction scheme provides a satisfactory explanation for the formation of equal amounts of biaryl and benzoic acid. The importance of reaction (120) is very much reduced by ferric benzoate. A rate equation with the following expression was observed in the analogous reaction in benzene[74], it is likely that a similar rate law is also obeyed in this system.

$$-\frac{d[P]}{dt} = k_1[P] + k_1'[P] \qquad \text{......} \quad (123)$$

P, k_1 and k_1' have their usual meaning as given previously. The termination reactions are between unlike radicals (reaction (116)) i.e. the direct oxidation of σ-complexes by benzoyloxy radicals. This reaction becomes important if by some means, benzoyloxy radicals are stabilised, and hence their concentration in solution is increased. Gill and Williams[16a] observed a similar rate equation in the decomposition of benzoyl peroxide in bromobenzene where reactions analogous to (116) is the main product formation step.

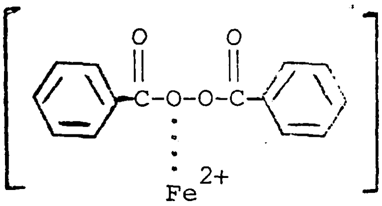
It is necessary to discuss the possible roles played by ferric benzoate in this reaction. Ferric benzoate could have participated in this reaction in the following ways.

(i) Ferric benzoate may have participated in the reaction at an earlier stage by co-ordinating with the oxygen atom of the carbonyl group of the peroxide molecule to form a weakly bonded π-complex. There are examples in the literature of π-complex formation between benzoyl peroxide or benzoyloxy radicals with solvent molecules[141]. Gill and Williams[16a] suggested that benzoyloxy radicals in bromobenzene are stabilised by the formation of a charge transfer π-complex which stabilised the benzoyloxy radicals from decarboxylation, and allowed its concentration in solution to build up. As a result there were efficient hydrogen abstractors present in solution which enabled the oxidation of σ-radicals to biaryls to proceed readily. Analogous π-complex formation reaction has also been suggested between benzoyl peroxide and tertiary amine molecules before by Imoto and Takemoto[142] and also by Horner[143]. Horner suggested the following structure for the complex (14).



(14)

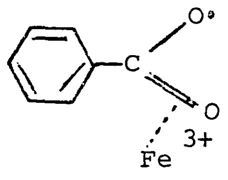
Complex formation between benzoyl peroxide molecules with ferrous ions has also been reported by Hasegawa and Nishimura[141], who also provided evidence for ferrous-oxygen bond formation in rhe transition state. The following structure[15] was suggested for the activated complex which involved a co-ordination of a peroxidic oxygen to the ferrous ions, probably accompanied by an electron jump from the ion, giving rise to the observed



(15)

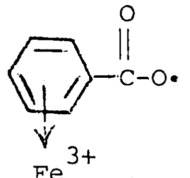
accelerated rate of decomposion of benzoyl peroxide in this system. Orr and Williams[144] also proposed such complex formation between hydroperoxide molecules and ferrous ions. Dailly[74] suggested that a π-complex could be formed between the oxygen atom of the carbonyl group of benzoyl peroxide and ferric benzoate. This can occur probably owing to the ionic character of the ferric to carboxylate bond. Though many of these transition metal carboxylates are essentially covalent compounds, electrical conductivity measurements show that metal-carboxylate bonds exhibit some ionic character[145]. Such a complexation reaction can result in an accelerated rate of decomposition of the peroxide. However, the kinetic results[74] revealed that the complexation did not assist the homolysis of the peroxide.

(ii) In order for reaction (116) to be an important termination step, the benzoyloxy radicals once generated should be saved from decarboxylation by some stabilisation mechanism probably involving a charge transfer complex similar to that suggested by Gill and Williams[16a]. Analogy with this mechanism of stabilisation of benzoyloxy radicals is sought in this system. The metal carboxylates have intermediate activities as ligand or electron transfer oxidants[63]. Taube[64] pointed out that an attached group in such a system is strongly polar. Probably this polar character of the metal carboxylate provides an analogy of stabilisation of benzoyloxy radicals to that described by Gill and Williams[16a]. The complex could have the following structures (16) and (17).



(16)

or



(17)

It is essential also to discuss how the catalyst (ferric ion) is regenerated in this reaction. If there were no way by which the ferrous ions formed could be oxidised to ferric ions again, a stoichiometric amount of ferric benzoate would be required and would result in an accumulation of ferrous ions in solution. There are two possible ways by which the catalyst could be reformed:

(a) The ferrous ions could be oxidised to the ferric state by the well-documented induced decomposition of benzoyl peroxide by ferrous ions[141], reaction (124).

$$Fe^{2+} + (Ph{\cdot}CO{\cdot}O)_2 \longrightarrow Fe^{3+} + PhCO_2^{-} + Ph{\cdot}CO{\cdot}O{\bullet} \qquad \ldots\ldots \quad (124)$$

Hey, Liang and Perkins[75] in an investigation of the effect of transition metal benzoates on the decomposition of benzoyl peroxide in benzene, also suggested that reaction (124) (with cuprous instead of ferrous ions) is the catalysed-regenerating step. The following mechanism was proposed, although without any supporting kinetic data.

$$(PhCO{\cdot}O)_2 + Cu^+ \longrightarrow PhCO{\cdot}O{\cdot}Cu^+ + PhCO{\cdot}O{\cdot} \quad \ldots\ldots \quad (125)$$

$$PhCO{\cdot}O{\cdot} \longrightarrow Ph{\cdot} + CO_2 \quad \ldots\ldots \quad (126)$$

$$Ph{\cdot} + PhH \longrightarrow \sigma{\cdot} \quad \ldots\ldots \quad (127)$$

$$\sigma{\cdot} + PhCO{\cdot}O{\cdot}Cu^+ \longrightarrow Ph\text{-}Ph + PhCO_2H + Cu^+ \quad \ldots\ldots \quad (128)$$

Based on the results obtained in a detailed kinetic study Dailly[74] argued that the above mechanism is inconsistent with the kinetic results. No autocatalysis was observed in the decomposition of benzoyl peroxide in benzene in the presence of ferric benzoate, nor is the unimolecular decomposition of peroxide greatly influenced by the metal salt. The rate of reaction should speed up, as ferrous ion is formed, to a maximum rate. As this did not happen when it is well known that ferrous ions will induce the decomposition this could be due to the reasons that:

(a) the kinetics were not sensitive enough and/or

(b) they were not correctly interpreted.

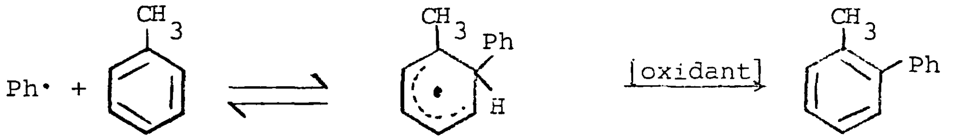
Another likely path for the regeneration of ferric ions to form ferrous ions is by reaction (118) which involves the direct oxidation of ferrous ion by benzoyloxy radical resulting in the formation of a benzoate anion which ultimately forms a molecule of benzoic acid, reaction (119). Alternative (b) (reaction 118) would be the more important contributor as this reactions would proceed at a rate faster than reaction (124). (c.f. a rate constant, approaching the diffusion controlled process has been determined for the following quite similar reaction by Walling[146]

$$Fe^{2+} + OH{\cdot} \xrightarrow{k} Fe^{3+} + OH^- \qquad k = 3 \times 10^8 \text{ mol}^{-1} \text{ l sec}^{-1}$$

while a rate constant of 360.8 mol^{-1} l sec^{-1} was calculated for reaction (124) at 80^o in ethanol).

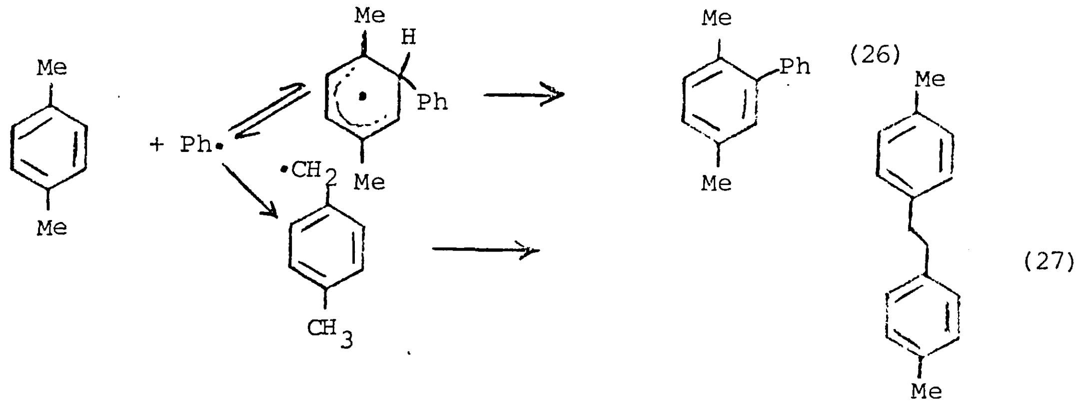
It is noted that the proportion of o-methylbiphenyl formed in the presence of ferric benzoate is higher than that in an uncatalysed reaction. The formation of o-isomer is accelerated more than the rate of formation of m- and p-isomers. Similar features were observed by Hey, Liang and Perkins[75]. There are two possible explanations for the increase of the o-isomer in the metal ion catalysed reactions.

(i) The first possibility is that the addition of phenyl radicals to toluene is reversible, then it is expected that 2-methylphenylcyclohexadienyl radicals will have a greater tendency to dissociate than its isomers owing to the greater steric effect associated with a methyl substituent in the ortho-position.



...... (129)

Consequently in the presence of an efficient oxidising agent for σ-complexes, which would inhibit the occurrence of the reverse reaction, a larger proportion of 2-methylbiphenyl would result. However, it is usually held that[19a,b,c] the initial addition step of phenyl radicals to benzene is effectively an irreversible process which is also the rate determining step in the actual arylation process. This generalisation was inferred from a lack of hydrogen isotope effect on the recovered substrate in this reaction. However, recently Kobayashi et al[25] reported the presence of an isotope effect at the crowded 2-position of m-dinitrobenzene in a phenylation reaction. It was pointed out that[19] the isotope effect could arise from the solvent effect of dimethylsulphoxide. Nonhebel et al[26a,b] have recently also postulated reversible addition of phenyl radicals to p-xylene and o-dichlorobenzene. The following mechanism was proposed by them to explain the slightly larger increase in yield of 4,4'-dimethylbibenzyl than that of 2,5-dimethylbiphenyl with increase in temperature.



However, this observation could also be accounted for if the two competing processes (26) and (27) have different activation energies. The increase in importance of the two reactions with increase in temperature would then not be the same. Rondestredt and Blanchard^{43} have shown that the extent of bibenzyl formation is temperature dependent. They reported that no detectable quantity of bibenzyl was formed below 25° but a substantial amount of it was detected at 60-68° by infrared spectroscopy in the phenylation of toluene with N-nitrosoacetanilide. Thus it appeared that bibenzyl formation required a higher temperature. If this is so, the larger increase of bibenzyl observed by Nonhebel *et al* could be due to the higher activation energy required for the formation of 4-methylbenzyl radicals, as suggested above.

In the reaction with *o*-dichlorobenzene, the decrease in the ratio of the yield of 2,3-dichlorobiphenyl to that of 3,4-dichlorobiphenyl with rise in the reaction temperature could arise from the greater tendency of 2,3-dichlorobiphenyl than 3,4-dichlorobiphenyl to undergo side reactions at elevated temperatures.

From the above considerations, it appears that there is no compelling evidence that the increase in the yield of 2-methylbiphenyl in this reaction is due to the reversibility of the addition of phenyl radicals to toluene.

(ii) As an alternative explanation, it is not unreasonable to suggest that the three isomeric methylphenylcyclohexadienyl radicals dimerise at different rates. If the rate of dimerisation of the 2-isomer is greater than the other isomers, in reactions where dimerisation is important, the loss of the 2-isomer may be more significant than loss of the other isomers. In the metal salt-catalysed reactions where the importance of dimerisation is greatly diminished, a greater proportion of 2-methylbiphenyl was formed at the expense of σ-radical dimers. This seems to be a more likely explanation for the increased proportion of 2-methylbiphenyl formed in the ferric benzoate catalysed reaction.

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

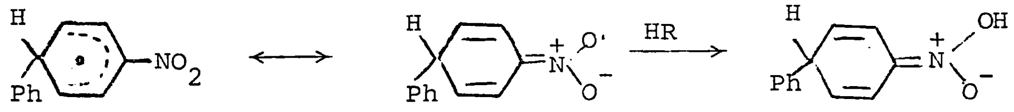
The tolyl benzoates formed in this reaction were not investigated, though there are reports[147] on their formation under favourable conditions, but as revealed by gas chromatography, they are only formed in small amounts (less than 1%).

II The effect of additives in the competitive reaction of benzoyl peroxide in benzene-toluene system.

(a) The decomposition of benzoyl peroxide in equimolar mixture of benzene and toluene

The discovery that the inclusion of a small amount of m-dinitrobenzene in the decomposition of benzoyl peroxide in toluene and in isopropylbenzene caused a reduction of bibenzyl and 2,3-dimethyl, 2,3-diphenylbutane formation[139] created uncertainty concerning the relative reactivities of alkylbenzenes as estimated by competitive reactions where nitrobenzene was used as a standard. In these reactions the yields of bibenzyls are found to be greatly reduced. In the estimations of rate factors from the competitive reaction of toluene and nitrobenzene[138] the assumption was made that the amount of side chain relative to nuclear attack was the same in the competitive reaction as in toluene alone. In view of the effect nitro-compounds were subsequently found to have on bibenzyl formation, this assumption must have been invalid. As a result the rate factors determined for toluene would be too low and require redetermination. In addition to this observation, recently there was a report[148] that nitrobenzene is unsuitable for use as a standard solvent in competition reactions where a hydrogen donor is present. Under such conditions the nitrophenylcyclohexadienyl radicals could abstract an hydrogen atom at their nitro-group, at the expense of transferring their hydrogen atoms to give nitrobiphenyl. This observation casts further doubt on the validity of rate factors of alkylbenzenes.

The results now reported (Table 37) provide further evidence that different proportions of bibenzyl are formed in competitive reaction from those formed in the reaction with toluene alone. There is less side-chain attack in the competitive reactions with benzene as standard solvent.



Scheme (45)

Table 37

Extent of side-chain attack

Reaction	Side chain attack	Nuclear attack
Toluene alone	23.8%	76.3%
Competitive reaction with benzene as standard solvent	17.4	82.6%

The lower proportion of side-chain to nuclear attack does not necessarily mean that fewer benzyl radicals are generated in these reactions. It is more likely that the benzyl radicals are diverted to form products other than bibenzyl. There are two possible ways in which this may occur. There are additional phenylcyclohexadienyl radicals available for disproportionation and combination reactions with benzyl radicals in the competitive reactions. The benzyl radicals are expected to undergo cross disproportionation or combination reaction more easily with the unsubstituted $\sigma-$ radicals than with methylphenylcyclohexadienyl radicals, probably for steric reason. Consequently more benzyl radicals are diverted from bibenzyl formation. Some of the rate factors which have been reported for the phenylation of toluene are listed in Table 38.

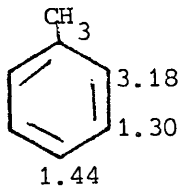
Table 38

${}^{PhCH_3}_{PhH}K$	Standard solvent	Fo	Fm	Fp	Reference
1.23	$PhNO_2$	2.50	0.71	1.00	Hey, Orman, Williams (149)
1.46	$PhNO_2$	2.68	0.70	2.02	Davies, Hey, Summers (55)
2.58	$\underline{P}$-$Cl_2C_6H_4$	4.70	1.24	3.55	Davies, Hey, Summers (55)
1.77	PhH	2.87	1.37	2.14	Gadalla & Elofson (85)
1.68	PhH	3.30	1.09	1.27	Simamura *et al*. (57)
1.81	PhH	3.38	1.30	1.44	This work

The rate factors obtained in the present work are higher than those reported by Hey, Orman and Williams[149]. This is probably due to the reason given earlier in this section, (i.e. more accurate analytical method was employed in the present studies). The present values agree well with some of the more recent results of Gadallah and Elofson[85] and Simamura and co-workers[57], even though phenyl radicals were generated from different sources. However the values reported by Davies, Hey and Simamura[55] are much higher than those obtained in this work, probably due to the fact that those workers used p-dichlorobenzene as a standard solvent and the rate factors were not determined directly from competitive reactions with benzene, instead by making use of conversion equations. As it can be shown from results obtained from the present studies, the use of conversion equations in the reactions in the absence of additives can give rise to erroneous results (section 3.A.VI page 212).

The major products biphenyl, methylbiphenyls, bibenzyl and benzoic acid are probably formed by the same mechanism in the phenylation in benzene or toluene alone; with the additional possibility of dimerisation and disproportionation reactions between phenylcyclohexadienyl, methylphenylcyclohexadienyl and benzyl radicals. From kinetics, the dimerisation and disproportionation reactions are probably the main termination reactions in this system.

Although the rate factors for toluene have been up-dated in the sense that the values determined, with the help of the accurate gas chromatographic analysis, are more reliable, they may not be more reliable indices of the reactivity of toluene, because of the high proportion of resin formation in this reaction. For the same reason the values obtained by Gadallah and Elofson[85] (50% yield) are also subject to the common criticism of the validity of rate factors[47].



The partial rate factors of toluene

The partial rate factors also revealed some anomalies. A value of 1.30 for the relative attack of the m-position of toluene appears unreasonable because the m-position is expected to be as reactive as one of the six positions of benzene. To bring this value to one, the relative rate has to be decreased to 1.39 which is beyond experimental error. The apparent activations of the m-position could be accounted for by the following suggestion. Phenyl radical is not the only species involved in selecting between the competing solvent molecules, if it is so, a value of unity for Fm should be obtained. Therefore different species must also involve in the selection process, e.g. a precursor of phenyl radical such as benzoyloxy radical or even benzoyl peroxide, both of which have longer life times than phenyl radicals. These species involved in the formation of complexes with toluene molecule through some weak attractions. Weak intermolecular attractive forces such as Van der Waal's forces would be sufficient for the reagent to discriminate between benzene and toluene. Since phenyl radical reacts with aromatic substrates with a rate approaching diffusing-controlled process (a second order rate constant of 7×10^7 l mol^{-1} s^{-1})[150] which implies that if complexation occurs between phenyl radical or its precursor with toluene molecules, phenyl radical subsequently generated could not show a random attack on the competing benzene molecules and toluene molecules. The phenyl radical formed would be in a closer vicinity of toluene molecules hence their attack on toluene is favourable, therefore leading to a higher reactivity of toluene molecules than benzene. This complication makes the relative rate and partial rate factors determined in this reaction invalid as reactivity indices of toluene molecules in the phenylation reaction.

(b) The effect of m-dinitrobenzene and nitrobenzene on the decomposition of benzoyl peroxide in an equimolar mixture of benzene and toluene

In a series of competitive reactions containing variable amounts of nitrobenzene and m-dinitrobenzene as additives, the yields of biaryls and benzoic acid were enhanced while that of bibenzyl is reduced. (Table 9, Figures 3 and 4). Consequently the rate factors calculated from the results obtained from these experiments should provide a truer picture of the reactivity of toluene with respect to benzene.

The importance of dimerisation and disproportionation reaction between the σ- radicals is greatly reduced in these systems. The yields of the biaryls and benzoic acid are probably increased by the nitro-group effect.

The effects of nitro-compounds on the relative rate and partial rate factors of toluene are shown in Figures 5, 6 and 7 and Table 40.

The relative rates and the partial rate factors in these reactions revealed some interesting features. In the presence of nitro-compounds, there is a levelling effect of the relative rates and the partial rate factors to a limiting value. The relative reactivity of the m-position of toluene has been reduced to a value approaching unity which is expected if the phenylation reaction involved the same species in the selecting process. These observations could be accounted for if the complexation between benzoyloxy radicals or benzoyl peroxide with toluene is no longer an important process and that the same species is involved in selecting the competing substrates. In this reaction the complexation between phenyl radical or its precursor with the nitro-compound may be a more favourable process than that between toluene and the precursor of phenyl radicals. As a result, the phenyl radicals subsequently generated would show a random attack on the competing solvent molecules. As phenyl radical is

The decomposition of benzoyl peroxide in an equimolar mixture of toluene and benzene containing nitrobenzene

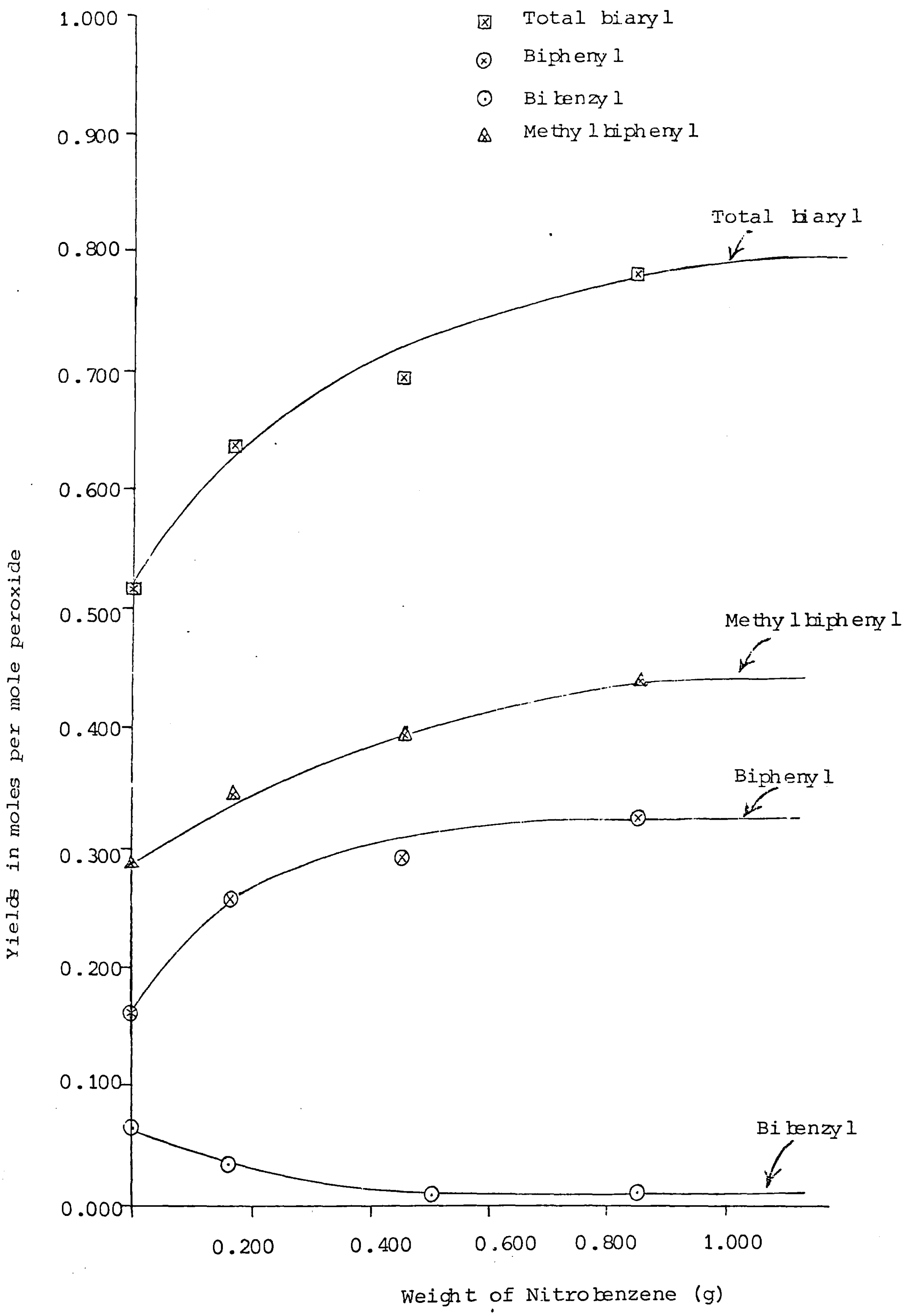


FIGURE 3

The decomposition of benzoyl peroxide in an equimolar mixture of benzene and toluene containing m-dinitrobenzene

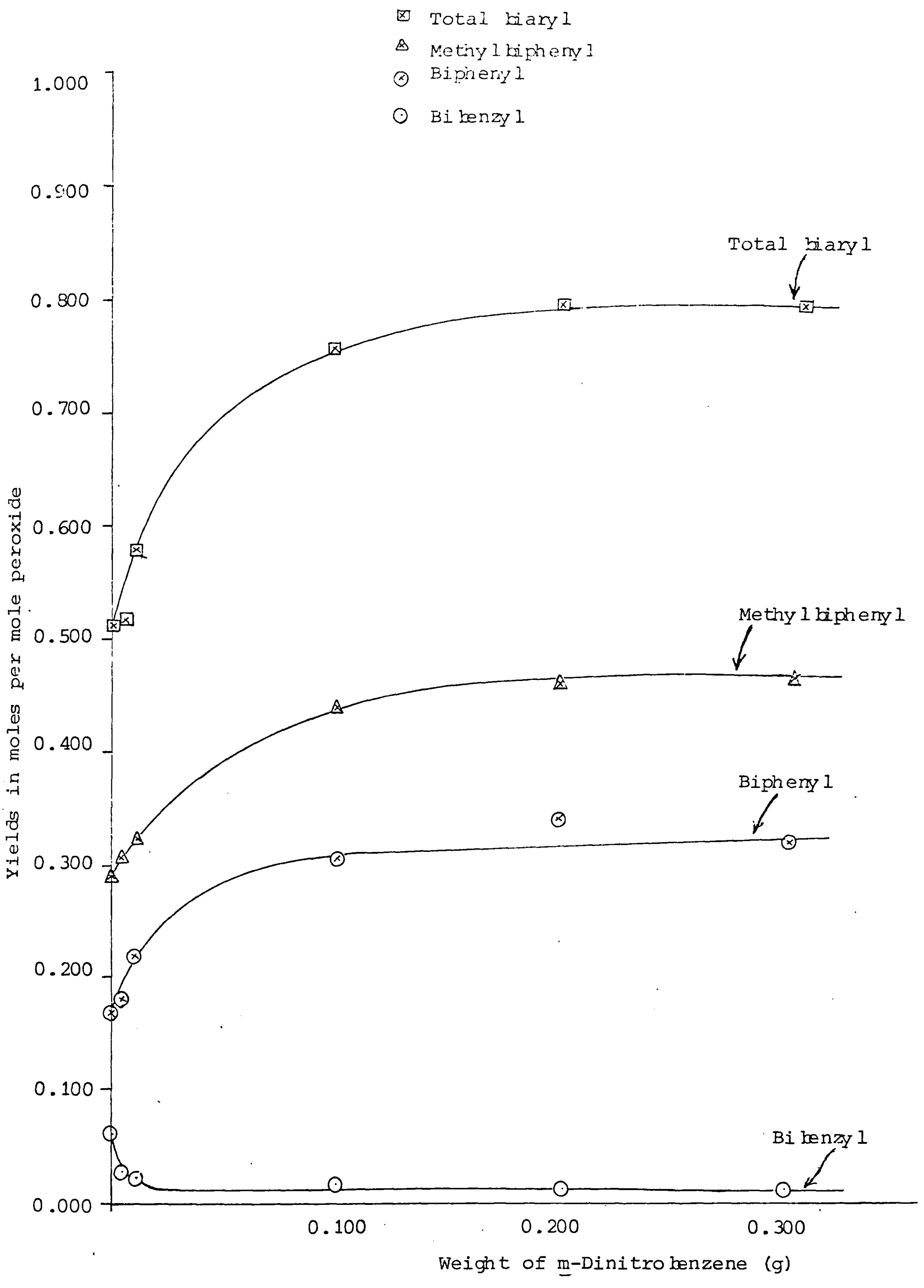


FIGURE 4

a very reactive species in aromatic substrates (cf. page167) hence the two molecules would approach the same reactivity in the absence of complexation between toluene and the precursor of phenyl radical. So the random attack of phenyl radicals on the two solvent molecules gives rise to the formation of a larger proportion of phenylcyclohexadienyl radicals which have a greater tendency to undergo dimerisation reaction in the absence of an oxidation agent. This fact becomes evident when we consider that the yield of biphenyl in the decomposition of benzoyl peroxide in benzene is seldom more than 0.4 mole per mole of benzoyl peroxide in the absence of additive while its yield is increased to more than 0.9 mole per mole in the presence of additives, e.g. aromatic nitro-compounds. So in the presence of nitro-compounds, the larger proportion of unsubstituted σ-radicals in the present system would be efficiently intercepted and converted to biphenyl by the nitroxide radicals. The nitroxide radicals have a less marked effect on the methylphenylcyclohexadienyl radicals.

The limiting value of relative rate in the presence of nitrobenzene (>0.4 g) agrees moderately well with the values reported recently by Davies, Hey and Summer[55] in the competitive reaction of toluene with nitrobenzene as standard (Table 39).

Table 39

$^{\text{PhCH}_3}_{\text{PhH}}K$	Partial Rate factors Fo	 Fm	 Fp	References
1.46	2.68	0.70	2.02	Davies, Hey, Summers(55)
1.36	2.48	1.02	1.12	The present work.

Table 40

The effect of nitrobenzene and m-dinitrobenzene on the rate factors of toluene in the competitive reactions

Experiment Number	Additive g (m/m)	Relative Rate $\frac{PhCH_3}{PhH}K$	Partial Rate Factors		
			Fo	Fm	Fp
17 & 18	Nil	1.81	3.38	1.30	1.44
	Nitrobenzene				
19 & 20	0.1598 g (0.210)	1.34	2.54	0.87	1.19
Mean of 21 & 22	0.4512 (0.592)	1.36	2.40	1.01	1.31
23	0.8578 (1.125)	1.36	2.48	1.02	1.15
	m-Dinitrobenzene				
24	0.007 g (0.007)	1.69	2.80	1.21	2.12
25 & 26	0.0152 g (0.015)	1.49	2.59	0.98	1.76
27 & 28	0.1035 g (0.100)	1.42	2.61	1.02	1.26
29	0.2004 g (0.192)	1.48	2.62	1.14	1.36
30 & 31	0.2999 g (0.288)	1.45	2.59	1.08	1.39

The effect of additives on the relative rate factors $^{CH_3}_{H}K$ in the decomposition of benzoyl peroxide in an equimolar mixture of benzene and toluene at 80°

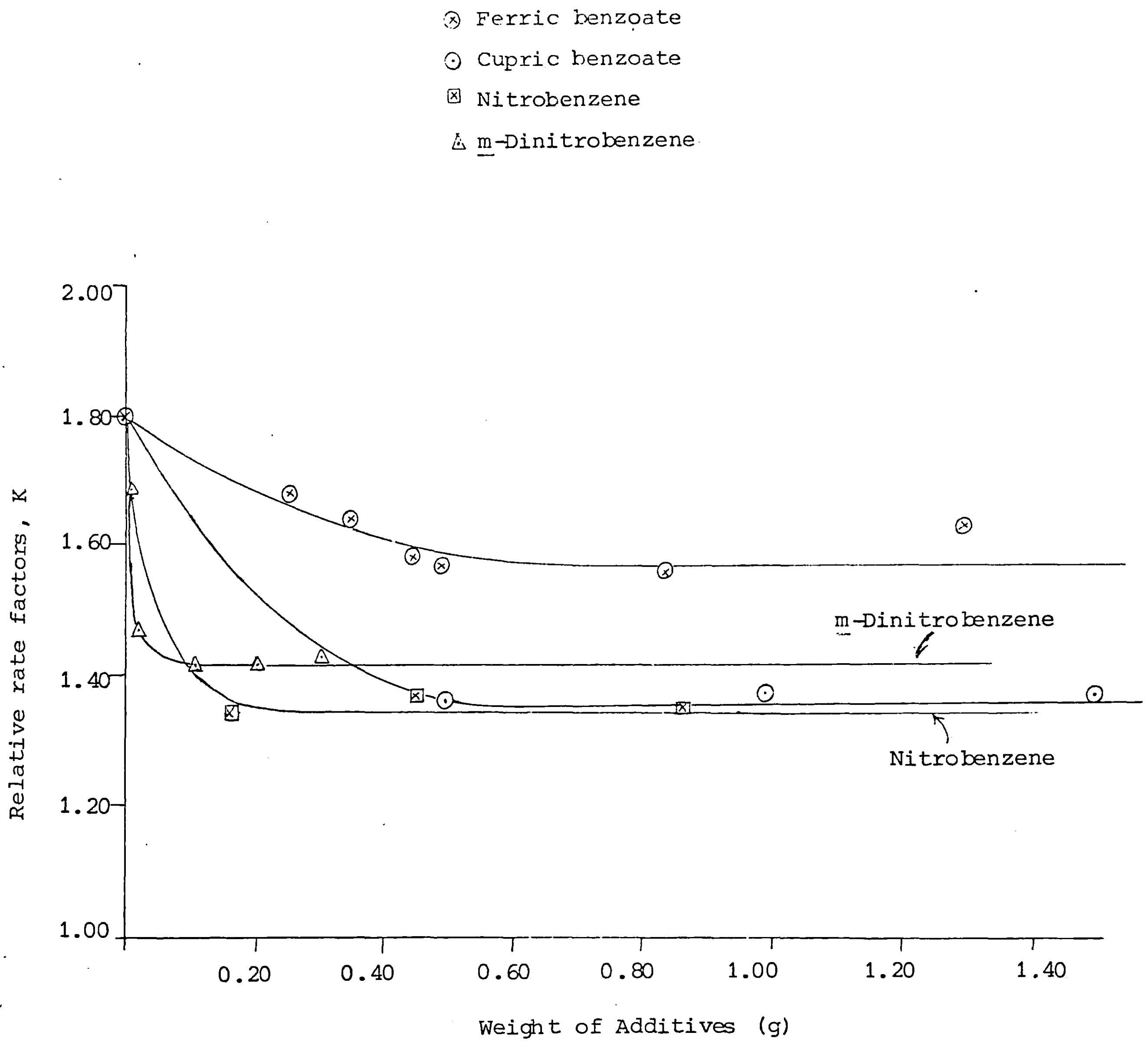


FIGURE 5

The variation of partial rate factors with concentration of nitrobenzene in the decomposition of benzoyl peroxide in equimolar mixture of toluene and benzene

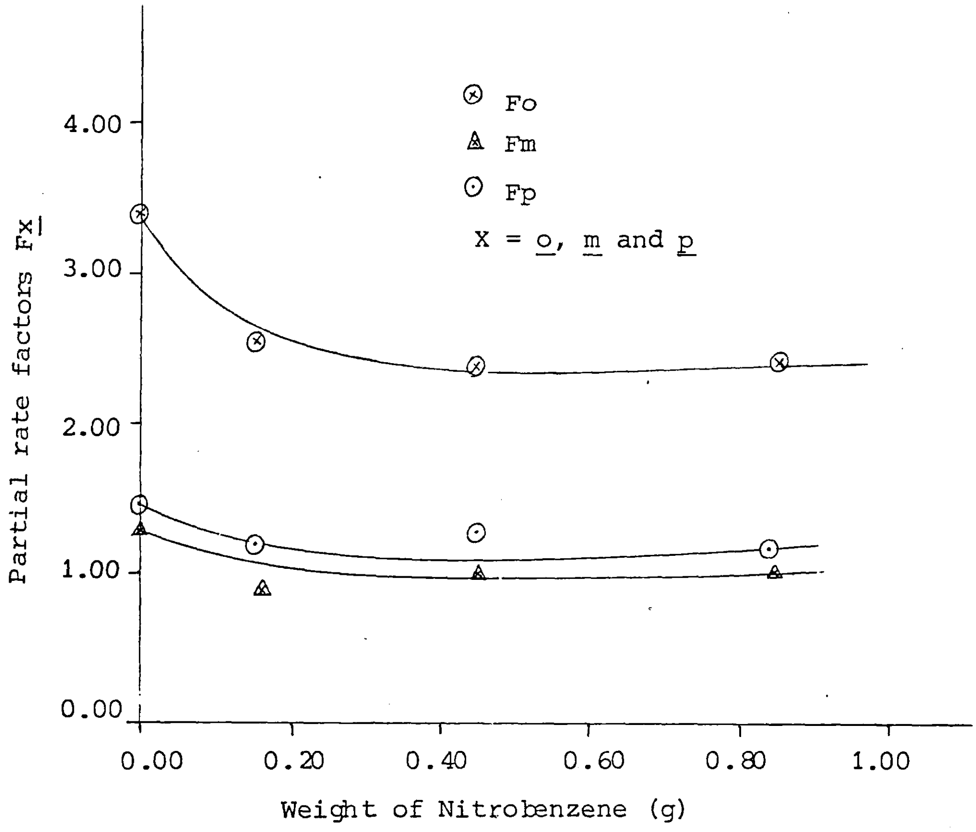


FIGURE 6

The variation of partial rate factors of toluene with concentration of m-dinitrobenzene in the decomposition of benzoyl peroxide in equimolar mixture of toluene and benzene

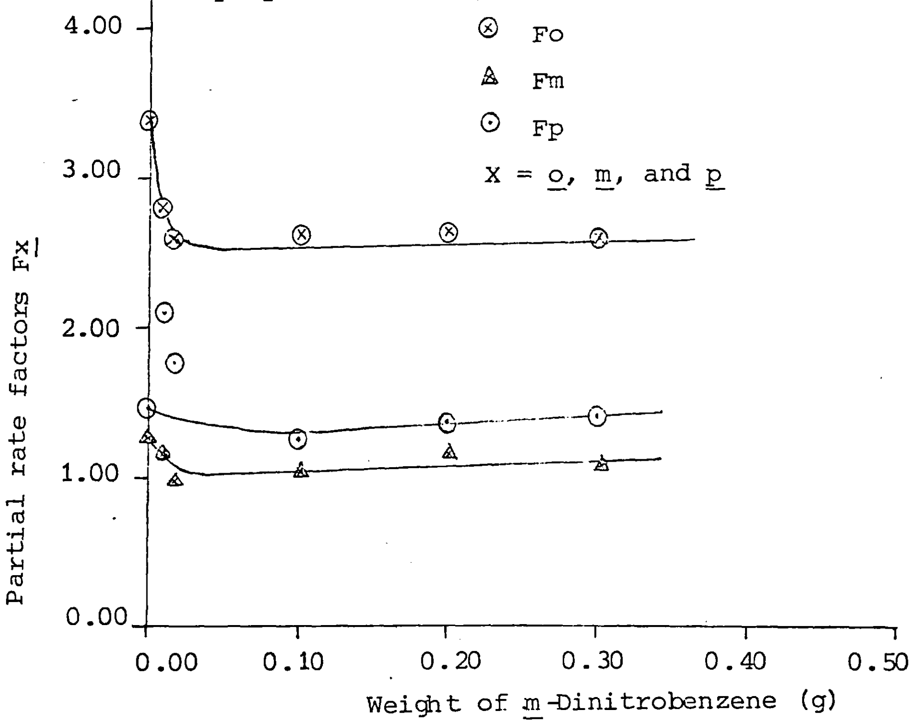
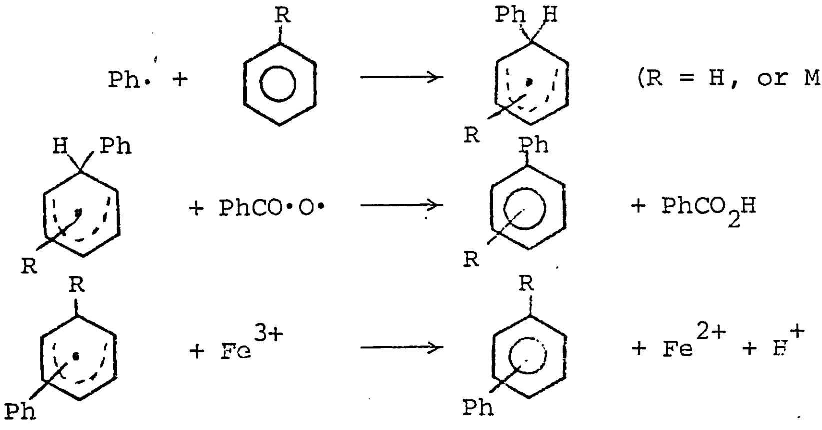


FIGURE 7

(c) The effect of ferric benzoate and cupric benzoate on the decomposition of benzoyl peroxide in equimolar mixture of benzene and toluene

The addition of ferric and cupric benzoates to the competitive phenylation of toluene and benzene produces a similar lowering of the values of relative rate with increase in catalyst concentration as that observed in reactions with nitro-compounds as additives. The partial rate factors follow the same trend. The metal salts probably exert the same influence on these reactions as they have shown in reaction in toluene alone. It is unreasonable that the effect of metal salts in an equimolar solution of benzene and toluene would be different from the effects they have in reactions in benzene or toluene alone, unless solvent complexation is important. Consequently, a similar mechanism to that proposed for the reaction in toluene alone can account for the formation of biaryls and benzoic acid in the competitive reactions.

$$(PhCO{\cdot}O)_2 \longrightarrow 2PhCO{\cdot}O{\cdot} \longrightarrow 2Ph{\cdot} + 2CO_2 \quad \ldots\ldots (130)$$



(R = H, or Me) ...... (131)

$+ PhCO_2H$ ...... (132)

$+ Fe^{2+} + H^+$ ...... (133)

$$PhCO{\cdot}O{\cdot} + Fe^{2+} \longrightarrow PhCO_2^- + Fe^{3+} \quad \ldots\ldots (134)$$

$$Fe^{2+} + (PhCO{\cdot}O)_2 \longrightarrow PhCO_2^- + PhCO{\cdot}O{\cdot} + Fe^{3+} \quad \ldots\ldots (135)$$

$$PhCO_2^- + H^+ \longrightarrow PhCO_2H \quad \ldots\ldots (136)$$

Table 41

The effect of cupric benzoate and ferric benzoate on the rate factors of toluene in the competitive reaction

Experiment Number	Additive g (m/m)	Relative Rate $^{CH_3}_{H}K$	Partial Rate Factors		
			Fo	Fm	Fp
Mean of 17 & 18	Nil	1.81	3.38	1.30	1.44
	Cupric benzoate				
32 & 33	0.5000 g (0.132)	1.36	2.66	0.92	1.00
34 & 35	0.9998 g (0.264)	1.36	2.70	0.88	1.09
36	1.5002 g (0.396)	1.37	2.66	0.89	1.13
	Ferric benzoate				
37	0.2547 g (0.038)	1.68	3.23	1.08	1.46
Mean 38 & 39	0.3497 g (0.052)	1.64	3.18	1.10	1.27
Mean of 40 & 41	0.4459 g (0.067)	1.58	3.06	.099	1.39
42	0.5504 g (0.082)	1.56	2.92	1.04	1.43
43	0.8474 g (0.126)	1.55	2.87	1.07	1.43
44	1.3032 g (0.194)	1.64	2.98	1.06	1.72

The decomposition of benzoyl peroxide in equimolar mixture of benzene and toluene containing ferric benzoate

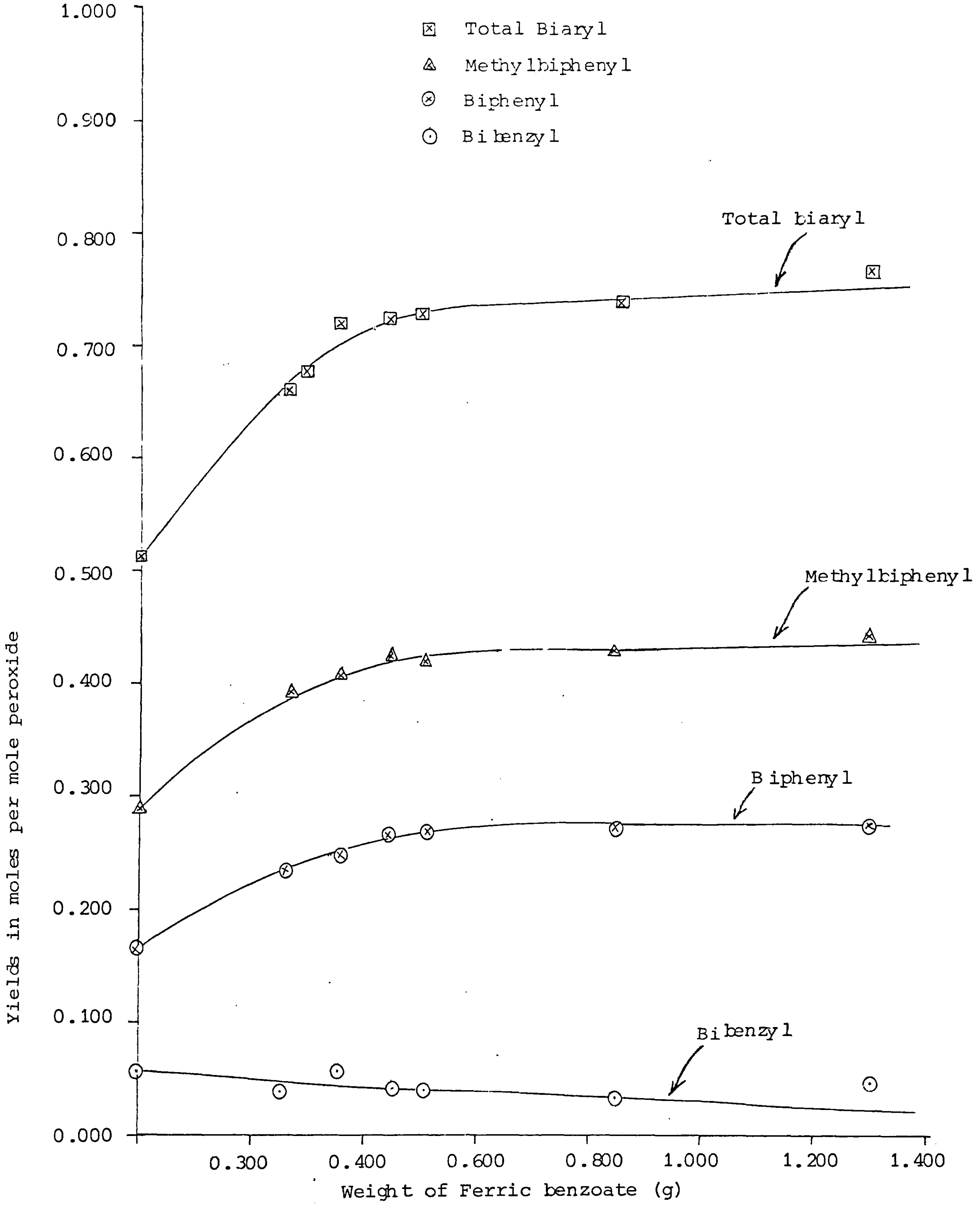


FIGURE 8

The decomposition of benzoyl peroxide in an equimolar mixture of benzene and toluene containing cupric benzoate

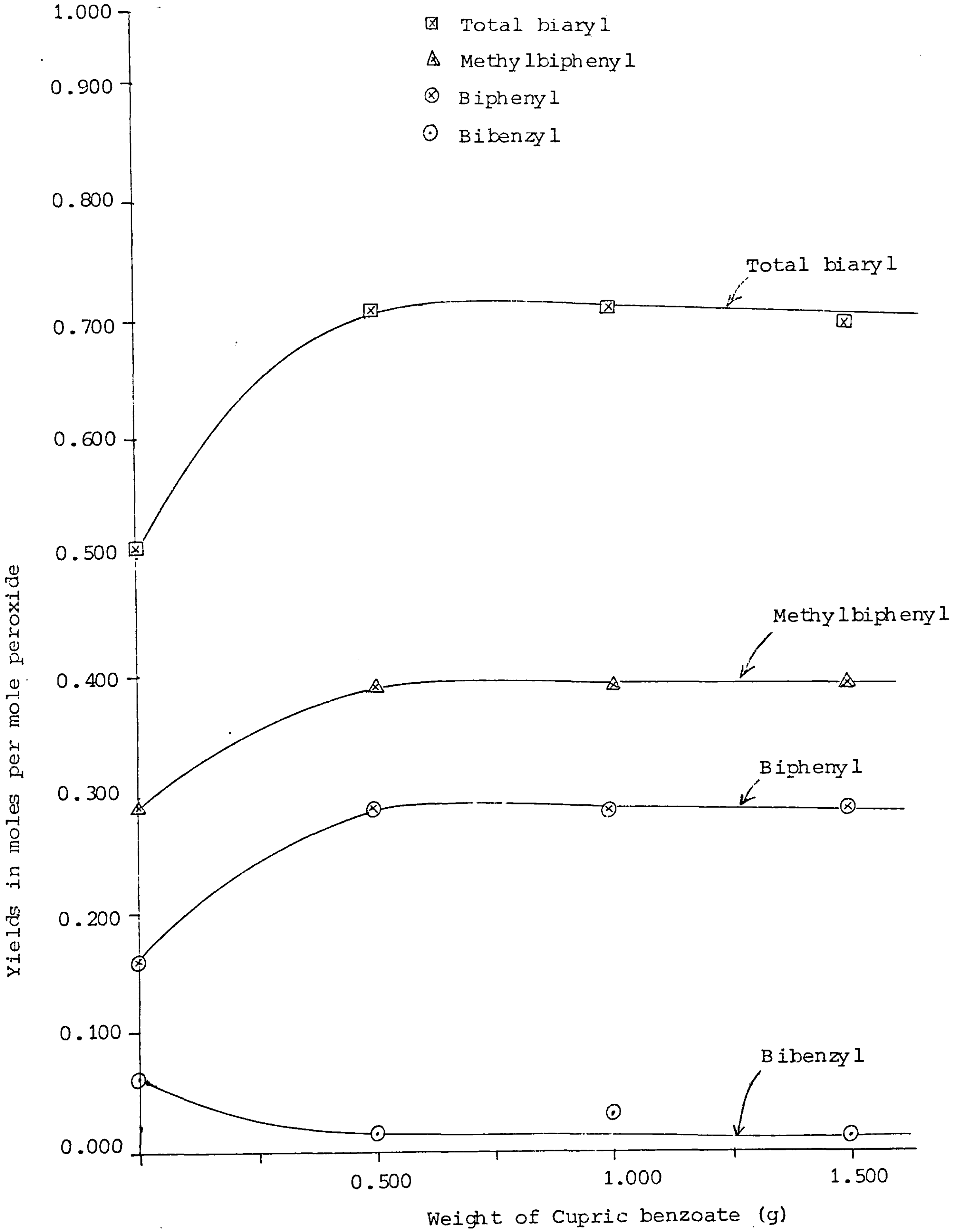


FIGURE 9

The variation of partial rate factors with concentration of cupric benzoate in the decomposition of benzoyl peroxide in equimolar mixture of toluene and benzene

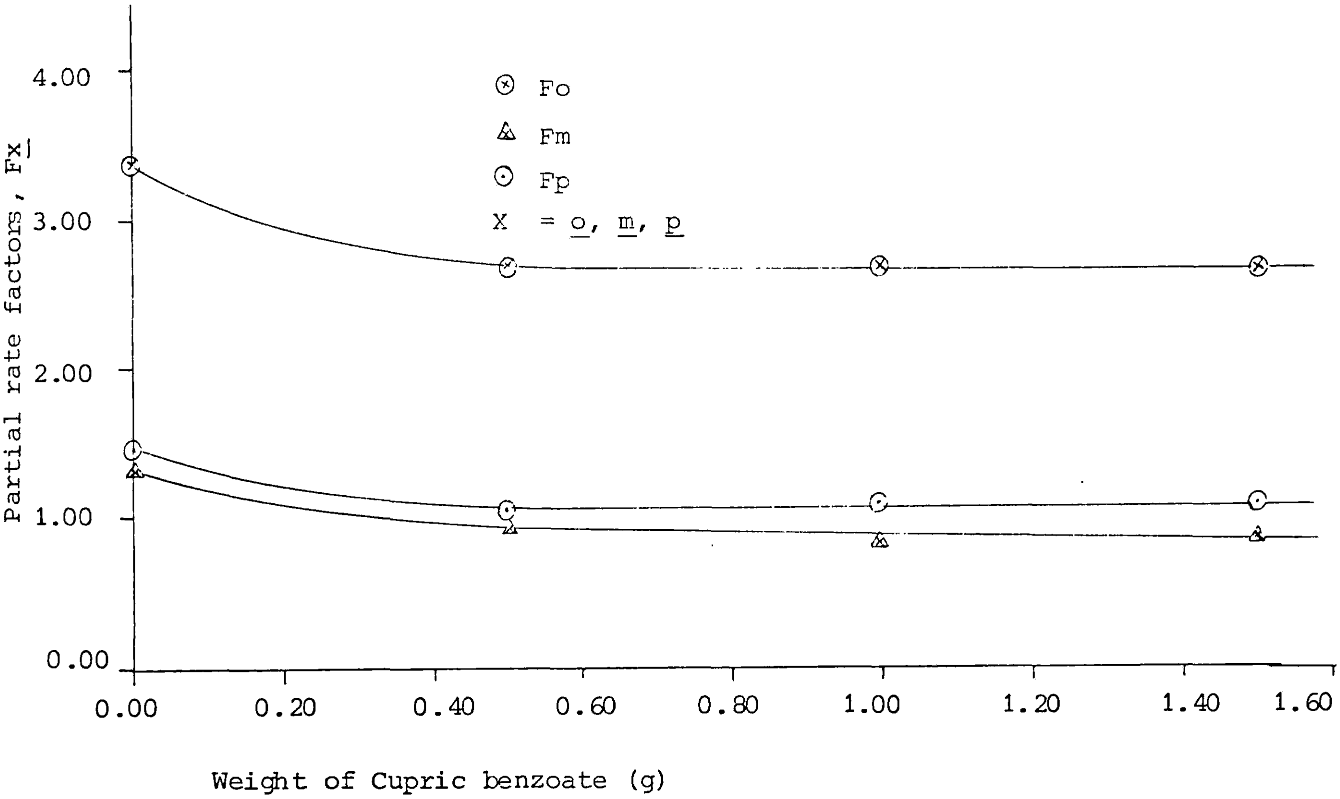


FIGURE 10

The variation of partial rate factors with concentration of ferric benzoate in the decomposition of benzoyl peroxide in equimolar mixture of toluene and benzene

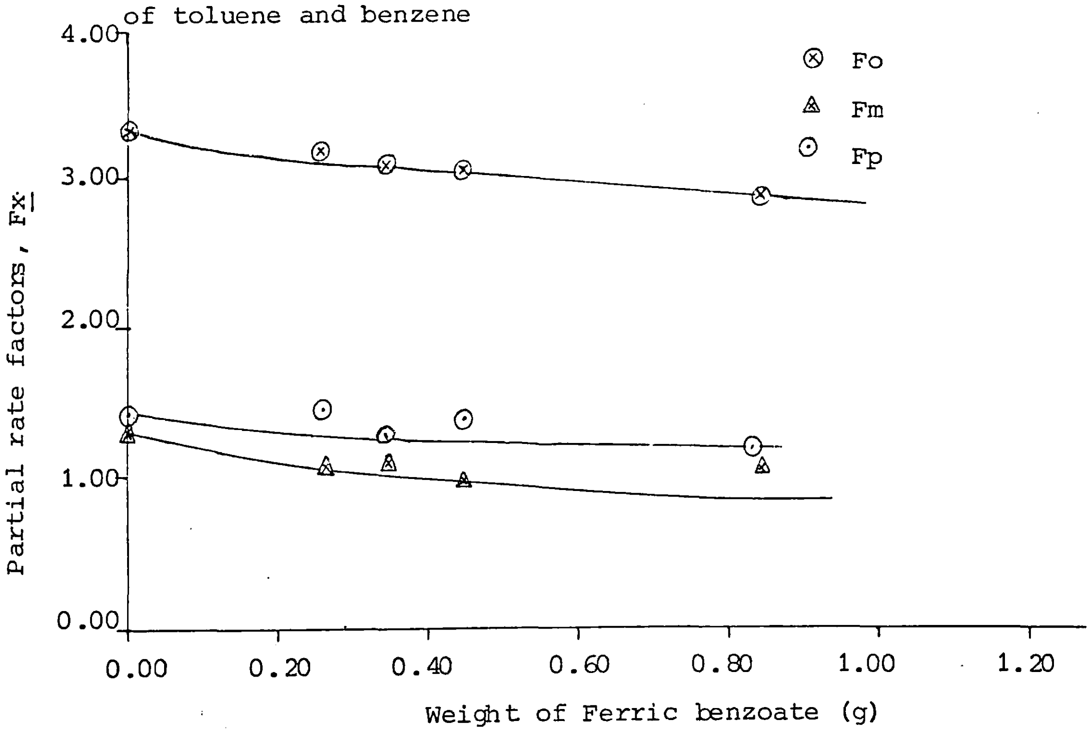


FIGURE 11

The variation of the relative rates and partial rate factors with catalyst concentration is illustrated in Figures 5, 10 and 11 and Table 4 and that for the variation of the major products is illustrated in Figures 8 and 9. The explanations suggested (page 168) to account for the similar trend caused by nitrobenzene and m-dinitrobenzene probably are also applicable in these metal ion catalysed reactions. The initial complexation of the peroxide molecule with the metal salts and the subsequent stabilisation of benzoyloxy radicals could be more important in these systems. The rate factors obtained in the presence of metal salts, for reasons similar to those given for the nitro-group catalysed reactions, are more reliable indices of the reactivity of toluene towards phenylation reactions than those observed from uncatalysed reactions (Table 38). The values of K obtained (Table 41) show that toluene is slightly more reactive than benzene than reported before[7].

(d) The effect of additives on the decomposition of benzoyl peroxide in a system containing various molar proportions of benzene and toluene

The relative rate factors for the competitive phenylation reaction containing varying molar ratios of benzene and toluene with and without additives are summarised in Table 42. A relative rate factor of 1.79 for the reaction containing toluene and benzene in a molar ratio of 2.95 agrees well with the value from the competitive reaction containing equimolar mixture of benzene and toluene in the absence of additive. However, a value of 1.32 is obtained for the reaction containing a molar ratio of 0.328 of toluene to benzene. On the other hand, more consistent values are obtained in the presence of additives. These values are also comparable to that obtained from the reaction containing an equimolar mixture of benzene and toluene. This observation suggests that the rate factors obtained in the absence of an efficient oxidising agent could be erroneous.

Table 42

The effect of varying substrate concentration on the relative rate of toluene at 80°. Peroxide concentration = 0.083 M (1.5 g/75 ml)

Additive g (mole/mole)	Substrate Ratio $[PhCH_3]/[PhH]$	Relative Rate K
Nil	1	1.81
Nil	2.947	1.79
Nil	0.328	1.32
m-Dinitrobenzene		
0.2999 g (0.288)	1	1.45
0.2501 g (0.241)	2.947	1.50
0.2532 g (0.243)	0.328	1.39
Cupric benzoate		
0.5000 g (0.132)	1	1.36
0.0998 g (0.026)	2.947	1.43
0.1010 g (0.027)	0.328	1.26
Ferric benzoate		
0.8474 g (0.126)	1	1.55
0.8033 g (0.119)	2.947	1.44
0.8020 g (0.119)	0.328	1.54

(e) Summary

From the above discussion it is clear that the rate factors depend on the concentration of the additives and approach a limiting value with the increase in additive concentration. The inclusion of additives inhibits the complicating side reactions. Consequently, the limiting results obtained in the presence of additives, which are also independent of the benzene/toluene ratio, are reliable indices of reactivity of toluene in the phenylation reaction. The values obtained under the influence of different additives agreed well with each other. The limiting value of the total rate factor is about 1.4. The best sets of total and partial rate factors obtained in the present studies are summarised in Table 43. The mean values are considered to be the best definitive set now available.

Table 43

Additive	Total Rate Factors	Partial Rate Factors		
	${}^{CH_3}_{H}K$	Fo	Fm	Fp
Nitrobenzene	1.36	2.48	1.02	1.15
m-Dinitrobenzene	1.44	2.57	1.05	1.41
Cupric benzoate	1.37	2.66	0.89	1.13
Ferric benzoate	1.58	2.92	1.06	1.53
Mean	1.4	2.7	1.0	1.3

III. The effect of additives on the decomposition of benzoyl peroxide

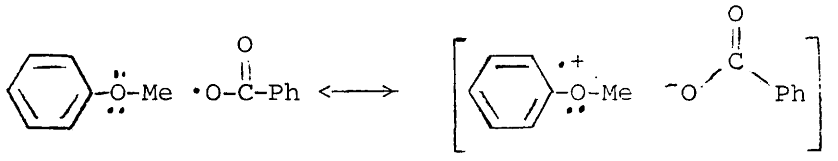
(a) The decomposition of benzoyl peroxide in anisole

(i) Methoxybiphenyls

The results of the phenylation reaction of anisole with benzoyl peroxide revealed several interesting features, (1) phenyl radicals exhibit a high selectivity at the o-position of the anisole molecule, (2) anisole is more reactive than benzene towards benzoyloxylation reaction, (3) the reaction is always accompanied by the formation of usually large amounts of benzoic acid, and (4) the reaction is characterised by high material balance; the recovery of phenyl group of the peroxide is always higher than 80%.

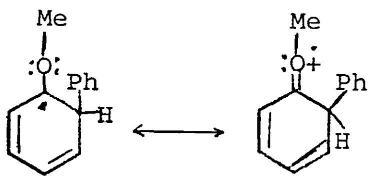
The high selectivity of the phenyl radicals at the o-position of anisole is inconsistent with the high reactivity of phenyl radicals with aromatic substrate[150] (cf. page 167). This fact could be explained if different species are involved in the selecting and the actual phenylation process. The contradicting observation of high selectivity and high reactivity could be rationalised if some preliminary association or complexation of a precursor of phenyl radical with anisole molecules occurs e.g. by a charge transfer complex formation. Complexation allows the precursor of phenyl radical to select the more reactive sites of the anisole molecules. The higher reactivity of the o-position suggests that an electrophilic species may be involved in the selecting process. Complexation is possible if there is a considerable difference between the distribution of electron density in the reagents and the substrate exists. The complexation in this reaction could happen in the following ways. The electrophilic benzoyloxy radicals may tend to associate themselves with the electron-rich site in the anisole molecules which is invariably the oxygen atom of the methoxy group, structure (18).

It is also possible that the benzoyloxy radicals form a loosely bound π-complex with the electron rich π-system of anisole.

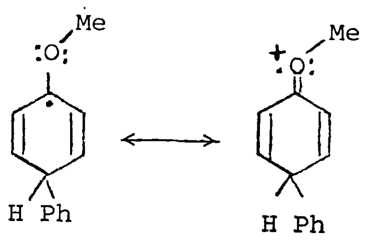

(18)

The benzoyloxy radicals stabilised in this manner could add to the anisole molecule to form the corresponding benzoyloxylated adduct or decarboxylate to afford phenyl radicals.

In the absence of a good oxidising agent, the benzoyloxy adducts are not efficiently intercepted and regenerate benzoyloxy radicals. On decarboxylation they give rise to phenyl radicals which add to anisole molecules to form the corresponding σ-radicals. Owing to their closer proximity to the o-position than other nucleus positions, the phenyl radicals subsequently formed attack the o-position most readily. The odd electron of the resulting σ-radicals of the o- and p- isomer is in conjugation with the oxygen atom of the methoxy group e.g. structures (19) and (20). The ability of the odd electron of the σ-radicals to delocalise to the oxygen atom of the methoxy group has two consequences namely (i) it facilitates the formation of the corresponding σ-radicals, (ii) it also facilitates the oxidation of the corresponding σ-complexes which are stabilised by such


(19)

and


(20)

conjugation effect. Therefore the rate of formation and the rate of oxidation of the *o*- and *p*- σ-radicals would be faster than those corresponding to the *m*- σ-radicals which are not stabilised by such conjugation. As a result, the *m*- σ-radicals are less readily formed and also less readily oxidised and tend to undergo dimerisation just as rapidly than σ-radicals involved in the phenylation of unsubstituted benzene. Jane-Marie Bonnier *et al*[52] have also reported the selective side reactions of σ-complexes in the phenylation of 4-methyl-3-phenylpyridine. Selective side reaction of σ-complexes was also observed in the phenylation of chlorobenzene with phenylazotriphenylmethane[151(a,b)].

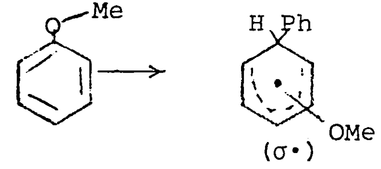
As a result of the complexation of benzoyloxy radicals with anisole molecules, the resulting phenyl radicals are restricted from attacking the three isomeric positions of anisole randomly. In addition to this complication, the greater resistance of the σ-radicals leading to the *m*-isomers than the *o*- and *p*-isomers to oxidise to biaryl , the isomer ratio determined in this reaction in the absence of an efficient oxidising agent is therefore a poor measure of the reactivity of the nuclear positions of anisole molecules towards the attack of phenyl radicals. It is more appropriate that the isomer ratio reflects the selectivity of benzoyloxy radicals on the various sites of anisole molecules.

The following reactions lead to the formation of major products in this reaction

$$(PhCO{\cdot}O)_2 \longrightarrow 2Ph{\cdot}CO{\cdot}O{\cdot} \qquad \ldots\ldots \ (137)$$

$$PhCO{\cdot}O{\cdot} \longrightarrow Ph{\cdot} + CO_2 \qquad \ldots\ldots \ (138)$$

Ph• +



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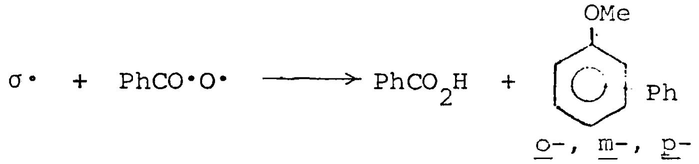

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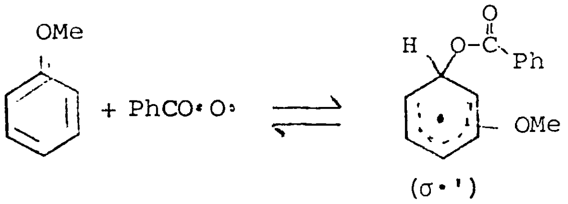

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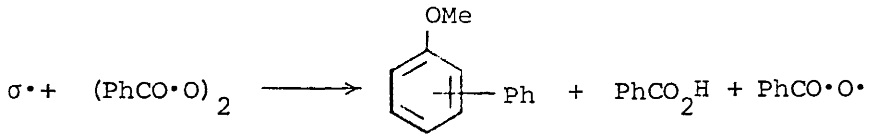

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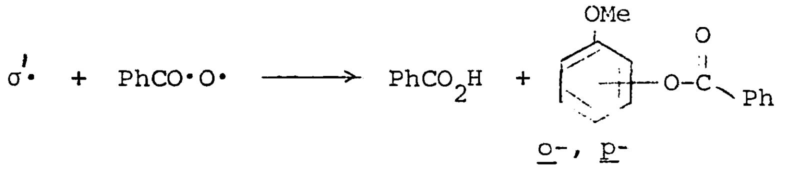


...... (143)

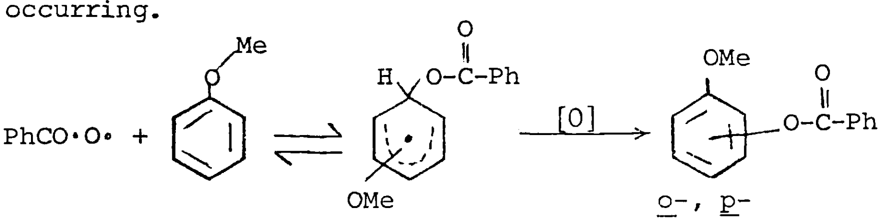
2 σ• ⟶ Dimerization and disproportionation products .... (144)

2 σ•' ⟶ Dimerization and disproportionation products....(145)

Reaction (140) is the main methoxybiphenyl formation reaction and is also the main termination step. This is based on the observation that high recovery of phenyl group is found in this reaction. The importance of termination by dimerization and disproportionation of σ-complex is correspondingly reduced in this system.

(ii) Methoxyphenylbenzoate

It is held that benzoyloxy radicals add reversibly to aromatic nucleus to form benzoyloxy-cyclohexadienyl intermediates, which are then oxidised to afford aryl benzoates[33, 36(a,b)]. Only o- and p-methoxyphenylbenzoates were detected in the present work. This observation agreed with the result of other workers[35(a),50]. The yield of benzoate ester detected in the present work is about 4% (on mole/mole basis) with a ratio of benzoyloxylated product to phenylated product about 0.07. The yield obtained in this reaction is much less than that reported in the presence of an oxidising agent where the benzoyloxylation adduct was trapped and oxidised to form the products, and prevented the reverse reaction from occurring.



...... (146)

Although an efficient oxidising agent (the benzoyloxy radicals stabilised by complexation) is present in solution in this reaction, owing to its low concentration, it cannot efficiently prevent the benzoyloxylated adduct from fragmenting to regenerate benzoyloxy radicals which then decarboxylate to give phenyl radicals, thereby resulting in low yields of ester in this reaction.

The low yield of ester observed in the present work disagrees with that reported by Lynch and Moore[35a] who detected a much higher yield of ester (20%, on mole per mole basis, with a ratio of 0.5 for the benzoyloxylated products to phenylated products). The isomer ratio reported by these workers ranging from 65 - 82% for the o-isomer and 18% to 35% for the p-isomer. However, the results obtained in the present work agreed well with the more recent work of McClelland, Norman and Thomas[50].

(iii) Benzoic acid

The yield of benzoic acid in this reaction is always too high to be accounted for by the formation of methoxybiphenyl and methoxyphenylbenzoate.

Table 44

Experiment Number	Methoxybiphenyls (m/m)	Methoxyphenyl-benzoates (m/m)	Benzoic acid
Mean of 57, 58, 59	0.412	0.037	1.176

Other mechanisms must be responsible for the amount of benzoic acid formed. It has been suggested by Augood and Williams[5] that side chain hydrogen abstraction occurs, and more recently McClelland, Norman and Thomas[50] also reported the detection of the products of side chain hydrogen abstraction. Traces of benzene were detected in the present studies. Consequently, side chain hydrogen abstraction by benzoyloxy radicals must account for, at least some of the benzoic acid formed. A minor contribution could also come from the hydrogen abstraction by benzoyloxy radicals from the hydro-aromatic products, a general reaction which becomes significant when the benzoyloxy radicals are stabilised[152]. Another contribution could come from the induced decomposition of benzoyl peroxide by phenol which contaminated the anisole sample, according to the following reaction[153].

$$\mathrm{PhOH} + (\mathrm{PhCO{\cdot}O})_2 \longrightarrow \mathrm{PhO{\cdot}} + \mathrm{PhCO_2H} + \mathrm{PhCO{\cdot}O{\cdot}} \quad \ldots\ldots \ (147)$$

Though the sample used for the present investigation has been shown gas chromatographically to be free from phenol ($\not> 0.05\%$) it is possible that some phenol is formed during the reaction. Free radicals can effect the dealkylation of ethers: Cowley, Norman and Waters[154] have found that methyl radicals effect dealkylation of anisole, and Kharasch and Huang[155] have shown that many phenol ethers can be dealkylated by free radicals, thus lending some support to this possible explanation of the formation of some of the excessive benzoic acid.

$$PhOCH_3 + PhCO\cdot O\cdot \longrightarrow (PhOCH_3)^{+\cdot} + PhCO_2^- \qquad \ldots\ldots (148)$$

$$(PhOCH_3)^{+\cdot} + PhCO\cdot O\cdot \longrightarrow Ph\overset{+}{O}{=}CH_2 + PhCO_2H \qquad \ldots\ldots (149)$$

$$Ph\overset{+}{O}{=}CH_2 + H_2O \longrightarrow PhOH + CH_2O + H^+ \qquad \ldots\ldots (150)$$

In a duplicate set of experiments t-butylhydroperoxide was deliberately added to the reaction mixture prior to the start of the reaction to find out if it could also participate, as phenol is thought to, in an induced decomposition of benzoyl peroxide hence giving high yields of benzoic acid. However, there was no significant change in the benzoic acid yield, and the product distributions were also essentially unaltered. So t-butylhydroperoxide cannot cause an induced decomposition of benzoyl peroxide. The reaction was not investigated further.

(b) The effect of *m*-dinitrobenzene and pentafluoronitrosobenzene on the decomposition of benzoyl peroxide in anisole

Table 45

Experiment Number	Additive (m/m)	Methoxy-biphenyls Yield (m/m)	Methoxyphenyl-benzoates Yield (m/m)	Benzoic acid
Mean of 57, 58, 59	Nil	0.412	0.373	1.176
Mean of 60 and 61	*m*-Dinitrobenzene (0.5760)	0.369	0.085	1.213
Mean 62 and 63	Pentafluoro-nitrobenzene (0.009)	0.395	Not determined	Not determined

The inclusion of m-dinitrobenzene and pentafluoronitrosobenzene in the reaction did not cause an increase in the yield of methoxybiphenyl but a slight decrease. The lack of an increase in the yield of biaryl is not unexpected as it has already been suggested in the preceding section that an efficient oxidising agent (benzoyloxy radicals) for the methoxyphenylcyclohexadienyl radicals exist. However, it is surprising to note that nitro-compounds only increase the yield of methoxyphenylbenzoate slightly (to about 9% yield, on a mole per mole basis). From the isomer distribution of methoxybiphenyls it is evident that m-dinitrobenzene must have participated in this reaction. The markedly different isomer ratios of methoxybiphenyls in the reaction containing m-dinitrobenzene and that containing pentafluoronitrosobenzene suggests that the compounds have different effects in this reaction.

Table 46

Experiment Number	Additive (m/m)	Methoxybiphenyls Isomer Ratio o-	m-	p-	Methoxyphenylbenzoates Isomer Ratio o-	p-
Mean of 57, 58, 59	Nil	73.7	11.8	14.5	71.5	28.5
Mean of 60 and 61	m-Dinitrobenzene 0.576	67.4	20.7	11.9	57.8	42.2
Mean of 62 and 63	Pentafluoronitrosobenzene 0.009	73.8	15.2	11.0	Not determined	

In the reactions containing m-dinitrobenzene, a more nearly statistical distribution of isomers is obtained showing that the phenyl radical is less selective towards the various positions of the anisole molecule in the presence of m-dinitrobenzene. This shift of the isomer ratio could be due to the following reason: m-dinitrobenzene may have participated in the formation of a π-complex with the benzoyloxy radicals, reducing the tendency of these radicals to complex with the anisole molecule. As a result, on decarboxylation of the benzoyloxy radicals, the phenyl radicals subsequently generated could attack the various position on anisole molecules more randomly to form the σ-intermediates. Therefore the isomer ratio represents the selectivity of phenyl radicals. These σ-intermediates are quantitatively oxidised to provide biaryl by the action of the arylnitroxide radical according to the mechanism proposed in page 150, to account for the effect of m-dinitrobenzene in the phenylation reaction in toluene. In the presence of arylnitroxide radicals, an efficient oxidising agent, the oxidation of the three isomeric σ-intermediates would be indiscriminate, and consequently the σ-intermediates were qunatitatively transformed to biaryl, the dimerization reaction of the σ-intermediates of the m-isomers being prevented. Thus the isomer ratios provide a better index of the reactivity of the various sites towards phenyl radicals than those obtained in the absence of m-dinitrobenzene and is therefore valid for the calculation of partial rate factors.

In contrast to the effect of m-dinitrobenzene, pentafluoronitrosobenzene showed little effect on the isomer ratio of methoxybiphenyls. The presence of five strongly electron withdrawing fluorine atoms renders the π-system somewhat electron deficient, it also causes the nitroso-group to be relatively less electron-rich. This effect may cause the complexation of the benzoyloxy radicals, with the pentafluoronitrosobenzene an unfavourable process. As a result, the complexation between the benzoyloxy radicals and anisole still exists, therefore giving rise to the same isomer ratio observed in the absence of additives.

(c) The effect of oxygen and air on the decomposition of benzoyl peroxide in anisole

Table 47

Additive	Experiment Number	Methoxybiphenyls Yield (m/m)	Methoxybiphenyls Isomer Ratio			Methoxyphenylbenzoates Yield (m/m)	Methoxyphenylbenzoates Isomer Ratio		Benzoic Acid
			o-	*m*-	*p*-		*o*-	*p*-	
Nil	Mean of 57 58 and 59	0.412	73.7	11.8	14.5	0.037	71.5	28.5	1.176
Under oxygen	Mean of 64, 65, 66, 67 and 68	0.168	65.7	22.2	12.1	0.286	36.1	63.7	1.289 (Mean of 67 and 68)
Under air	Mean of 79 and 70	0.341	67.2	19.8	13.0	0.186	38.9	61.2	Not determined

Oxygen and air both affected the yield and the isomer ratios of the phenylated and benzoyloxylated products. The yield of methoxyphenylbenzoate was increased by about 8 times, but on the other hand, the yield of methoxybiphenyl was lowered to about 25% of that observed in the absence of oxygen. The shift of isomer ratio of methoxybiphenyls is in the same direction as that observed from the reactions in the presence of an oxidising agent, e.g. *m*-dinitrobenzene, cupric and ferric benzoates. However, the isomer ratio of methoxyphenylbenzoate is reversed with the *p*-isomer formed in a greater proportion (60-66%). The effect of oxygen in this reaction is in contradiction to the results of Cazes, Howe, Morrison and Samkoff[48], who reported an increase in the yield of methoxybiphenyl from 0.5 to 1.35 mol/mole under the influence of oxygen with the isomer ratio unaffected. We also noted greatly different results for experiments repeated under their identical conditions[159]. With such observations, their results could not be accepted without reservation. Since the yield of methoxybiphenyl found in the present work reduced so drastically, it would hardly expect all isomers to be equally affected,so change in isomer ratio is not surprising.

The isomer ratio with oxygen is not significant.

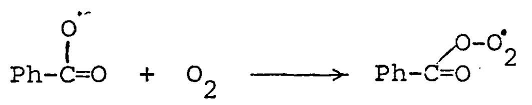
The decrease in yield of methoxybiphenyls in this reaction is considered to be due to the fact that phenyl radicals are trapped by oxygen molecules by the following mechanism resulting in the formation of phenol.

$$\text{Ph}\bullet + O_2 \longrightarrow \text{PhO}_2\bullet \qquad \ldots\ldots \quad (151)$$

$$\text{PhO}_2\bullet + \text{RH} \longrightarrow \text{PhO}\bullet\text{OH} + \text{R}\cdot \qquad \ldots\ldots \quad (152)$$

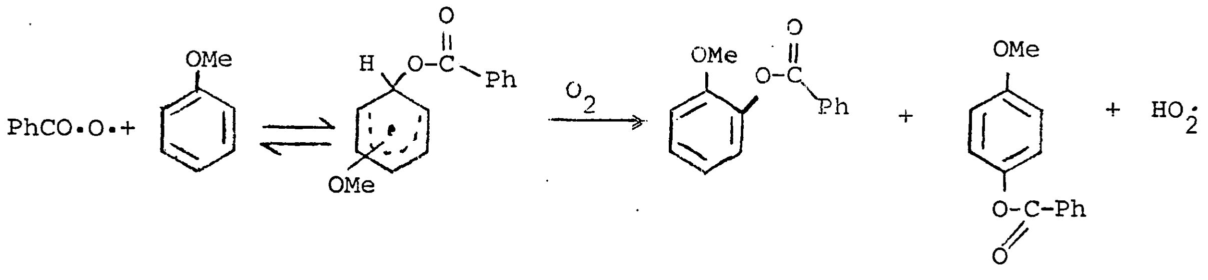
$$\text{PhO}\bullet\text{OH} \longrightarrow \text{PhO}\bullet + \bullet\text{OH} \qquad \ldots\ldots \quad (153)$$

The greater effect of oxygen than air on the decrease in methoxybiphenyls' formation also provides further support for this mechanism of diverting phenyl radicals from phenylation. The wider spread of the yield obtained in these reactions probably reflects the differences in flow rate of the gas in these reactions. It is difficult to reproduce the same flow rate in a different set of experiments. However, the benzoyloxy radicals are not trapped, this is probably due to the resultant formation of the unfavourable weak peroxidic bond.



$$\text{Ph-}\overset{\text{O}^{\bullet}}{\overset{|}{\text{C}}}\text{=O} + O_2 \longrightarrow \text{Ph-}\overset{\text{O-O}^{\bullet}_{2}}{\text{C}}\text{=O} \qquad \ldots\ldots \quad (154)$$

The increase in yield of the benzoate is consistent with the reversible addition of benzoyloxy radicals to anisole. In the presence of an efficient oxidising agent the reverse reaction is prevented.



...... (155)

The reason for the shift in isomer ratio of the benzoate is not clear, possibly the effect of the methoxy substituent in the oxidation step could be responsible.

(d) The effects of ferric benzoate and cupric benzoate on the decomposition of benzoyl peroxide in anisole.

Table 48

Experiment Number	Additive (m/m)	Methoxybiphenyls				Methoxyphenylbenzoates			Benzoic Acid (m/m)
		Yield (m/m)	Isomer Ratio *o*-	*m*-	*p*-	Yield (m/m)	Isomer Ratio *o*-	*p*-	
Mean of 57 58 and 59	Nil	0.412	73.7	11.8	14.5		71.5	28.5	1.176
Mean of 71 and 72	Cupric benzoate (0.100)	0.453	70.2	19.3	10.5	0.365	69.0	31.0	1.043
Mean of 73 and 74	Ferric benzoate (0.102)	0.518	70.3	18.1	11.6	0.126	60.7	39.3	0.949

The inclusion of transition metal salts in the reaction affected the isomer distribution pattern of methoxybiphenyls and the yields of methoxyphenylbenzoates. However, the salts have little effect on the total yield of methoxybiphenyls whereas they exert a great effect on the benzoyloxylation reaction. The yield of the benzoate ester was increased by 1300% by cupric benzoate and about 400% by ferric benzoate. Very similar isomer ratios are obtained for the methoxybiphenyls produced with both catalysts, suggesting a similarity of the effect of the two transition metal salts on these reactions. Side reactions of the σ-radicals are therefore minimal and the isomer ratio obtained approached a true measure of the reactivity of the various positions on the ring for phenylation provided that complexation of the radicals or its precursors with anisole does not favour the attack of any particular site. From the more nearly statistical distributions of isomer ratio than in the absence of additives it is evident that the latter complication is unimportant; it is more likely that the benzoyloxy radicals or benzoyl peroxide would complex with the more polar transition metal salts as described in the reaction in toluene (page 158). The larger proportion of m-methoxybiphenyl in this metal salt catalysed reaction than in the uncatalysed reaction is resulted from a more random attack on anisole by phenyl radicals to give σ-intermediates which are quantitatively oxidised to give biaryl under the influence of metal ions, as discussed in the preceding sections for the reactions under the influence of m-dinitrobenzene. Presumably the transition metal salt played the same role in this system as suggested for reaction in toluene (p. 158), and the methoxybiphenyls were formed by a similar mechanism to that suggested for the formation of methylbiphenyls in the presence of transition metal salts.

The fact that a 13-fold increase in the yield of benzoyloxylated products could be explained if the formation of the σ-complexes for benzoyloxylation were much less easily reversible in the presence of metal benzoates because (a) rate of their formation increased or (b) rate of their fragmentation decreased or (c) rate of their oxidation to ester increased, or a combination of two or all three of these reasons. As a result less benzoyloxy radicals are available for hydrogen abstraction leading to a slight decrease in the yield of benzoic acid in this reaction.

IV. The Effects of Additives in the Competitive Reaction of Benzoyl Peroxide in Benzene and Anisole Systems

(a) The decomposition of benzoyl peroxide in an equimolar mixture of benzene and anisole

The relative rate and partial rate factors obtained in the present work and those reported by previous workers are summarised in Table 49.

Table 49

Relative Rate	Partial Rate Factors Fo	Fm	Fp	Reference
3.18	7.24	1.05	2.51	Experiment 77 and 78
2.01	4.2	0.87	1.9	48
2.71	5.6	1.23	2.31	55
1.96	3.9	1.0	1.92	85

The relative rate obtained in the present work is higher than that previously reported[48,137]. The isomer ratio obtained is similar to that for the reaction in anisole alone. The high reactivity of anisole towards phenyl radicals could also be related to the complexation reaction and to the greater tendency of the phenylcyclohexadienyl radicals than the substituted σ-radicals to undergo side reactions. The complex formation "ties up" benzoyloxy radicals with anisole molecules.

(b) The effects of *m*-dinitrobenzene and nitrobenzene on the decomposition of benzoyl peroxide in an equimolar mixture of benzene and anisole

Table 50

Experiment Number	Additive g(mole/mole peroxide)	Relative Rate K	Partial Rate Factors		
			Fo	Fm	Fp
Mean of 77 and 78	Nil	3.18	7.24	1.05	2.51
Mean of 79, 80 and 81	*m*-Dinitrobenzene 0.2022 g (0.1941)	1.87	3.78	1.18	1.32
Mean of 82 and 83	*m*-Dinitrobenzene 0.4546 g (0.4304)	1.76	3.50	1.13	1.28
Mean of 84 and 85	Nitrobenzene 0.2168 g (0.2842)	2.19	4.41	1.38	1.52
Mean of 86 and 87	Nitrobenzene 0.4940 g (0.6476)	1.69	3.43	1.04	1.20

The isomer distribution of both methoxybiphenyl and methoxyphenylbenzoates shows a close similarity to that observed in the reaction in anisole alone containing m-dinitrobenzene as additive (Table 50). The effect of the nitro-compounds are demonstrated in figures (12), (13) and (14). From the similarity in isomer ratio in the products, it is likely that the same effect of m-dinitrobenzene operating in the reaction in anisole alone is also operating in this reaction. In the presence of m-dinitrobenzene the effect which was observed in the relative rates K for toluene is also observed here, though the effect is greater here: the relative rate has decreased from 3.18 to about 1.8.

The more drastic effect on the relative rate K in this reaction than for reactions with toluene could be accounted for by the following consideration. In the presence of m-dinitrobenzene, the complexation of benzoyloxy radicals with anisole is no longer an important phenomenon. On the contrary, the benzoyloxy radicals show a greater tendency to complex with the nitro-compound. Thus, a complicating factor in the uncatalysed reaction is removed by the presence of the catalyst. As a result, phenyl radicals could be freely formed from benzoyloxy radicals and could exhibit a random selection of the two competing solvent molecules. This would give rise to the formation of more phenylcyclohexadienyl radicals. As already suggested (page171), in the absence of additives the phenylcyclohexadienyl radicals are more prone to dimerisation reaction than the substituted phenylcyclohexadienyl radicals. However, this difference becomes much less important in the presence of m-dinitrobenzene since both types of radicals are then oxidised readily to give biaryls. Thus the biphenyl yield is increased, whereas the yield of methoxybiphenyls which was high even in the absence of additives, since the corresponding σ-complexes are almost quantitatively oxidised to biaryls, shows little scope for increase. The value of K as measured in the presence

The effect of additives on the relative rate factor ${}^{MeO}_{H}K$ in the decomposition of benzoyl peroxide in an equimolar mixture of anisole and benzene at 80°

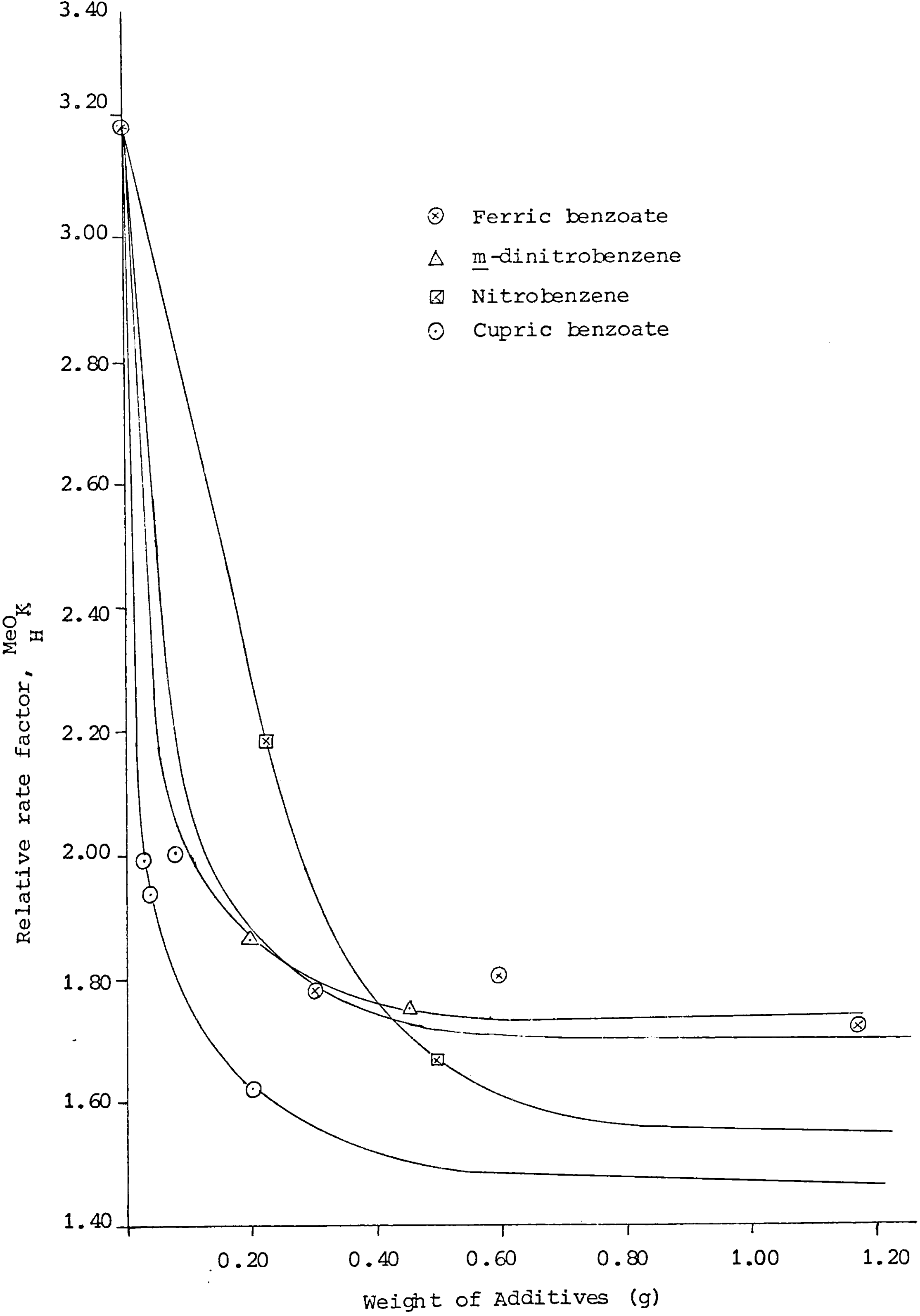


FIGURE 12

The variation of partial rate factors with concentration of nitrobenzene in the decomposition of benzoyl peroxide in equimolar mixture of anisole and benzene

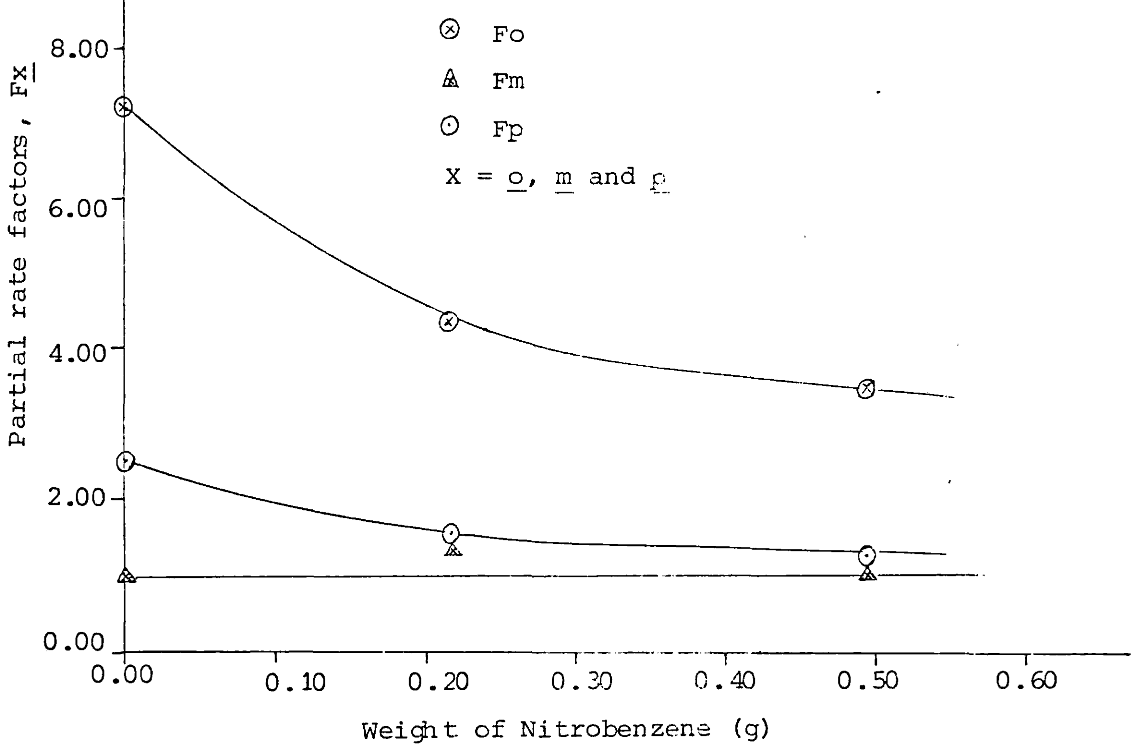


FIGURE 13

The variation of partial rate factors with concentration of m-dinitrobenzene in the decomposition of benzoyl peroxide in equimolar mixture of anisole and benzene

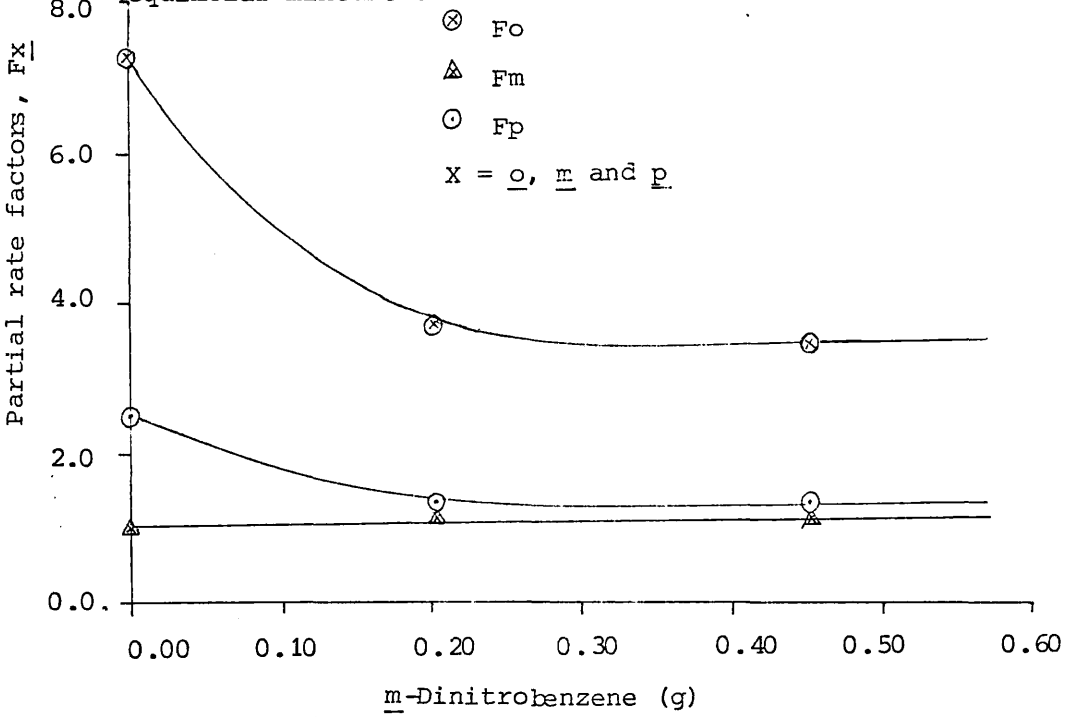


FIGURE 14

of m-dinitrobenzene is therefore lower than in its absence, and should be a better measure of the true relative reactivity of anisole.

A similar trend of reactivity was also observed in reactions with added nitrobenzene. Since the relative rate and the partial rate factors obtained in both nitrobenzene and m-dinitrobenzene are similar, the explanations suggested for the m-dinitrobenzene catalysed reactions are also applicable here.

The nitro-arenes also exert a great effect on the partial rate factors of the o- and p-positions of anisole while the m- is practically unaffected (c.f. Table 50). This fact provides further support of the idea that in the absence of additive benzoyloxy radicals also involved in selecting the two competing substrates ie. benzene and anisole molecules. In the presence of nitro-compounds the reactivity of o- and p-positions decreased drastically. The decrease in reactivity is caused by the removal of the preliminary selection by the electrophilic benzoyloxy radicals on the o- and p-positions which are relatively electron-rich. This arises from the elimination of the complexation reaction between benzoyloxy radicals and anisole molecules. The benzoyloxy radicals tend to form complex with the nitro-compounds. On subsequent decarboxylation of benzoyloxy radicals, the phenyl radicals generated would have no polar preference and would be non-selective both intra-molecularly and inter-molecularly, therefore causes a reduction in the partial rate factors of the o- and p-positions. Since the m-position is the least sensitive to polar effect, so the removal of the above complication has little effect on its reactivity.

(c) The effect of ferric benzoate, cupric benzoate and cupric p-toluate on the decomposition of benzoyl peroxide in an equimolar mixture of benzene and anisole

Table 51

Experiment Number	Additive g (mole/mole peroxide)	Relative Rate			
		K	Fo	Fm	Fp
Mean of 77 and 78	Nil	3.18	7.24	1.05	2.51
	Ferric benzoate				
Mean of 88 and 89	0.3053 g (0.045)	1.79	3.84	0.87	1.34
Mean of 90 and 91	0.5979 g (0.089)	1.81	3.83	0.90	1.36
Experiment 92	1.1857 g (0.176)	1.72	3.66	0.89	1.25
	Cupric benzoate				
Mean of 93 and 94	0.0206 g (0.006)	1.99	4,08	1.19	1.39
Experiment 95	0.0400 g (0.011)	1.94	3.98	1.15	1.36
Experiment 96	0.0800 g (0.021)	2.08	4.30	1.26	1.38
Mean of 97 and 98	0.2000 g (0.053)	1.62	3.31	0.98	1.12
	Cupric toluate				
Mean of 99 and 100	0.0404 g (0.010)	1.56	3.19	0.95	1.05

These catalysts also lead to lower apparent relative reactivities of anisole. The isomer ratio in these reactions is similar to that observed in reactions catalysed by nitro-arenes. As usual the recovery of phenyl groups is good so the extent of the side reaction is minimal in this catalysed reaction.

The variation of partial rate factors with concentration of ferric benzoate in the decomposition of benzoyl peroxide in equimolar mixture of anisole and benzene

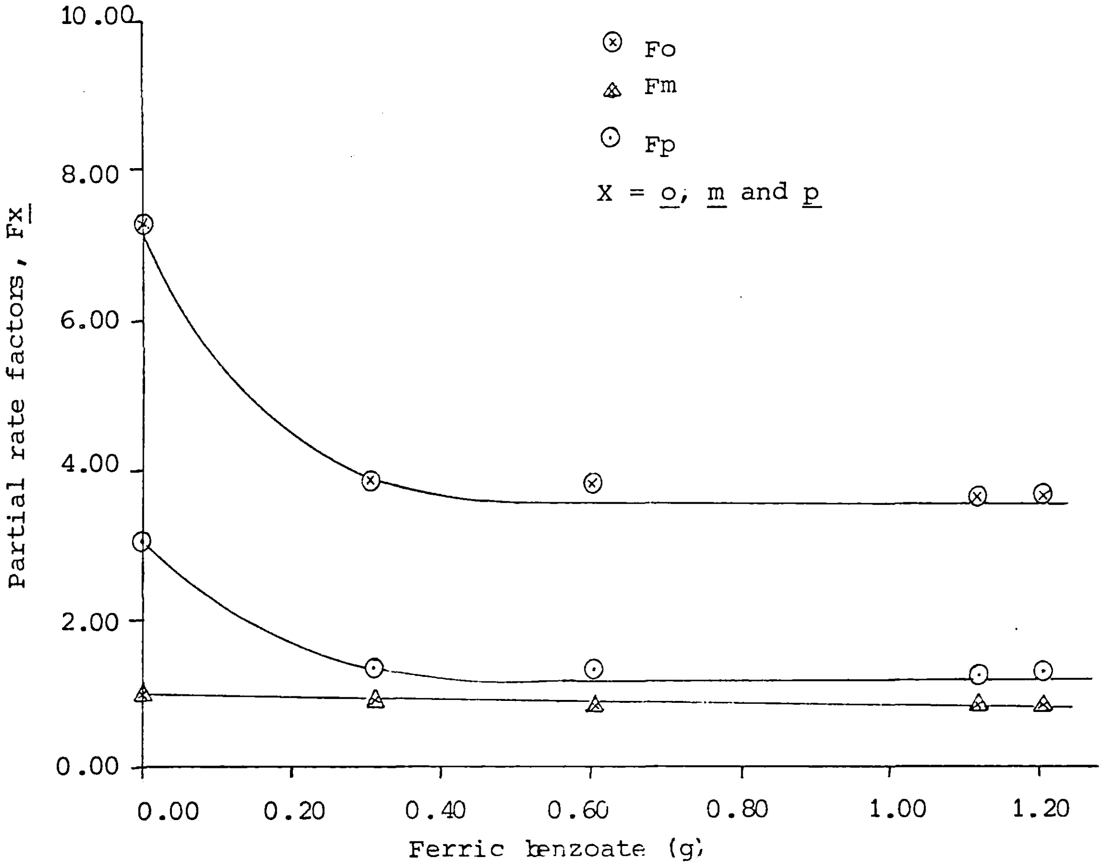


FIGURE 15

The variation of partial rate factors with concentration of cupric benzoate in the decomposition of benzoyl peroxide in equimolar mixture of anisole and benzene

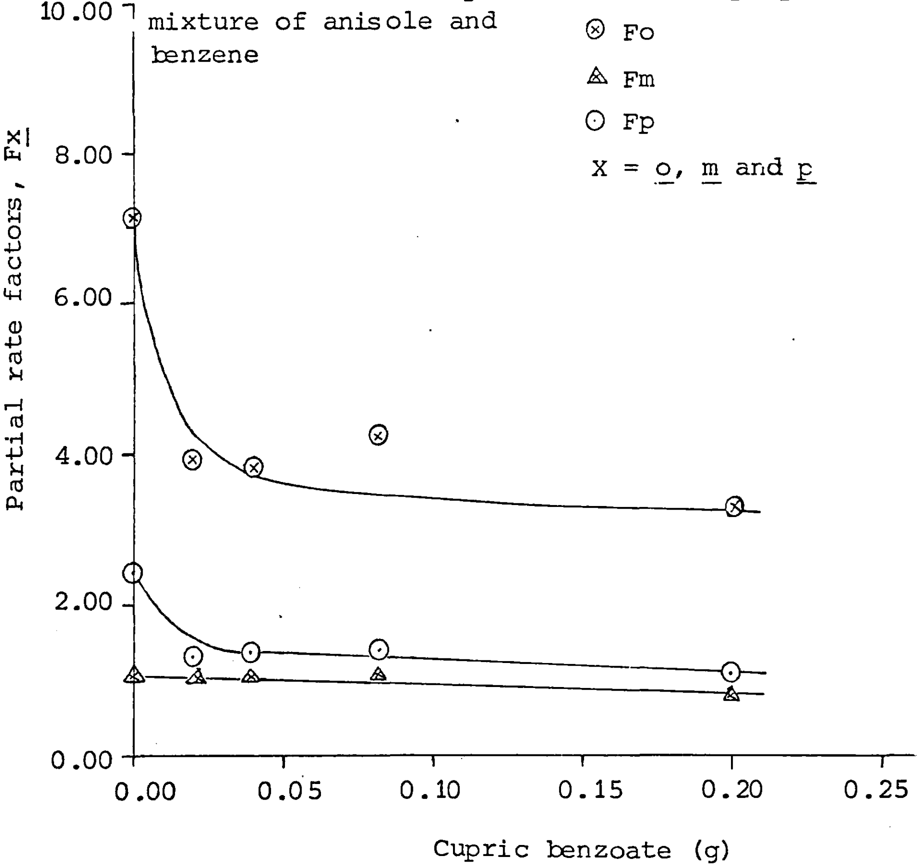


FIGURE 16

The rate factors are summarised in Table (51) and the effects of the metallic benzoates on relative rates is demonstrated in figures (12), (15) and (16). The explanation of the variation of K values and the partial rate factors obtained in these experiments could have the same origin as suggested for reaction containing nitro-compounds; i.e. the benzoyloxy radicals or benzoyl peroxide molecules tend to form complexes with the metal salts rather than with anisole molecules eliminates complications, and leads to a truer picture of the relative reactivities. The phenyl radical again turns out to be less selective than it appears to be in the uncatalysed reactions. Again as with the other catalysts selective dimerisation of unsubstituted phenylcyclohexadienyl radical is prevented by catalysis by their oxidation to biphenyl and this also results in a reduced value of K for anisole.

The above explanation for the effect of ferric benzoate on the rate factors is also applicable in the cupric benzoate and cupric p-toluate catalysed reactions. It is noted that the yield of benzoic acid in the transition metal salts catalysed reaction is always less than that observed in the uncatalysed reactions.

(d) The decomposition of benzoyl peroxide in a solution containing various molar ratios of anisole and benzene

The changing of the molar ratio of the competing substrates also has some effect on the value of relative rate compared to the value obtained from the corresponding reactions containing equimolar mixture of the two competing solvents. The lowering of the relative rates in the presence of additives is also observed here. The result obtained shows a close similarity to the values found in reaction containing an equimolar mixture of anisole and benzene in reaction with the appropriate additives.

Table 52

Experiment Number	Additive g (m/m)	Molar Ratio of anisole and benzene	Relative Rate
Mean of 77 & 78	Nil	1.0	3.18
Mean of 101 & 102	Nil	2.817	2.41
Mean of 103 & 104	Nil	0.308	2.92
	m-Dinitrobenzene		
Mean of 82 & 83	0.4546 (0.436)	1.0	1.76
Mean of 105 & 106	0.2569 (0.251)	2.817	1.66
Mean of 197 & 198	0.3131 (0.301)	0.308	1.22
	Cupric benzoate		
Mean of 97 & 98	0.2000 (0.053)	1.0	1.62
Mean of 109 & 110	0.1757 (0.047)	2.817	1.69
Mean of 111 & 112	0.1742 (0.046)	0.311	1.72
	Ferric benzoate		
Mean of 90 & 91	0.6004 (0.089)	1.0	1.81
113	0.5882 (0.087)	2.819	1.78
114	0.5778 (0.086)	0.311	1.67
Mean of 115 & 116	0.7953 (0.118)	0.2047	1.70

Consequently, the explanations which have been advanced in the preceding section are also applicable here. The close similarity of the results also provide a further check for the reliability of the rate values obtained in reactions containing equimolar mixture of anisole and benzene. Therefore the relative rate obtained from reaction in the absence of additive did not provide a true measure of the intra-molecular and inter-molecular reactivity of anisole. As it has been discussed in the preceding section the results in the presence of additives provide reliable indices of the reactivity of anisole molecules.

(e) Summary

The results of phenylation reactions in anisole suggest two conclusions: (1) benzoyloxy radicals form complexes with anisole and (2) in the absence of additive side reactions of σ-radicals can be selective. The inclusion of additives such as nitro-arenes, metal benzoates serves two functions (1) they suppress the complexation reaction of benzoyloxy radicals with anisole molecules (2) they prevent the side reactions of various σ-radicals. Therefore the results obtained under these conditions reflect the true intra-molecular and inter-molecular reactivity of anisole and benzene towards phenyl radicals.

The best set of relative rate and partial rate factors is given in the following table. These values are obtained by taking the mean value of the limiting values obtained from graphs (12) - (16) in the presence of additives e.g. nitrobenzene, m-dinitrobenzene, ferric benzoate, cupric benzoate and cupric p-toluate.

Table 53

Relative Rate	Partial Rate Factors		
K	Fo	Fm	Fp
1.7	3.4	1.0	1.2

V. The Effect of Some Additives on the Decomposition of Benzoyl Peroxide in t-Butylbenzene

Table 54

Experiment Number	Additive g (mole/mole peroxide)	t-Butylbiphenyls (m/m)	Isomer Ratio			Benzoic Acid (m/m)
			o-	m-	p-	
Mean of 117 and 118	Nil	0.585	19.6	56.9	23.5	0.402
Mean of 119 and 120	m-Dinitrobenzene 0.2636 g (0.379)	0.433	23.4	55.2	21.4	0.445
Mean of 121 and 122	Cupric benzoate 0.1039 g (0.041)	0.484	24.7	51.8	23.5	0.635
Mean of 123 and 124	Ferric benzoate 0.6049 (0.134)	0.495	20.7	52.6	26.8	0.4405

The reaction products in this reaction were not fully investigated in the present work. The major products detected are t-butylbiphenyls and benzoic acid. Little biphenyl (< 1%), which is probably formed by the union of two phenyl radicals, was also detected in the present studies.

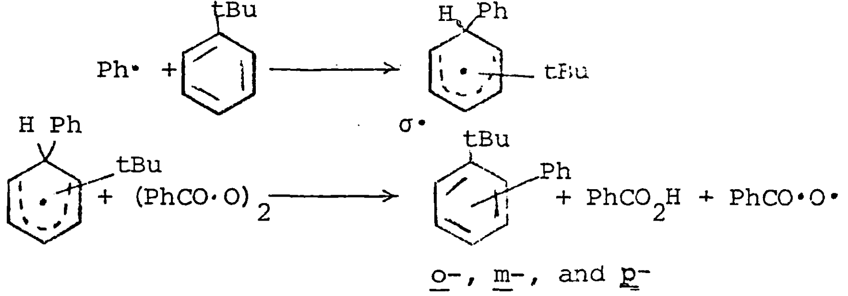
The phenylation of t-butylbenzene is complicated by a steric effect arising from the bulky t-butyl group, and which greatly suppresses the reactivity of the o-position. From the results listed in Table 54 oxidising agents in the reaction did not increase the yield of t-butylbiphenyls. The presence of oxidising agents in the reaction did not increase the yield of t-butylbiphenyls and the isomer ratio changes are not great. It seems that the additives did not participate in the reaction. m-Dinitrobenzene did not cause an increase on the yield of the biaryl probably because there is difficulty in reducing it to the corresponding nitroso-compound. The reducing agent in this reaction would be the various σ-intermediates resulting from the attack of t-butylbenzene by phenyl radicals. Presumably due to steric hindrance, the reduction of m-dinitrobenzene by σ-radicals is expected to proceed with difficulty. Consequently the m-dinitrobenzene, added as a catalyst, competes with t-butylbenzene for the phenylation reaction. The absence of a catalytic effect could also be partly due to steric hindrance to any oxidation of these bulky σ-complexes.

The absence of any effect of the metal salts in increasing yields of biaryl is largely due to the very low (almost zero) solubility of the metal salts in t-butylbenzene.

The t-butylbiphenyls and benzoic acid are formed according to the following mechanism; with the termination reaction occurring between σ-radicals.

$$(PhCO{\cdot}O)_2 \longrightarrow 2PhCO{\cdot}O{\cdot} \qquad \ldots\ldots \quad (156)$$

$$PhCO{\cdot}O{\cdot} \longrightarrow Ph{\cdot} + CO_2 \qquad \ldots\ldots \quad (157)$$



...... (158)

...... (159)

$$2\sigma{\cdot} \longrightarrow \text{Dimerisation and disproportionation products} \qquad \ldots\ldots \quad (160)$$

(a) <u>The effect of additives in the decomposition of benzoyl peroxide in benzene-t-butylbenzene system</u>

The results of the yields of biaryls and benzoic acid are given in Table (17). The relative rate and the partial rate factors for phenylation obtained in the present work from reactions in the absence of additive, together with some literature values were shown in the following Table (55).

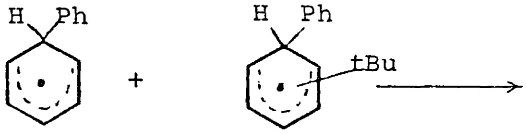
Table 55

Relative Rate	Partial Rate Factors			Reference
K	Fo	Fm	Fp	
1.06	0.59	1.74	1.72	Mean of Experiment 125 and 126
0.64	0.46	0.94	1.0	149
1.09	0.70	1.64	1.81	55

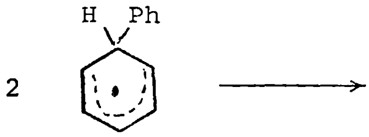
The rate values obtained in the present studies are higher than that reported by Cadogen, Hey and Williams[155b], and those of Cazes et.al.[48] but are more in line with the values published recently by Davies, Hey and Summers[55]. The relative rate (106) indicates that t-butylbenzene is about as reactive as benzene towards phenylation. However, the lower total yield of biaryls in the present reaction (0.50 mole/mole) casts doubt on the significance of the relative rate, since the side reactions of the σ-radicals may be important therefore the apparent rate factors could be misleading.

(b) The effect of m-dinitrobenzene and nitrobenzene on the decomposition of benzoyl peroxide in an equimolar mixture of benzene and t-butylbenzene

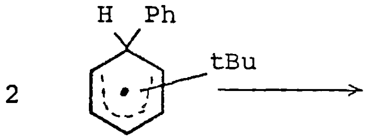
Unlike the reaction in t-butylbenzene alone, the yield of t-butylbiphenyls is increased by about 10% in the competitive reaction containing m-dinitrobenzene (Table 18), but the yield of biphenyl is increased to a much greater extent (over 40%). The enhanced yield of the biaryl is accompanied by a similar increase in the yield of benzoic acid. These observations indicate that the nitro-group effect is operating in this system. Now the m-dinitrobenzene could be reduced easily by the unsubstituted phenylcyclohexadienyl radicals to the corresponding nitroso-compounds which ultimately forms the nitroxide radicals, (page150), the species responsible for the oxidation reaction. The increase in yield of t-butylbiphenyls could be due to the nitro-group effect.



Dimerisation and disproportionation products ...... (161)

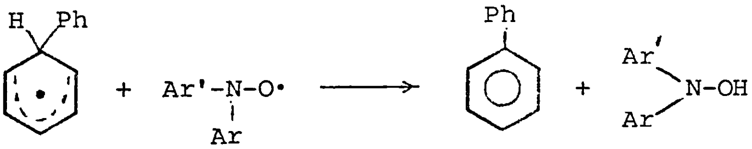


Dimerisation and disproportionation products ...... (162)



Dimerisation and disproportionation products ...... (163)

In the absence of nitro-compound the contribution of reactions (161) and (162) to residue formation would be more important than that of reaction (157) because of steric hindrance of the t-butyl group. In the presence of nitroxide radicals, the following reaction is very favourable and proceeds readily where the phenylcyclohexadienyl radicals are efficiently oxidised to biphenyl.



Consequently the extent of reactions (161) and (162) is greatly reduced so that more t-butylbiphenyl is formed. Similar enhancement of yield of biaryls and benzoic acid is also observed with nitrobenzene added as an oxidising agent. This observation could be accounted for by the similar explanation.

The lowering of the relative rates in the presence of m-dinitrobenzene and nitrobenzene is also observed here. The partial rate factors also show some interesting feature: the reactivity of m- and p-positions is preferentially lowered while that of the o-position is practically unaffected. The low reactivity of o-position is not unexpected because the o-position is deactivated by the steric effect from the bulky t-butyl group. The high value of Fm in the uncatalysed reaction is anomalous for reasons as described before (page 167). This position is expected to have a value of unity if the selecting process between the two competing solvents involved the same species. Therefore the large partial rate factors of the m- and p-positions (both of which are reduced to a value closer to unity in the presence of nitro-compounds) indicates that initial complexation also occurs between the precursor of phenyl radicals and t-butylbenzene molecules thereby increases the reactivity of the m- and p-positions. In this system, the complexation is likely to occur between benzoyloxy radicals and t-butylbenzene through some weak Van der Waal's forces. Since the benzoyloxy radicals have a longer lifetime than phenyl radicals hence intra-molecular selection within t-butylbenzene molecule is likely. As a result the attack of the sterically unfavourable o-position is avoided. This complexation is lifted in the presence of nitro-compounds (page 168). 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.

(c) The effect of ferric benzoate and cupric benzoate on the decomposition of benzoyl peroxide in an equimolar mixture of benzene and t-butylbenzene

Table 56

Experiment	Catalyst (m/m of Peroxide)	Relative Rate	Partial Rate Factors		
		K	Fo	Fm	Fp
Mean of 125 and 126	Nil	1.06	0.59	1.74	1.72
Mean of 133 and 134	Ferricbenzoate (0.089)	1.02	0.61	1.56	1.77
Mean of 131 and 132	Cupric benzoate (0.011)	0.73	0.51	1.09	1.16

The presence of ferric benzoate in the reaction mixture has little effect on the yield of biaryl. The relative rate and partial rate factors in this reaction are also practically unaffected, they show a close similarity to the values obtained from the uncatalysed reaction. This lack of effect of ferric benzoate could be due to some structured features of the catalyst. This is possibly due to the reason that ferric benzoate has a greater tendency to coagulate in this system (probably arises from its low solubility in the present system) to form polymeric complex which further lowers its solubility and efficiency for complexation with the reagent. Hence it could not remove the complexation of benzoyloxy radicals with t-butylbenzene.

The relative rate and partial rate factors obtained with cupric benzoate as catalyst fall in the same range as that observed in the reaction containing nitro-compounds. The yield of biaryls was also increased in this reaction. These observations show that cupric benzoate, unlike ferric benzoate, has a catalytic effect in this system. Though the solubility of cupric benzoate is also low in this system. However, unlike ferric benzoate which requires a fairly large quantity to exhibit a catalytic effect, cupric benzoate being a stronger oxidising agent, a little of it dissolved in solution is sufficient to show its effect. Cupric benzoate might have influenced the reaction by the same mechanism as suggested for nitro-compounds.

(d) Summary

As it has been shown that nitro-compounds and cupric benzoate could prevent the complexation between a precursor of phenyl radicals and t-butylbenzene, the rate factors obtained from reactions under the influence of these additives should provide a reliable measure of the reactivity of t-butylbenzene towards the phenylation reaction by benzoyl peroxide. The best set of reactivity index for t-butylbenzene in the phenylation reaction with benzoyl peroxide is given below. These are obtained by taking the mean values of the rate factors from the reactions catalysed by m-dinitrobenzene, nitrobenzene and cupric benzoate.

$^{t\text{-}Bu}_{H}K$	Fo	Fm	Fp
0.8	0.5	1.2	1.2

VI. The Competitive Reactions of Equimolar Mixtures of Two Mono-Substituted Benzenes

(a) Anisole and toluene system

The yields of methoxybiphenyls and methylbiphenyls and the relative rates determined in this reaction are listed in Table (19). By making use of the following conversion equations (169) and (170), these relative rates can be converted into the relative rate with respect to benzene as the standard solvent[156].

$${}^{PhX}_{PhH}K = {}^{PhX}_{PhY}K \cdot {}^{PhY}_{PhH}K$$

$${}^{PhY}_{PhH}K = {}^{PhX}_{PhH}K \Big/ {}^{PhX}_{PhH}K$$

where PhX and PhY represent the substituted benzenes.

The results are summarised in Table (20). The same striking feature of lowering relative rate in the presence of additives observed in the previous section is also observed here (Table 57). This observation supports the explanation advanced in the previous discussion, i.e. under the influence of the additive chosen the complication arises from the complexation between the substrates and the precursor of phenyl radical is eliminated and enables phenyl radicals to exhibit a more random attack on the competing substrates.

Table 57

Catalyst	Nil	*m*-Dinitrobenzene	Cupric benzoate	Ferric benzoate
${}^{MeO}_{CH_3}K$	1.62	1.33	1.25	1.35

The results obtained by using the conversion equation in the absence of additive showed slight disagreement with that determined from the competitive reactions between the substrates and benzene. This might be ascribed to the formation of complexes of different stabilities between the substrates (toluene and anisole) with the reagent. However, good agreement is obtained in the presence of additives. This finding supports the conclusion that the rate factors determined in the absence of additives are not reliable indices of reactivity. The present results also confirmed that anisole is more reactive than toluene in the phenylation reaction by benzoyl peroxide. The best values of ${}^{MeO}_{CH_3}K$, ${}^{CH_3}_{H}K$ and ${}^{MeO}_{H}K$ are listed below, these values are calculated from the conversion equations by using the best values of ${}^{MeO}_{CH_3}K$, ${}^{CH_3}_{H}K$ and ${}^{MeO}_{H}K$.

Table 58

	${}^{MeO}_{Me}K$	${}^{CH_3}_{H}K$	${}^{MeO}_{H}K$
Best values obtained from the direct competitive reactions	1.3	1.4	1.7
Best values obtained by using the conversion equation	1.2	1.4	2.0

(b) Anisole and t-butylbenzene system

The yield of biaryls and the total rate factors with respect to benzene are summarised in Tables 32 and 33. The K values calculated are comparable with the values determined in direct competitive reactions with benzene as solvent, except for reactions containing no catalyst. The similar trend of lowering of K values observed in the competitive reactions with benzene in the presence of additive is also observed in this reaction. This observation could also be accounted for by the explanation given in the anisole/toluene system.

Table 59

Catalyst	Nil	*m*-Dinitrobenzene	Cupric benzoate	Ferric benzoate
${}^{MeO}_{tBu}K$	2.41	2.05	2.05	2.18

	${}^{MeO}_{tBu}K$	${}^{MeO}_{H}K$	${}^{tBu}_{H}K$
Best values obtained from direct competitive reactions	2.1	1.7	0.80
Best values obtained by using the conversion equation equation	2.1	1.8	0.84

(c) Toluene and t-butylbenzene system

The results are summarised in Tables (24) and (25). The total rate factors obtained by using the conversion equations for the reactions containing m-dinitrobenzene and cupric benzoate differ considerably from the values determined from the direct competitive reactions between toluene and benzene. It is only fortuitous that the use of the value ${}^{tBu}_{H}K = 1.00$ (i.e. the value determined from the competitive reactions between t-butylbenzene and benzene containing no additive or in the presence of ferric benzoate) for the calculations of ${}^{CH_3}_{H}K$ in the m-dinitrobenzene and cupric benzoate reactions provides values (1.24 and 1.40 respectively) which give better agreement with the experimental results. This discrepancy might arise from the greater uncertainty on the reliability of the experimental results in this system.

Table 60

Catalyst	Nil	m-Dinitrobenzene	Cupric benzoate	Ferric benzoate
${}^{CH_3}_{tBu}K$	1.55	1.33	1.40	1.56

	${}^{CH_3}_{tBu}K$	${}^{CH_3}_{H}K$	${}^{tBu}_{H}K$
Best values obtained from direct competitive reactions	1.4	1.4	0.8
Best values obtained by using the conversion equation	1.8	1.2	1.0

(d) Summary

The results obtained from the direct competition reactions between anisole, toluene and t-butylbenzene confirmed the following order of reactivity in the phenylation reaction with benzoyl peroxide.

PhOMe > $PhCH_3$ > PhH > t-BuPh

The lowering of relative rates in the presence of additives also support the conclusion that complexation occurs between the substrates and the reagent.

VII. Conclusion

The best set of reactivity indices for toluene, anisole and t-butylbenzene obtained in this work is summarised below.

Table 61

Summary of the rate factors for the systems studied in the presence of additives

Solvent	Relative Rate K	Partial Rate Factors Fo	Fm	Fp
Toluene	1.4	2.7	1.0	1.3
Anisole	1.7	3.4	1.0	1.2
t-Butylbenzene	0.8	0.5	1.2	1.2

B. Homolytic Aromatic Silylation

I. The Reaction of Phenyldimethylsilyl Radicals with Aromatic Hydrocarbons

(a) The reaction of phenyldimethylsilyl radicals with benzene

(i) The decomposition of azo-bis-isobutyronitrile or benzoyl peroxide in a benzene solution containing phenyldimethylsilane

The results are summarised in Table 62.

Table 62

Yields of products for the phenyldimethylsilane/benzene system

Experiment Number	Radical Initiator (Molar Concentration)	Molar Concentration of Phenyldimethylsilane ($PhMe_2SiH$)	Diphenyldimethylsilane (Ph_2SiMe_2)	Diphenyltetramethyldisilane ($(PhMe_2Si)_2$)
Mean of 160 and 161	AIBN (80°) (0.104 M)	0.100 M	1.9%	Detected, yield not determined
Mean of 162 and 163	AIBN (80°) (0.560 M)	0.230 M	10.8%	15.5%
Mean of 164 and 165	Benzoyl peroxide (80°, 0.040 M)	0.046 M	32.5%	<2%
166	t-Butyl peroxide (u.v. light, 0.068 M)	0.087 M	33.6%	23.4%
167	t-Butyl peroxide (u.v. light, 0.084 M)	0.059 M	7.5%	145%
168	u.v. light	0.070 M	23%	trace
169	u.v. light	0.744 M	6%	12%

AIBN = Bis(azo-isobutyronitrile)

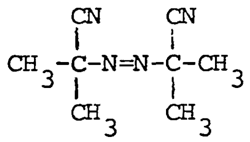
The reaction products in this reaction are not fully investigated only the major products are studied. The thermal decomposition of benzoyl peroxide in a benzene solution of phenyldimethylsilane gave aromatic substitution product (diphenyldimethylsilane) (21), up to 35% yield, and

and substitution occurred to a less extent with azo-bis-isobutyronitrile as radical initiator (7-14%). The dimerisation product, tetramethyldiphenyldisilane $(PhMe_2Si)_2$ (22), of the silyl radicals was also detected in these reactions therefore providing evidence for the homolytic nature of the reaction.

The formations of diphenyldimethylsilane (Ph_2SiMe_2) (21) and tetramethyldiphenyldisilane $(PhMe_2Si)_2$ (22) are consistent with a homolytic aromatic substitution reaction which involves silyl radical intermediates and could be accounted for by the following mechanism

$$P \xrightarrow{\Delta} 2R\cdot \qquad \ldots\ldots \quad (164)$$

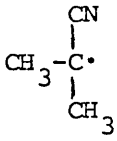
where P =



$$CH_3-\underset{CH_3}{\overset{CN}{C}}-N{=}N-\underset{CH_3}{\overset{CN}{C}}-CH_3$$

or $(PhCO\cdot O)_2$

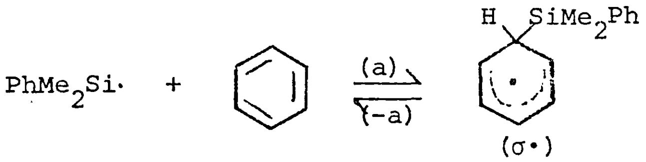
R· =



$$CH_3-\underset{CH_3}{\overset{CN}{C}}\cdot$$

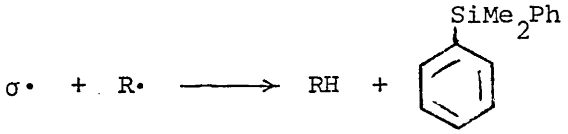
, PhCO·O· or Ph·

$$R\cdot + PhMe_2SiH \longrightarrow RH + PhMe_2Si\cdot \qquad \ldots\ldots \quad (165)$$



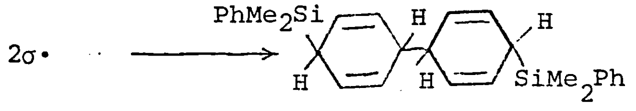
(σ·)

...... (166)



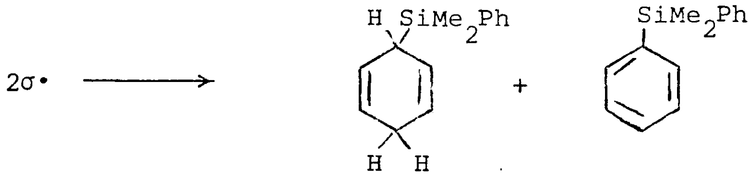
(21)

...... (167)



and other isomers

.... (168)



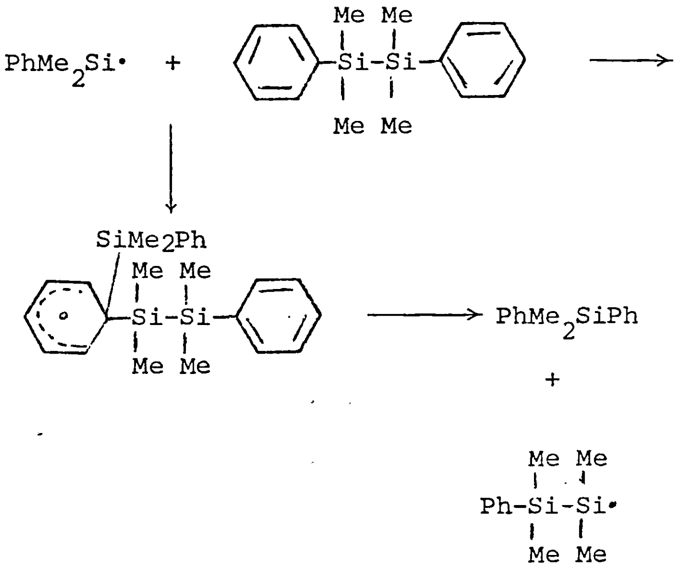
...... (169)

$$2\ PhMe_2Si\cdot \longrightarrow \underset{(22)}{PhMe_2Si - SiMe_2Ph}$$ ...... (170)

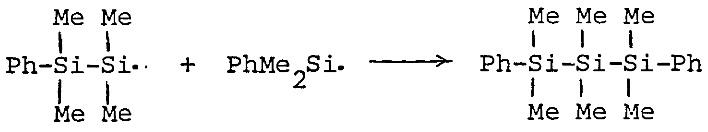
Diphenyldimethylsilane was formed by the addition-displacement mechanism, the silyl radicals add to the benzene nucleus to form the cyclohexadienyl adduct. In the presence of an radical initiator, these σ-intermediates could be aromatised by radicals derived from the initiator or by phenyldimethylsilyl radicals. In the latter, the starting phenyldimethylsilane is regenerated. The contribution from the disproportionation and dimerisation routes in this reaction would be important, as shown by the poor material balance in these reactions. The formation of the polymeric residue accounted for the rest of the silyl radicals.

The formation of the dimer (22) of the silyl radicals indicated that these radicals are not very reactive towards benzene. This observation is also consistent with the postulated reversible addition reaction of silyl radicals to benzene to form the σ-intermediates[21,115(b),216]. In the absence of an efficient oxidising agent, the combination reaction of two silyl radicals to form dimers could compete more favourably with the oxidation of σ-radicals.

There are a number of unidentified peaks (trace quantities) in the gas chromatograms of the products of these reactions, when the temperature of the gas liquid chromatographic column (Apiezon grease column) was raised to 230°C. A larger portion of polymeric compounds might be too involatile to be eluted at this temperature. The dimerisation and disproportionation products of the σ-intermediates might account for some of the unidentified peaks. However, where no radicals initiator was included to catalyse the reaction (e.g. direct photolysis of phenyldimethylsilane in benzene), there was a trace peak in the chromatogram after the one due to diphenyldimethylsilane. This trace peak was possibly due to the dihydroaromatic product resulting from the disproportionation reaction of σ-radicals. Besides the dimerisation of the silyl radicals to give high boiling residue; other processes such as that given below could also divert the aromatic silylated products diphenyldimethylsilane and the dimer tetramethyldiphenyldisilane (22) to form other involatile compounds.



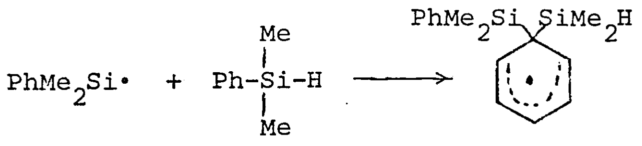
...... (171)



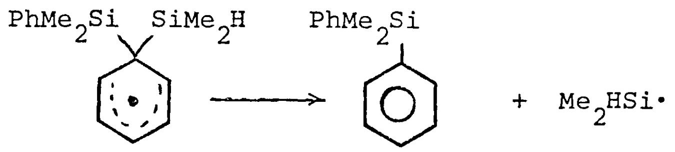
$$\mathrm{Ph{-}\overset{Me}{\underset{Me}{Si}}{-}\overset{Me}{\underset{Me}{Si}}\cdot} + \mathrm{PhMe_2Si\cdot} \longrightarrow \mathrm{Ph{-}\overset{Me}{\underset{Me}{Si}}{-}\overset{Me}{\underset{Me}{Si}}{-}\overset{Me}{\underset{Me}{Si}}{-}Ph}$$

...... (172)

Diphenyldimethylsilane could also be formed from the following redistribution reaction as a minor contributor.



...... (173)



...... (174)

The reactions (168) and (171) for the formation of diphenyldimethylsilane are further supported by the fact that even in reaction in toluene or anisole there is always formed 2 - 3% of diphenyldimethylsilane.

Relatively more dimer of the silyl radicals ($PhMe_2Si\cdot$) was obtained when bis(azo-isobutyronitrile) was employed as a radical initiator than when benzoyl peroxide was used. This observation may be due to the fact that 2-cyanoisopropyl radicals are less efficient as a hydrogen abstractor than benzoyloxy or phenyl radicals so that the reverse reaction of (163) is more prevalent in the former reaction.

(ii) <u>The photolysis of t-butyl peroxide in a benzene solution containing phenyldimethylsilane</u>

The results are summarised in Table (62), experiment numbers (153) and (154). Substitution product occurred up to 33% under favourable conditions, however, lower yield (7.5%) was obtained when large amounts of t-butylperoxide was included in the photolytic reactions, (experiment number (151)). Dimer of phenyldimethylsilyl radicals was also detected in varying quantities (14.5 to 23.4%).

The products could also be accounted for by the mechanism suggested in the preceding section. In reactions where t-butylperoxide was employed as radical initiator the silyl radicals were formed in the following manner.

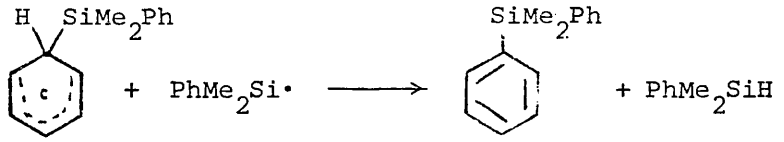
$$(CH_3)_3C\text{-}O\text{-}O\text{-}C(CH_3)_3 \xrightarrow{h\nu} 2(CH_3)_3C\cdot O\cdot \qquad ...... (175)$$

$$(CH_3)_3C\cdot O\cdot + PhMe_2SiH \longrightarrow (CH_3)_3COH + PhMe_2Si\cdot \qquad ...... (176)$$

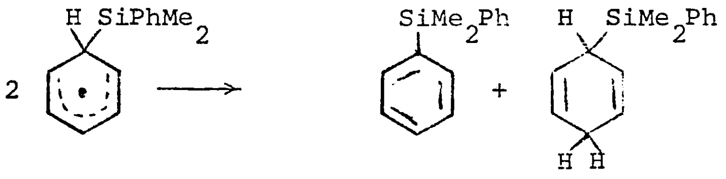
From the similarity of the products formed, phenyldimethylsilyl radicals are also believed to have been formed from the direct photolysis of a solution containing phenyldimethylsilane in benzene. In this reaction diphenyldimethylsilane was obtained in yield varying from 6%

$$PhMe_2SiH \xrightarrow{h\nu} PhMe_2Si\cdot + H\cdot$$

to 33% depending on the experimental conditions. No attempt in this work has been made to detect hydrogen or any organic reduction products formed (if any). In this reaction the transformation of the σ-radicals to binuclear aromatic product is probably caused by phenyldimethylsilyl radicals or by disproportionation.



...... (177)



and other isomers .... (178)

The ratio of the yields of diphenyldimethylsilane and dimer varied with the concentration of phenyldimethylsilane, being lowered with higher concentration of hydrosilane. This is probably due to the fact that at higher concentration the stationary concentration of silyl radicals is higher and so more favourable for the dimerisation reaction.

In both the thermolytic and photolytic reactions a compound with the same retention time of biphenyl is obtained (with yields varied from 0.01 to 0.06 mole per mole of phenyldimethylsilane consumed). The photolysis of benzene under the same conditions also forms trace amounts of a compound with the same retention time as biphenyl.

From the above considerations, the best methods of silylating benzene with phenyldimethylsilyl radicals are (i) by the thermal decomposition of an equimolar mixture of benzoyl peroxide and phenyldimethylsilane in benzene at 80^{o} for 72 hours, and (ii) by the photolysis of an equimolar mixture of t-butylperoxide and phenyldimethylsilane in large excess of benzene at room temperature for 100 hours or longer. However, the choice of benzoyl peroxide as the radical initiator has one disadvantage when the reactions of silyl radicals with substituted benzenes are investigated. The competing phenylation reaction will complicate the analysis of the reaction products.

(b) The photolysis of phenyldimethylsilane in toluene

Photolysis of toluene solution containing t-butylperoxide and phenyldimethylsilane gave bibenzyl as the major product, together with some nuclear substituted products. The analysis of the reaction products by gas chromatography was difficult as the latter products are only formed in minor amounts whereas the predominant g.l.c. peak due to bibenzyl masked the peaks of other products. Therefore the reaction was not investigated further.

$$(t\text{-BuO})_2 \xrightarrow{h\nu} 2t\text{-BuO}\cdot \qquad \ldots\ldots \quad (179)$$

$$t\text{-BuO}\cdot + PhCH_3 \longrightarrow t\text{-BuOH} + PhCH_2\cdot \qquad \ldots\ldots. \quad (180)$$

$$2PhCh_2\cdot \longrightarrow (PhCH_2)_2 \qquad \ldots\ldots \quad (181)$$

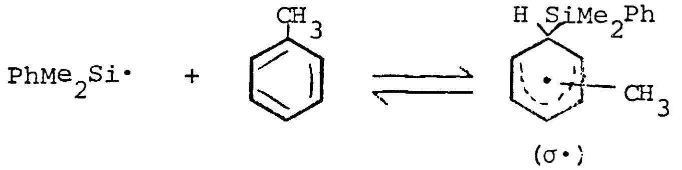
Some of the bibenzyl could also be contributed by the following reaction, as some bibenzyl is formed in the photolysis of toluene alone. Consequently direct photolysis of a solution containing phenyldimethylsilane

$$PhCH_3 \xrightarrow{h\nu} PhCH_2\cdot + H\cdot \qquad \ldots\ldots \quad (182)$$

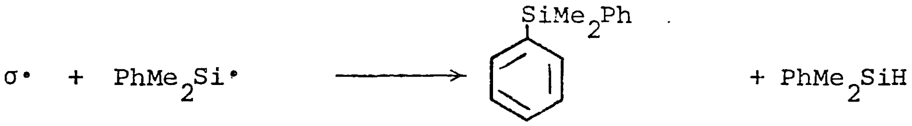
$$2PhCH_2\cdot \longrightarrow (PhCH_2)_2 \qquad \ldots\ldots \quad (183)$$

in toluene was performed. It was found that the bibenzyl yield is greatly reduced. The aromatic substitution products were probably formed by the homolytic aromatic substitution reaction. These products were obtained in low yield ($\sim$ 12%). The results are summarised in Table (26).

$$PhMe_2SiH \xrightarrow{h\nu} PhMe_2Si\cdot + H\cdot \qquad \text{......} \quad (184)$$

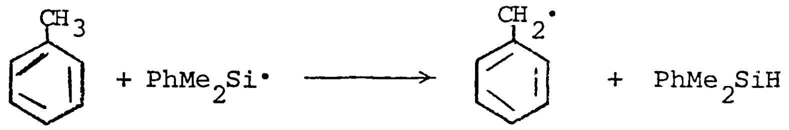


...... (185)



...... (186)

$$2\sigma\cdot \longrightarrow \text{Dimerisation and disproportionation products} \qquad \text{......} \quad (187)$$



...... (188)

...... (189)

Diphenyldimethylsilane detected in this reaction is probably formed by the redistribution reaction as described before (page 221). The reaction was carried out once.

(c) The reaction of phenyldimethylsilyl radicals with naphthalene

Table 63

The reactions of silyl radicals with naphthalene at 130°

Experiment Number	α-(Phenyldimethylsilyl)-naphthalene	β-(Phenyldimethylsilyl)naphthalene	Isomer Ratio	
			α-	β-
Mean of 173 and 174	18.1%	6.9%	74%	26%

The thermal decomposition of t-butylperoxide in naphthalene containing the hydrosilane at 130° afforded α- and β-silylated naphthalenes, (yields varied from 18 to 31%), diphenyltetramethyldisilane (21) and at least two unidentified peaks, some of which could be due to binaphthyls, because peaks with similar retention times are observed from the reaction mixture obtained by the thermal decomposition of benzoyl peroxide in naphthalene.

The α- and β-silylated naphthalenes are probably formed according to the general reaction scheme of homolytic aromatic silylation (page 218).

II. The Reaction of Phenyldimethylsilyl Radicals with Halobenzenes.

(a) The reaction of phenyldimethylsilyl radicals with chlorobenzene

Table 64

The products of the reaction of silyl radicals with chlorobenzene

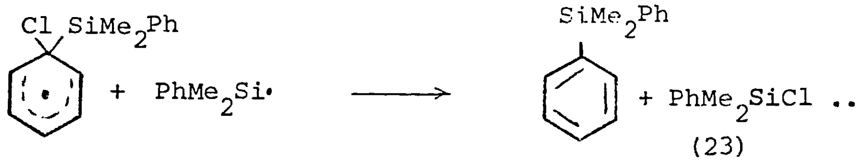
Experiment Number	Diphenyldimethylsilane (Ph_2SiMe_2)	Diphenyltetramethyldisilane ($(PhMe_2Si)_2$)	Chlorobiphenyls		
			Yield	Isomer Ratio	
				2	3 & 4
Mean of 171 and 172	51.6%	10.2%	22.1	52.8%	47.2%

The thermal decomposition of t-butylperoxide in a solution of phenyldimethylsilane in chlorobenzene at 130° for 24 hours gave the following products: diphenyldimethylsilane (in ∼ 50% yield) phenyldimethylchlorobenzene (23), o-, m- and p- chlorophenyl, tetramethyldiphenyldisilane (21) and a number of unidentified peaks.

There are two ways by which the silyl radicals appear to react with chlorobenzene: (a) an addition-displacement reaction or (b) a direct abstraction of the chlorine atom from chlorobenzene to produce phenyl radicals. Attack by silyl radicals other than at the 1-position apparently does not occur. This is possibly due to the nucleophilic nature of the silyl radicals which predominantly attack the relatively electron deficient 1-position and avoid the relatively electron rich π-system of the benzene ring.

(a)

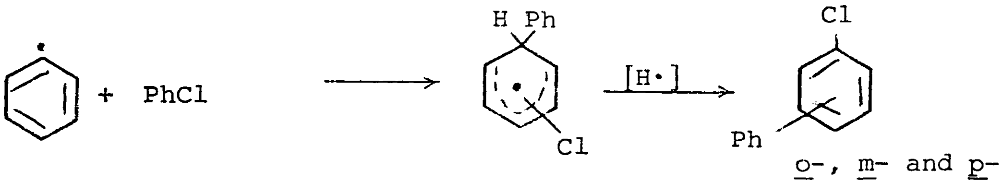
...... (190)



(191)

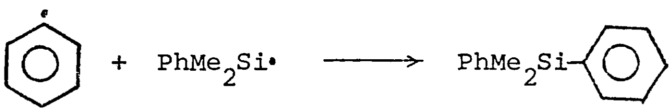
(b)

...... (192)



...... (193)

The yield of phenyldimethylchlorosilane was not determined due to the readily hydrolysis of this compound in air. Diphenyldimethylsilane may be formed by radical recombination of phenyl radicals with phenyldimethylsilyl radicals (eq. 191) or by an addition displacement mechanism (a).



...... (194)

The latter is more likely, particularly in view of the detection of chlorodimethylphenylsilane. This allows an approximate estimation of the ratio of the addition displacement reaction to the halogen abstraction reaction by comparison of the yields of diphenyldimethylsilane and chlorobiphenyls. An indication of the relative importance of addition to halogen abstraction processes is given by the ratio of the yields of chlorobiphenyls to diphenyldimethylsilane (0.61).

Table 65

Heat change of abstraction of halogen atoms from halobenzenes by trimethylsilyl radicals

X	D(Ph-X)kcal mol^{-1} (158)	D(Me_2Si-X)kcal mol^{-1} D(Me_2Si-X)kcal mol^{-1} (a)	ΔH(kcal mol^{-1})
Cl	85	104	-19
Br	71	87	-16
I	61	78	-17

(a) values taken from Table(3)

The above table shows that all these halogen abstraction reactions would be exothermic and therefore feasible. The presence of chlorobiphenyls among the products is consistent with this. The isomer ratio of the chlorobiphenyls is comparable with that obtained from the phenyl radicals generated from known sources[6a,7]. This provides further evidence of the participation of phenyl radicals in this reaction.

(b) The reactions of phenyldimethylsilyl radicals with p-dichlorobenzene

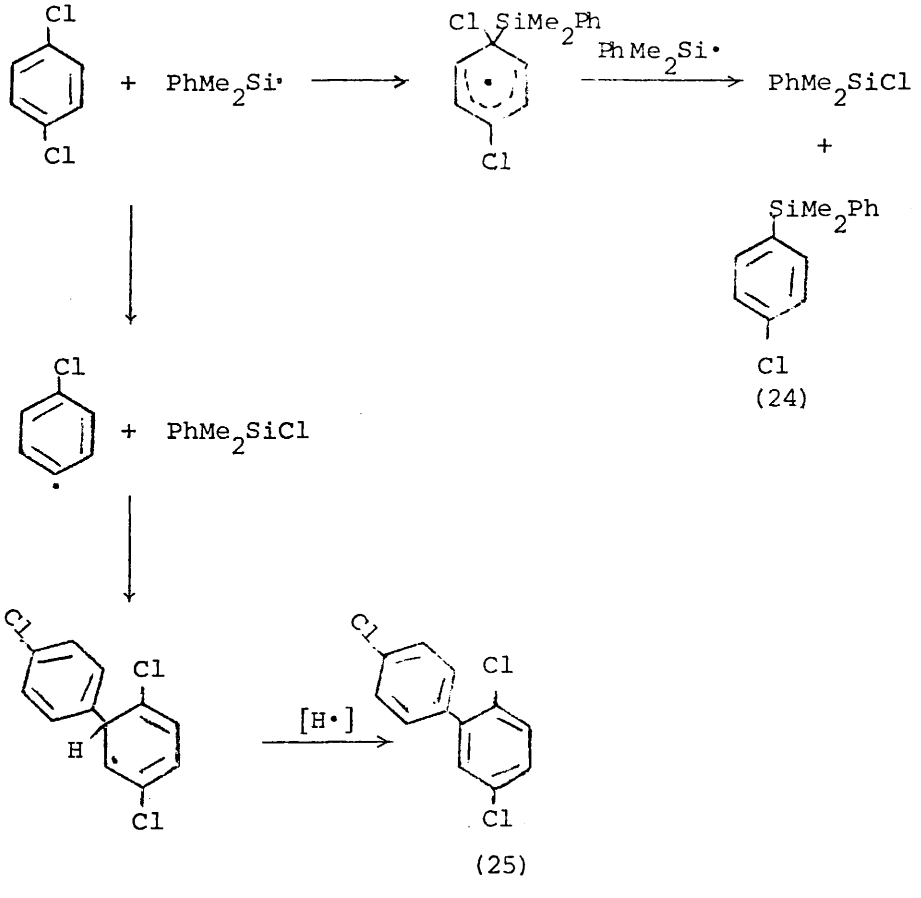
The results are summarised in the following table.

Table 66

The products of the reactions of silyl radicals with p-dichlorobenzene

Experiment Number	p-chloro-(phenyl-dimethylsilyl)-benzene (24)	Diphenyltetramethyl disilane	2,4',5-trichloro-biphenyl (25)
Mean of 195 & 196	10.4%	4.2%	5.4%

The reactions of silyl radicals with p-dichlorobenzene gave the following products: o-chlorophenyldimethylphenylsilane (24), 2,4',5-trichlorobiphenyl (35) and tetramethyldiphenyldisilane (22). These products were probably formed by the competition of the addition-displacement and halogen abstraction mechanism. The predominantly attack of 1-position by the silyl radicals provides further evidence of the nucleophilic nature of silyl radicals.



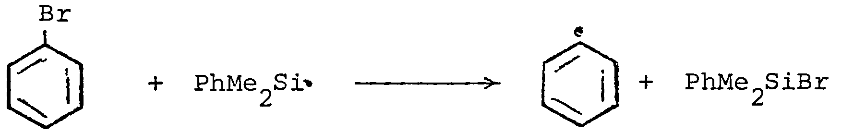
... (195)

...... (196)

(c) The reactions of phenyldimethylsilyl radicals with bromobenzene

The major products detected in this reaction are o-, m- and p-bromobiphenyls together with a little biphenyl. A little benzene was also detected. Tetramethyldiphenyldisilane was not detected in this reaction and also no diphenyldimethylsilane was formed.

The major products obtained in this reaction suggest that the direct bromine abstraction from bromobenzene by silyl radicals is a favourable reaction in this system, possibly because of the relatively weaker carbon-halogen bond in bromobenzene compared to that in chlorobenzene. The isomer ratio of bromobiphenyls formed is similar to that formed from other homolytic phenylation reactions. A trace of biphenyl was detected possibly formed by union of phenyl radicals or by their attack on the 1-position of bromobenzene. The absence of diphenyldimethylsilane in the reaction products ruled out the importance of the addition-displacement process in this reaction. The absence of any detectable amount of the dimer of the original silyl radicals in this reaction indicated that these silyl radicals are very reactive towards bromobenzene. In one reaction while t-butylperoxide alone was allowed to decompose in bromobenzene at 130°, only a trace of bromobiphenyls was detected at the end of the reaction. No attempts were made to determine the yield of bromosilanes for the reason given for chlorosilanes. The main reaction is therefore as follows:-



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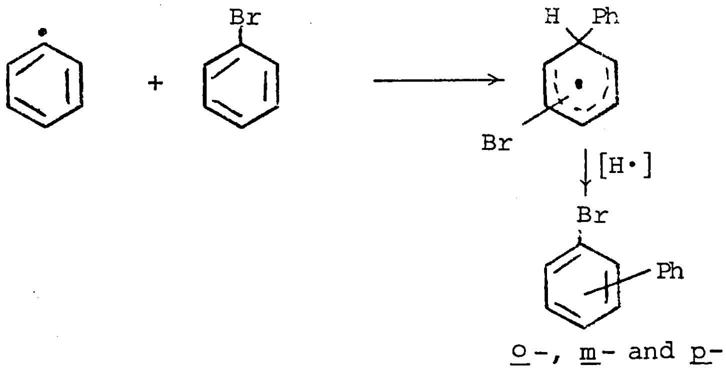

...... (198)

The reaction in iodobenzene was qualitatively shown to produce mainly iodo-biphenyls, and is therefore similar to that in bromobenzene.

III. The Reactions of Phenyldimethylsilyl Radicals with Anisole.

Table 67

The products of the reactions of silyl radicals with anisole

Experiment Number	Diphenyldimethylsilane	Diphenyltetramethyldisilane	Phenyldimethylsilylanisole			
			Yield	Isomer Ratio		
				o-	m-	p-
Mean of 179 and 180	6%	5.5%	17.5%	42%	39%	19%

The reaction of silyl radicals with anisole is complicated. Amongst the products, o-, m- and p-(phenyldimethylsilyl)anisoles (26), diphenyldimethylsilane and tetramethyldiphenyldisilane were identified (Table 67). These products are consistent with the homolytic nature of the reaction. The silyl radicals are formed by the now well-established homolytic aromatic substitution reaction. The isomer ratio of the silylanisoles is 45%. 35% and 20% for the o-, m- and p- isomers respectively. The higher m/p ratio observed in this reaction than in phenylation reaction is consistent with the nucleophilic nature of silyl radicals as being shown in the previous discussion (page 226).

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